COMPLEXES OF ETHYLXANTHATE AND N,N-DIETHYLDITHIOCARBAMATE AND THEIR ADDUCTS WITH SOME NITROGEN BASES

BY

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A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

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MARCH, 1971

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ABSTRACT

This thesis concerns first row transition metal complexes, of ethylxanthate (Xan) and diethyldithiocarbamate (dtc). Complexes of the type $M(Xan)_2$ and $(NEt_4)M(Xan)_3$ where M = Mn, Fe, Ni and Zn have been prepared and studied. It was found that Cr(II) and Co(II) could not be stabilized in the presence of ethylxanthate, due to their tendency to oxidize while Cu(II) was instantaneously reduced. The $(NEt_4)M(dtc)_3$ complexes could not be prepared and evidence is presented which challenges the reported existence of $NaCo(dtc)_3$. In an attempt to decrease the tendency of the divalent metal atoms to oxidize, the reactions between $MCl_2 \cdot nH_2O$ and KXan have been studied in the presence of 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen). These resulted in the formation of complexes of the type $M(Xan)_2 \cdot B$ (where M = Mn, Fe, Co, Ni or Zn and B = bipy or phen). When B = bipy and M = Fe, Co or Ni, two species which are crystallographically different are obtained. Similar reactions with dtc result in similar complexes, except when M = Ni.

The infra-red spectra (between 200 cm^{-1} and 2000 cm^{-1}) are discussed and some empirical assignments are made. The visible and near infra-red spectra as well as room temperature magnetic moments are explained in terms of ligand-field theory and an apparatus is described to study the magnetic susceptibilities as a function of temperature. Results of conductance studies in nitromethane and molecular weight studies are also discussed.

The results of these studies are consistent with high spin octahedral metal ions, with the possible exceptions of $Mn(Xan)_2$ and $Fe(Xan)_2$ for which low magnetic moments were obtained.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr. D. G. Holah for suggesting the topic for this study and for his continuous encouragement and generous financial support.

I would also like to extend my appreciation to Dr. T. Griffith and staff for making available most of the instruments used to measure the physical properties of the complexes, Mr. K. Sumpter for his frequent assistance with glass-work, Mr. J. Butler and staff for continual mechanical assistance and to Dr. I. Hoodless for many helpful suggestions with regard to writing this thesis.

Finally, I must convey my thanks to my wife, Pearl, for her moral support and typing assistance, and to Mrs. Dianne Conrad for her conscientious typing of the final copy of this thesis.

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1. INTRODUCTION

1.1-General:

That interest in metal complexes of sulfur-containing ligands has increased markedly in the last two decades is attested by the appearance of two very recent reviews on this topic.[1,2] Despite the fact that most 1,1-dithiolate studies have involved dithiocarbamates* (see FigureI), both these species and O-alkyldithiocarbonates (i.e: xanthates**) (see Figure II) have been found to interact strongly with metals and the resultant complexes are the basis of one of the above mentioned reviews[2].

Complexes of both types of ligands find wide industrial use, as well as applications in analytical

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*If $R' = R'' = C_2H_5$, the ligand will be abbreviated dtc^-. If R' and R'' are unspecified, the ligand will be abbreviated R_2dtc^-. If R' and R'' are specified, but not both equal to C_2H_5, the standard symbols for the alkyl group will be inserted in place of "R_2".

**If $R = C_2H_5$, the ligand will be abbreviated as "Xan^-". In all other cases the abbreviation, "$RXan^-$" will be used unless the alkyl group is specified, in which case its standard abbreviation will be inserted in place of "R".

chemistry. For example, mining industries having discovered the usefullness of xanthates as flotation agents, have used them to process such ores as chalcopyrites, galena, antimonite and sphalerite[3]. Extraction data have been compiled[4] for iron(III), cobalt(II), nickel(II) and copper(II). It is reported that if xanthate is added to a solution containing zinc(II) sulfate and cobalt ions (oxidation unspecified but presumably trivalent), the cobalt will precipitate in preference to the zinc ions[5]. Treatment of the precipitate with sodium sulfide regenerates the xanthate as the sodium salt[6]. When nickel and cobalt are simultaneously removed from solution by flotation with xanthate species, the nickel can be separated from the cobalt by washing with ammonia solution[7]. This results in a soluble $Ni(NH_3)_x(RXan)_y$ complex, leaving the cobalt behind. Alternatively, the xanthate can be removed from the nickel complex by treating the flotate with sodium hydroxide to give nickel(II) hydroxide and water-soluble sodium xanthate[8]. The cobalt xanthate complex does not react under these conditions.

The quantitative determination of silver(I) by precipitation of the insoluble silver(I) xanthate species was first reported by Deshmukh and Saraswathi[9]. In 1969 the method was reported[10] to be suitable for the determination of copper, silver, lead, nickel, cadmium and zinc. For the last three metals, the alkyl group must be n-propyl, n-butyl and n-hexyl, respectively, or longer. Alternatively, the concentration of xanthate in aqueous solution can be determined by titrating, at a pH value between seven and eleven (with ammonium hydroxide), with a standard solution of copper(II) ions (which are reduced to form copper(I) xanthate), using potassium ferrocyanide as an indicator[11].

Alkylxanthates have also found uses as lubricants[12], thermal stabilizers[13] and corrosion inhibitors[14]. Despite their toxic properties toward animals[15] (depression, slow movement, bristled hair, difficult respiration, tremors and convulsions), they have also been utilized as fungicides[16].

The practical uses and toxic properties of dithiocarbamates, which have been extensively reviewed elsewhere[17], will not be dwelled upon here.

Of some importance to this thesis is the decomposition of 1,1-dithiolates. Thus, the decomposition of xanthic acid[18], which is independent of oxygen[19], but catalyzed by quarternary ammonium salts[20] at pH values of six or greater, has been found to have an activation energy (E_A) of 17.5 k'cal./mole at pH values less than six[21]. It is also true that some transition metal xanthates are not particularly stable. For example[22], bis(n-butylxanthato)zinc(II) is decomposed by n-butanol at 110° C. to give carbon disulfide, di(butoxy)carbon sulfide and tetra(butoxy)methane among the products. Also, the decomposition of bis(alkylxanthato)nickel(II), with alkyl groups of hydrogen, methyl or ethyl, upon heating to give unsaturated hydrocarbons has been reported[23]. Transition metals have been found to catalyze the iodine oxidation of 1,1-dithiolates from the structure shown in Figure III to that shown in Figure IV, the extra sulfur atom coming either from decomposition of the dithiolate or from elemental sulfur, if it has been incorporated into the reaction medium[24]. Likewise, the incorporation of divalent metal complexes of xanthate enhances the ability to add sulfur atoms to olefines[25]. Finally, the reaction of amines with tris(alkylxanthato)cobalt(III) results in the formation of dithiocarbamates[26]. Ninety-five percent conversion has been reported.

Dithiocarbamates also are susceptible to decomposition. The ability of these species, and others, to oxidize (RS^-) to $(RS)_2$ has been reported[27] to be:

$$((C_2H_5)_2dtc)_2 > (C_6H_5CS_2)_2 > (C_6H_5C(O)S)_2 > (C_6H_5S)_2.$$

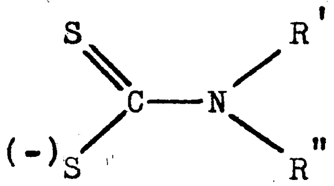
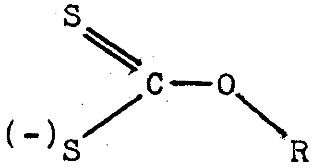


Figure I



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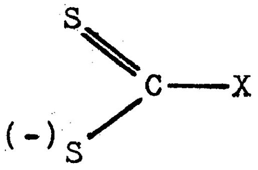

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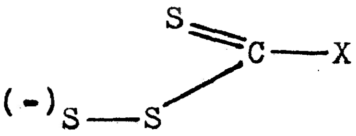


Figure IV

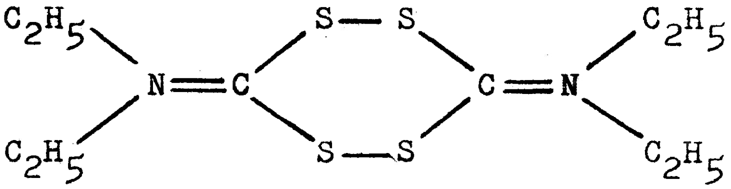


Figure V

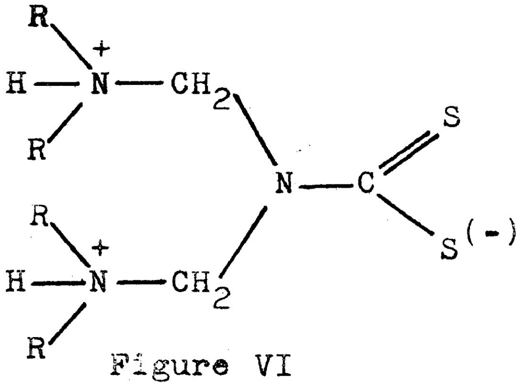


Figure VI

In acid medium (a pH value between 4.6 and 6.3), diethyldithiocarbamate is oxidized to tetraethylthiuram disulfide, between 0.4 volts and 1.0 volts, and to oxygen-containing species between 1.2 and 1.4 volts[28]. In the presence of chloride ions in chloroform solution, tris(diethyldithiocarbamato)iron(III) or bis(diethyldithiocarbamato)chloroiron(III) species can be oxidized[29] to form a tetrachloroiron(III) complex with the s-tetrathian dimer shown in Figure V. A carbon-nitrogen stretching frequency at 1568 cm^{-1} is in accord with this. Similar compounds involving this dimer can be formed with the tetrachlorocobaltate(II) and hexachloroantimonate(II) cations[29]. Finally, the ability to form metal(II) complexes of a cationic dithiocarbamate (e.g: Figure VI) has been demonstrated[30].

1.2-Stabilities of Bis and Tris Complexes of Xanthates and Dithiocarbamates:

Reactions of sodium diethyldithiocarbamate with the divalent first row transition metal halides produce bis(diethyldithiocarbamato)metal(II) complexes with chromium, manganese,iron, nickel, copper and zinc[31]. An unusual feature of these species[31] is that their structures approximate to square pyramidal dimers with chromium, manganese, iron, copper or zinc (see Figure VII) and a square planar monomer with nickel. Sodium tris(diethyldithiocarbamato)cobaltate(II) is the only tris dithiocarbamate complex of a divalent transition metal to be reported[32]. This conflicts with reports that cobalt(II) is spontaneously oxidized to cobalt(III) in the presence of dithiocarbamate[33] even when oxygen is excluded[31], and evidence will be presented in this thesis which seriously questions the existence of such an N,N-diethyldithiocarbamate complex of cobalt(II). A species originally believed[34] to contain the tris(dibutyldithiocarbamato)nickelate(IV) cation has since been suggested to be a resonance hybrid of this species (Figure VIII) and the (dibutyldithiocarbamato)-(tetrabutylthiuram disulfide)nickel(II) cation[35] (Figure IX).

The reason for the apparent inablility to form the tris(diethyldithiocarbamato)metallate(II) species has been suggested to be due to a significant contribution of the structure shown in Figure X(c) to the structure of the chelate[36]. This results in the formation of a stable bis complex which renders unlikely the rearrangement of the metal-sulfur bonds to form the tris complex. Confirmation of this hypothesis came from Nakamoto, <u>et al.</u>[37], who also suggested that this structure makes a greater contrib-

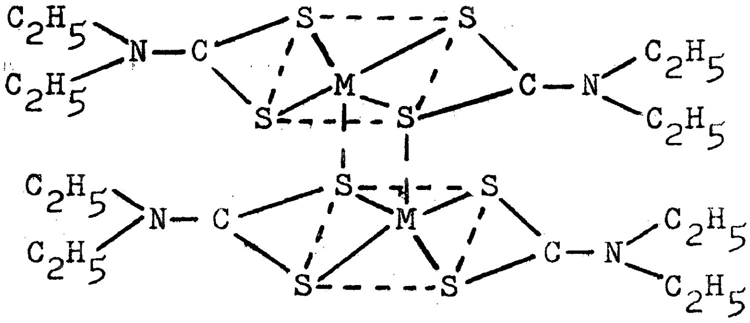
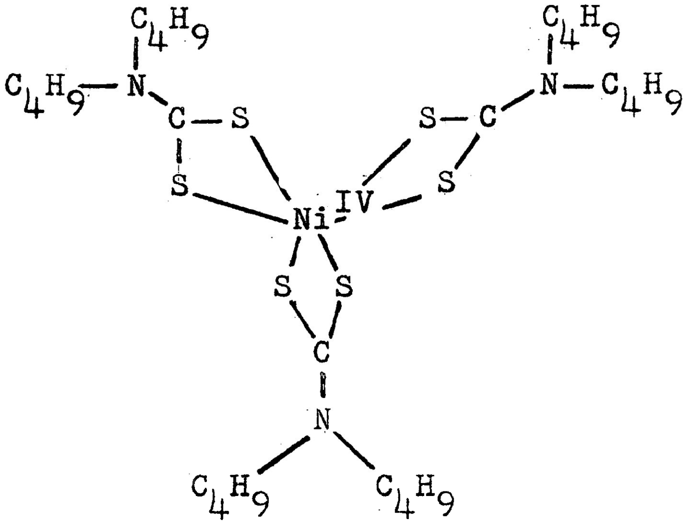


Figure VII



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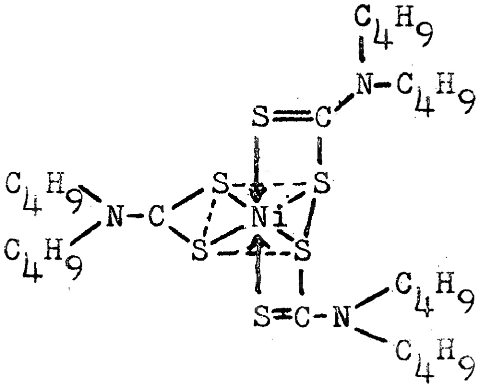

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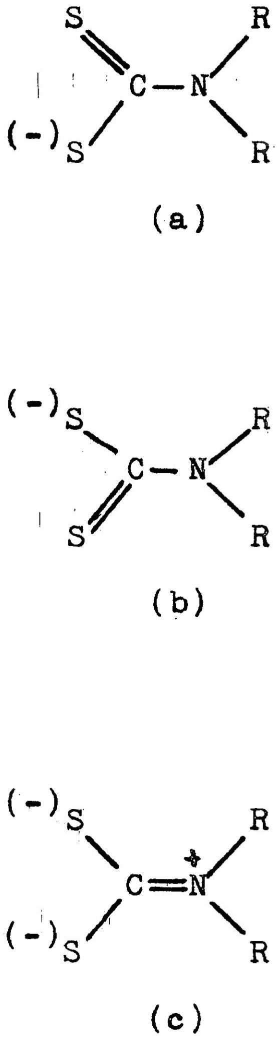
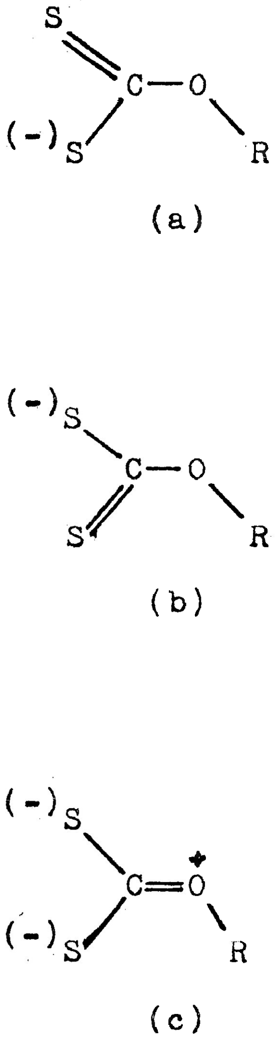

(a)

(b)

(c)

Figure X


(a)

(b)

(c)

Figure XI

ution to the structure of the complex than either of the structures shown in Figures X(a) and X(b).

Dithiophosphates (dtp^-), dithiocarbamates and xanthates have been found to occupy the following positions in the spectrochemical series[38]:

$$Br^- < Cl^- < dtp^- < F^- < R_2dtc^- <$$
$$RXan^- < H_2O < R_2S < NH_3 < SO_3^= <$$
$$NO_2^- \ll CN^-.$$

N.M.R. studies also suggest that the relative strengths of these ligands, as well as thioethylxanthate ($RSCS_2^-$), are[39]:

$$dtp^- < R_2dtc^- < RSCS_2^- < Xan^-.$$

It was noticed[38] that the ligand strength increases as the number of non-bonding electron pairs on the sulfur atom decreases (dtc^-=6, R_2S=4 and $SO_3^=$=2). This would imply that the dithiocarbamate ion has more electron density about the sulfur atom than does the xanthate ion. This is reasonable only if Figure XI(c) makes less contribution to the xanthate structure than does Figure X (c) to the dithiocarbamate structure. Previous independent and unrelated studies[36] resulted in the same conclusion as to the significance of the canonical shown in Figure XI(c). It is possible, therefore, that the bis(alkylxanthato)metal(II) complexes are not as stable as the corresponding dialkyldithiocarbamato complexes.

Although several bis(ethylxanthato)metal(II) complexes have been reported, including cadmium[40], palladium[41], platinum[41] and iron[42], it appears that only those of nickel and zinc have been examined crystallographically. While the nickel complex is square planar[43] (see Figure XII) like bis(diethyldithiocarbamato)nickel(II), the zinc complex is polymeric with the zinc atom being surrounded by a tetrahedron of sulfur atoms (Figure XIII), each coming from a different xanthate ion[44]. This difference in structure between the zinc complexes of diethyldithiocarbamate and ethylxanthate may reflect the difference in the electron donor ability of the nitrogen atom (for dithiocarbamate) and the oxygen atom (for xanthate). The fact that nickel(II) forms a tris complex with ethylxanthate[45] but not, as far as is known, with diethyldithiocarbamate may also reflect these different electron donor abilities. No bis(ethylxanthato)metal(II) species of either chromium or manganese appear to have been reported.

The square planar nickel(II)-dithiolate complexes have been studied in some detail. The dependence of the frequency of the d-d transition on the nickel-sulfur distance has been derived[46] to be

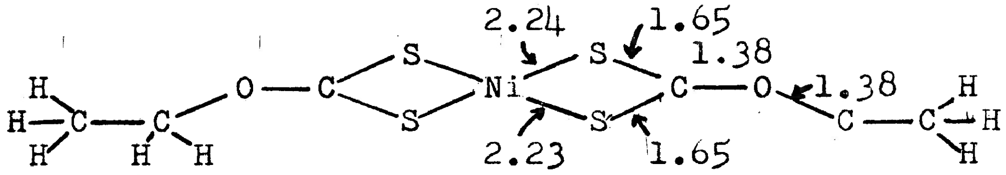


Figure XII

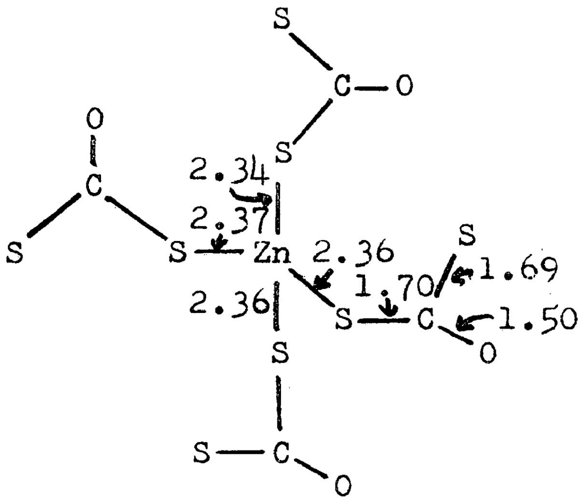


Figure XIII

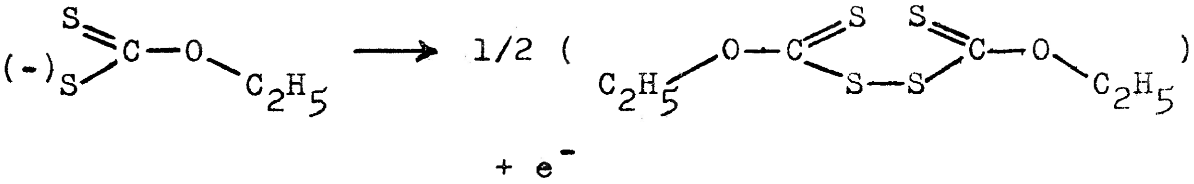
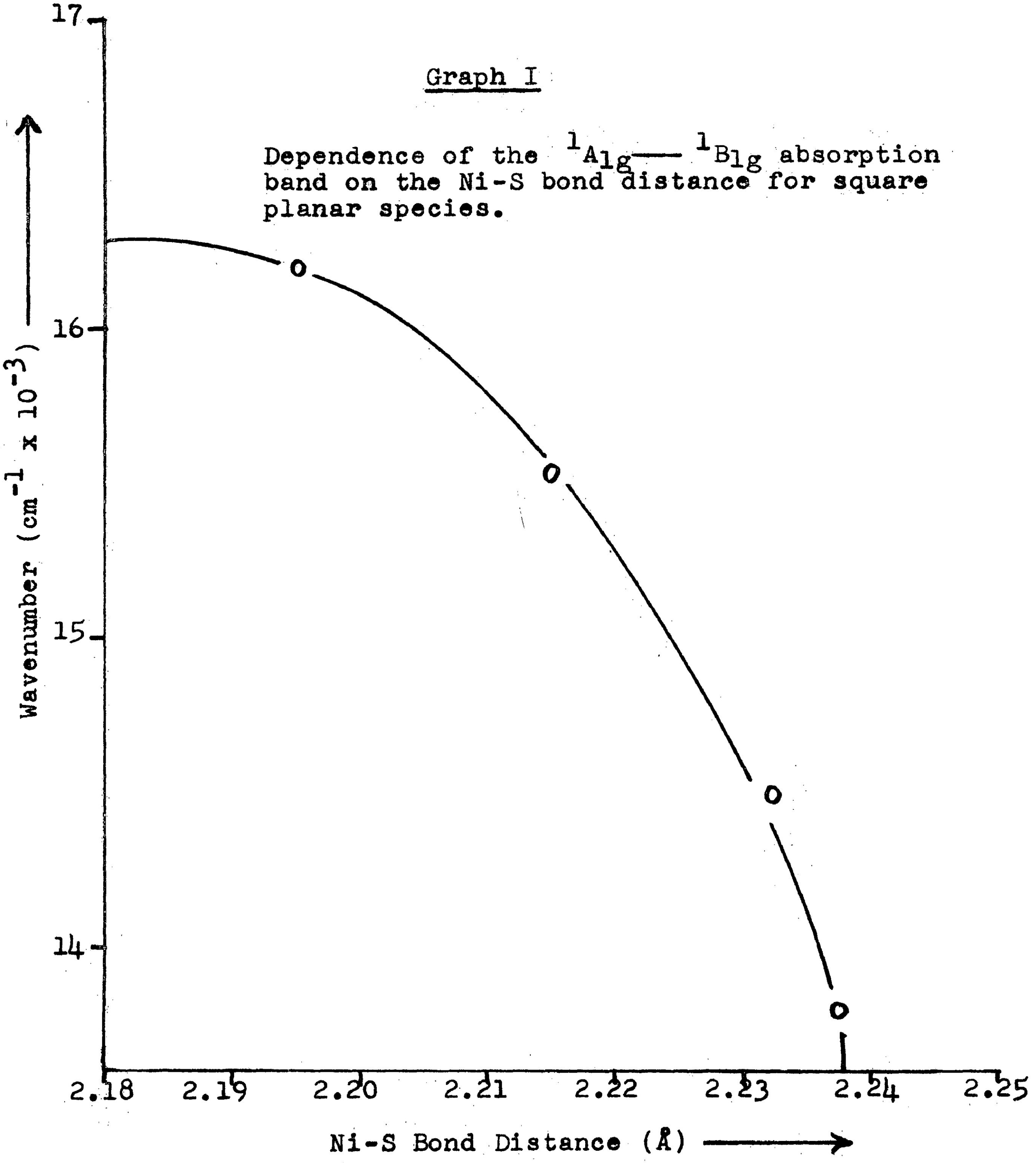


Figure XIV

as shown in Graph I. Since bis(ethylxanthato)nickel(II) has a nickel-sulfur distance[43] of 2.235 Å, its absorption band should occur about 14,500 cm^{-1}. Hence, its reported position[43] at 16,000 cm^{-1} requires verification. In solution, the band is found[43,38] between 15,500 cm^{-1} and 17,500 cm^{-1}, presumably depending on the solvent. A high extinction coefficient (about 67) is in keeping with a square planar species[75].

1.3-The Stability of Metal Oxidation States:

The stability of metal oxidation states in xanthate complexes is an intriguing phenomenon of these species. Of the many iron complexes to be reported (e.g: references 4,42,47,48,49,50), only one purports to involve the iron(II) species rather than the trivalent metal[42]. Virtually all chromium complexes involve a trivalent metal ion (e.g: references 10 and 51). The cobalt(II) ion has been reported to oxidize spontaneously to cobalt(III) in the presence of an alkylxanthate[52,54,55]. However it is possible[53] to form a bis(alkylxanthato)cobalt(II) complex, provided the alkyl group is large (e.g: isoamyl). Alternatively, the bis complex is reported[55] to form if the reaction between cobalt(II) and xanthate occurs in acid medium (e.g: pH value between 2.5 and 3.5



Graph I

Dependence of the $^1A_{1g}$ — $^1B_{1g}$ absorption band on the Ni-S bond distance for square planar species.

with sulfuric acid).

It has long been known[56] that n-butylxanthate will reduce copper(II) ions to copper(I). Confirmation of this report has recently been accomplished by two independent groups[57,58]. Indeed, this reduction forms the basis for the quantitative determination of alkylxanthate[11]. Also, nickel(II) has been reported[59] to reduce more easily in the presence of ethylxanthate. The explanation of these apparent anomolies became evident in 1968 when Shulman and Larinov reported[60] that the potential for the oxidation of ethylxanthate to diethyldixanthogen is 0.136 volts (see Figure XIV). Since the potential for the reduction of copper(II) to copper(I) is 0.15 volts, the potential for its reduction by ethylxanthate is +0.286 volts, making the reaction favorable. Similarly, silver[9] and gold[61] have been found to form monovalent complexes with alkylxanthates. The reduction of nickel(II) to metallic nickel has a potential of -0.23 volts. Hence in the presence of ethylxanthate, the "apparent" potential for the reduction is (-0.23+0.136) volts (i.e: -0.094 volts). This implies that the reductant need have a potential of only +0.094 volts rather than +0.23 volts.

The situation is further complicated, by several reports[3,4,62,63] of bis(alkylxanthato)copper(II) complexes. Indeed, it has been stated[63] that "from E.S.R. measurements of the reaction products between Cu(I) and $(RXan)_2$ in benzene solution, the formation of $Cu(RXan)_2$ was confirmed". Clearly, the ability or inability of copper(II) to reduce in the presence of ethylxanthate and of copper(I) to oxidize in the presence of dialkyldixanthogen requires further study.

There are also discrepancies regarding oxidation states in dithiocarbamate chemistry. Conflicting reports of the oxidation state of cobalt in diethyldithiocarbamate complexes have already been mentioned. In further work on this system, Bhatt and co-workers[64] have published studies purporting to include the bis(diethyldithiocarbamato)cobalt(II) complex despite a previous suggestion[65], by themselves, that the reaction between cobalt(II) sulfate and sodium diethyldithiocarbamate results in a complex in which the ratio between cobalt and the dithiolate is 1:3. Di(n-butyl)dithiocarbamate has also been shown[66] to oxidize metals such as copper(I), nickel(II), zinc(II), cadmium(II) and mercury(II).

1.4-Some Basic Adducts of Dithiolate Complexes:

It has been seen that the only bis(ethylxanthato)metal(II) complexes of first row transition metals to be studied extensively involve nickel(II) and zinc(II) (with one mention of iron(II)), while similar diethyldithiocarbamato complexes of chromium(II), manganese(II) and iron(II) are exceedingly air sensitive and the literature is contradictory regarding the oxidation state of cobalt in complexes with diethyldithiocarbamate. It is however significant that bis(diethyldithiocarbamato)1,10-phenanthrolinecobalt(II) is quite stable toward oxidation. It therefore appears that an investigation of the ability of nitrogen bases to stabilize some easily oxidized bis(ethylxanthato)metal(II) and bis(diethyldithiocarbamato)metal(II) complexes is warranted.

It has been suggested[45] that basic adducts of bis(dithiolato)metal(II) complexes will form more readily when the dithiolate is ethylxanthate than when it is diethyldithiocarbamate. This is probably a result of the dithiocarbamate species forming more stable complexes than the xanthate species, as has already been mentioned. The action of trisubstituted phosphines with bis(dithiolato)metal(II) complexes with palladium and platinum results[157] in a) the formation of a basic adduct and b) ligand substitution. When the dithiolate is diethyldithiocarbamate the reaction is very slow, as predicted. Also, if the dithiolate is diethyldithiophosphate, two moles of pyridine can be added, one at a time[69], to each mole of bis(diethyldithiophosphato)nickel(II). Studies of amine adducts of bis(dimethydithiocarbamato)zinc(II)[70] and bis(diethyldithiocarbamato)-zinc(II)[71] have been reported. The carbon-nitrogen stretching frequency shifts to lower energy in these adducts due to an increased electron density about the zinc atom.

The addition of pyridine to bis(ethylxanthato)-nickel(II) also results in a shifting of the carbon-oxygen stretching frequency to lower energy[45]. Pyridine has also been reported to break the iron-sulfur-carbon-sulfur ring in tris(alkylxanthato)iron(III), to form a pyridyl adduct[72]. Both these adducts of xanthate complexes have been found to have weaker metal-sulfur bonds and more ionic character than the corresponding adduct-free complex, as would be expected[72]. Unimolar amounts of copper(I) xanthate, bis(xanthato)nickel(II), and bis(xanthato)zinc(II) can accommodate 1,2 and 2 moles of pyridine, respectively[73]. A complex purported to be bis(ethylxanthato)2,2'-bipyridylnickel(II) was originally suggested to be four-coordinate[74], although Coucouvanis suggests it is probably six-coordinate[2]. Two independent groups[75,76] have recently verified, *via*.

spectrophotometric studies, that this complex is six-coordinate.

The nitrogen bases to be studied in this thesis are 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen). The potentials of various oxidation or reduction half-reactions of some metal complexes are listed in Table 1. It is evident that the potential for the reduction of bis(2,2'-bipyridyl)copper(II) in the presence of ethylxanthate would be 0.256 volts, indicating that is remains favorable. As the other potentials may be sufficiently negative to prevent the oxidation of the metals, the stabilization of these divalent states appears feasible.

It is interesting to compare the affinities for the first and second protons of 2,2'-bipyridyl and 1,10-phenanthroline. The data in Table 2, published by McBryde[81], show that 1,10-phenanthroline has a greater affinity for the first proton, but 2,2'-bipyridyl associates more strongly with the second proton. This is likely due to 2,2'-bipyridyl adopting a trans arrangement in solution (Figure XV). Hence the first proton can be attracted to both nitrogen atoms in 1,10-phenanthroline whereas the second must overcome the repulsion of the first proton. The stability constants of most metal chelates (i.e: $(ML_{n+1}) / (ML_n)(L)$) are usually about

Table 1

Some potentials for oxidation or reduction half-reactions.

Half-Reaction	E (volts)	Reference
$(Fe(bipy)_3)^{2+} \longrightarrow (Fe(bipy)_3)^{3+}$	-1.10	77
$(Fe(phen)_3)^{2+} \longrightarrow (Fe(phen)_3)^{3+}$	-1.10	78
$(Co(bipy)_3)^{2+} \longrightarrow (Co(bipy)_3)^{3+}$	-0.37	79
$(Cu(bipy)_2)^{2+} \longrightarrow (Cu(bipy)_2)^{+}$	0.12	80

Table 2

Stability constants for monoprotonated and diprotonated 2,2'-bipyridyl and 1,10-phenanthroline.

Stability Constant	L = bipy	L = phen
$\frac{(LH^+)\ (OH^-)}{(L)}$	$3.16 + 10^4$	$9.55 + 10^4$
$\frac{(LH_2^{2+})(OH^-)}{(LH^+)}$	10^{-5}	10^{-7}

ten times greater for 1,10-phenanthroline than for 2,2'-bipyridyl[82]. This may be due to some rotation about the C_9-C_{10} bond (see Figure XV) in 2,2'-bipyridyl, making at least one of the metal-nitrogen bonds weaker than for the rigid 1,10-phenanthroline (Figure XVI).

1.5-Structural Data:

Although x-ray K-absorption spectra have been utilized to study[83] the non equivalence of carbon-sulfur bonds in several bidentate sulfur ligands (including dialkyldithiocarbamates), many of the conclusions already reached as to the relative importance of the structures shown in Figures X(a), (b) and (c) for dialkyldithiocarbamates and Figures XI(a), (b) and (c) for alkylxanthates may be verified by an examination of data from detailed crystal structures.

The unusual coordination of the metals in the bis(diethyldithiocarbamato)metal(II) species has already been mentioned (section 1.2). Structural data on the nickel(II), copper(II) and zinc(II) complexes are listed in Table 3, along with numerous other complexes. The bis(diethyldithiocarbamato)-cadmium(II) complex is interesting in that it too exists as a square pyramidal dimer, the two halves being related by a center of symmetry[99]. The inter-

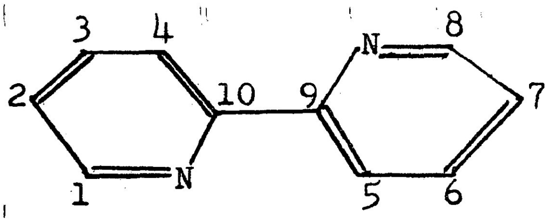


Figure XV

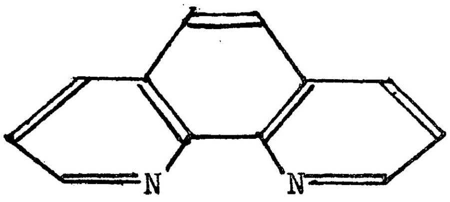


Figure XVI

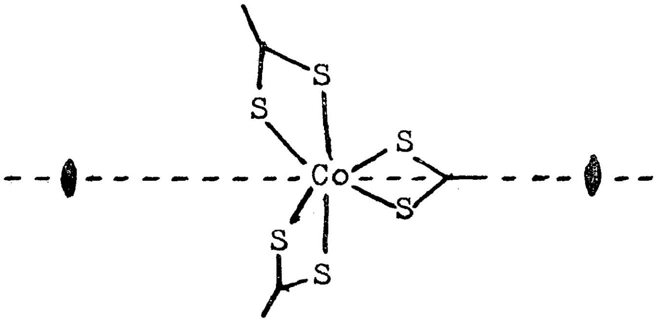


Figure XVII

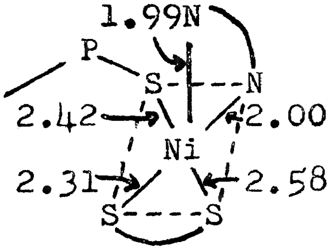


Figure XVIII

molecular metal-sulfur distance for this and the other dimers has been specified (Table 3). It is noticed also that the carbon-nitrogen stretching frequency varies by only about 90 cm^{-1}. This is helpful in assigning this peak in other complexes of diethyldithiocarbamate.

Several single-crystal studies have ascertained that the diethyldithiocarbamate complex of cobalt(III) belongs to the $C_{2/c}$ space group with a, b and c values of 14.10 Å, 10.29 Å and 17.04 Å respectively, leading Merlino to conclude that the structure shown in Figure X(c) makes about 40% contribution while the others contribute equally[90]. He asserts that this ratio of contribution is fairly constant regardless of the metal or configuration. Brennan and Bernal[101] suggest that the molecule deviates strongly from octahedral symmetry as shown in Figure XVII, with cobalt-sulfur distances of 2.270 Å, 2.268 Å and 2.263 Å, sulfur-carbon distances of 1.707 Å, 1.732 Å and 1.719 Å, and carbon-nitrogen distances of 1.315 Å and 1.303 Å. As carbon-sulfur double and single bond distances have been reported[103] at 1.57 Å and 1.80 Å, respectively, the carbon-sulfur distances reported for the cobalt(III) species[101] correspond to bond orders of 1.61, 1.70 and 1.65, respectively, (i. e: they appear to be very similar to those

Table 3

Structural data and C-N stretching frequencies for some dithiocarbamate complexes.

Compound	M-S (Å)	C-S (Å)	C-N (Å)	(C-N) $\mathrm{cm^{-1}}$	References
$\mathrm{Nadtc\cdot 3H_2O}$	1.3052	1.713 1.730	1.345	1477	84,85
$\mathrm{(dtc)_2}$	-	1.649 1.817	1.348	1495	86,68
$\mathrm{Fe(NO)(dtc)_2}$	2.30 2.28 2.26	-	-	-	87
$\mathrm{Fe(dtc)_2Cl}$	2.27 2.32	-	1.36 (1.31)	1500	88,89
$\mathrm{Co(dtc)_3}$	2.258	1.704	1.320	1489	36,90
$\mathrm{Ni(Rdtc)_2}$	2.208 2.211 2.218 2.224	1.68 1.70	1.38 1.37	1538	45,91,92
$\mathrm{(Cu(dtc)_2)_4}$	2.291 2.259 2.247	1.708	1.408	-	93
$\mathrm{Cu(dtc)_2}$	2.361 2.339 2.297 2.317* 2.851	1.717	1.34	1508	36,94,95,96
$\mathrm{Zn(dtc)_2}$	2.442 2.326 2.353 2.817* 2.390	1.728	1.326	1505	36,95,97
$\mathrm{Zn(Me_2dtc)_2\text{-}\cdot Pyr}$	(2.598 2.330 (2.612 2.325	(1.707 1.727 (1.707 1.732	-	-	98

Table 3, cont'd.

Compound	M-S (Å)	C-S (Å)	C-N (Å)	(C-N) cm^{-1}	References
$Cd(dtc)_2$	2.800 2.536	1.741 1.734	1.33	-	99,100
	2.544 2.547	1.725 1.714	1.33		
	2.644*				

*Intermolecular distance

reported by Merlino[90]). It seems unlikely that the slight difference in the reported carbon-sulfur disdistances (between the study done by Merlino[90] and that done by Brennan and Bernal[101]) constitutes a significant difference in the bond order.

An example of the structure of a basic adduct is illustrated by bis(dimethyldithiophosphato)2,9-methyl,1,10-phenanthrolinenickel(II) which has been found to have one monodentate and one bidentate dithiophosphate ligand, resulting in three unequal nickel-sulfur distances[104] (Figure XVIII).

Table 3 indicates that complexes of diethyldithiocarbamate often show similar carbon-sulfur bonds while the metal-sulfur bonds may not be equivalent. The carbon-nitrogen bond distances shown in this table verify the conclusion already mentioned, regarding the electron donation of the nitrogen atom. This results in a shortening of the carbon-nitrogen bond length from that of a single bond[105] (1.47Å) towards that of a double bond[105] (1.27Å). It follows, therefore, that canonical form X(c) makes a considerable contribution to the structure.

On the other hand, a lesser shortening of the carbon-oxygen bond distance in most xanthate species from that of a single bond[106] (1.42Å) towards that of a double bond[106] (1.12Å), is indicated in Table 4.

Table 4

Structural data for some xanthate complexes.

Compound	M-S (Å)	C-S (Å)	$C-S_2$ (Å)	C-O (Å)	References
KXan	3.321 3.387	1.72 1.69	1.66 1.67	1.34 1.35	107
$Ni(Xan)_2$	2.235	1.73	1.65	1.38	43
$Zn(Xan)_2$	2.362 2.337 2.364 2.369	1.70 1.70	1.61 1.69	1.42 1.33	44
$As(Xan)_3$	2.94 2.28	1.66	1.65	1.31	108
$Sb(Xan)_3$	3.00 2.52	1.70	1.59	1.36	109
$Pb(Xan)_2$	2.95 2.84 2.79 2.74	1.68 1.66	1.70 1.78	1.30 1.28	110
$Pb(i-PrXan)_2$·Pyridine	2.72 3.00	1.73	1.60	1.35	111
	2.83 2.90	1.57	1.74	1.43	
$CoXan_3$		1.67		1.67 1.36	48

Table 4, cont'd.

Compound	M-S (A)	C-S_1 (A)	C-S_2 (A)	C-O (A)	References
$CoXan_3$		1.67		1.67 1.36	48
$Ni(Xan)_3^-$	2.41(Average)				158

Hence, canonical form XI(c) appears to make less contribution to the structure of xanthates than does X(c) to that of dithiocarbamates. The minor contributions of canonical form XI(c) to the structure of the ligand was also implied[112] from a crystal study of tris(ethylxanthato)cobalt(III). Presumably this could also have been implied from a crystal study of tris(ethylxanthato)iron(III) which has been found[49] to crystallize in the same crystal system and space group ($R\bar{3}$), although earlier work[48] assigned different space groups to each compound. Finally, Table 4 also augments the suggestion, by Coucouvanis[2], that xanthate complexes often show unequal carbon-sulfur bonds.

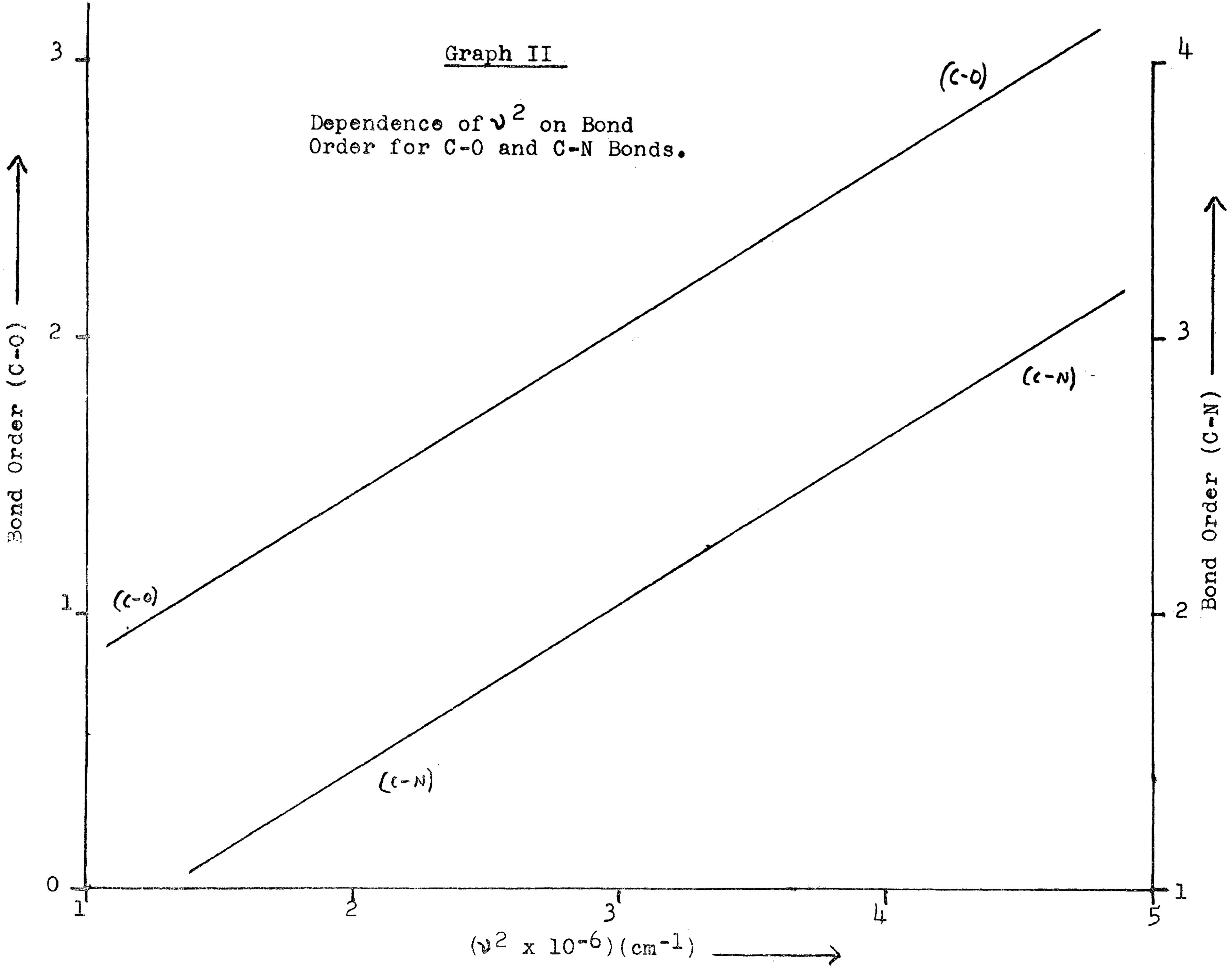
1.6-Infra-Red Spectra:

Having observed from the crystal structures that carbon-sulfur and metal-sulfur bonds in complexes of of ethylxanthate and diethyldithiocarbamate are not always equivalent, it follows that the assignment of the infra-red bands which are due to these bonds is of great interest. However, such studies are often difficult because of the complexity of such spectra and the resultant problems of assigning the many infra-red bands to various vibrational modes. For example, the carbon-sulfur stretching frequency in such complexes as bis(dithiocarbamato)lead(II)[121] and bis(diethyldithiocarbamato)nickel(II)[114] has been reported to be 622 cm^{-1} and 975 cm^{-1}, respectively. Presumably such major structural differences as might be implied by the great difference between the two reported stretching frequencies, should not be present in the two complexes.

Problems of interpretation also arise with complexes of such xanthates as n-butylxanthate[115]. In discussing bands in the 1130 cm^{-1} to 1137 cm^{-1} and 1200 cm^{-1} to 1277 cm^{-1} regions of the spectra of these complexes it has been stated that "no individual characteristic vibration exists for each group because the C-atom present in C-O, C=S and C-S has a smaller mass than the other atoms of the compounds and therefore their kinematic interaction is stronger and each characteristic vibration causes simultaneous changes in all three groups". Theoretical calculations suggest[116] that both the CO and C=S groups should absorb energy at approximately 1150 cm^{-1}. In the same article, these authors postulate the frequencies to be in the 1150 cm^{-1} to 1160 cm^{-1} (C=S) and 1010 cm^{-1} to 1080 cm^{-1} (CO) regions based on electronegativity considerations. In a subsequent publication[68] they reassess these assignments in the light of the spectra of additional complexes and conclude that the higher energy band corresponds to the C_1-O group (see Figure XIX) and the lower energy band to the C=S group. The assignments in this latter publication have been supported by other workers[117]. There are no other bands between 1020 cm^{-1} and 1070 cm^{-1} for $R_2C=S$ compounds when the sulfur atom is replaced by an oxygen atom[118]. Similarly, bands at 1110 cm^{-1} and between 1200 cm^{-1} and 1250 cm^{-1} for compounds with a C-O-C linkage are not observed in compounds without this linkage[118]. Further, the 1050 cm^{-1} band is not observed when the sulfur atom of ethylxanthate is replaced by selenium atoms[119].

The dependence of this C_1-O band as well as the $C\overset{\cdots}{-}N$ band of dithiocarbamate complexes on bond order has been shown by Fackler and Coucouvanis[120] to be as illustrated in Graph II. The $C\overset{\cdots}{-}N$ frequency has been assigned with overwhelming consistancy (e. g: Table 3), between 1480 cm^{-1} and 1570 cm^{-1}. It has also been suggested that a peak between 1418 cm^{-1} and 1437 cm^{-1} is due to a second $C\overset{\cdots}{-}N$ stretching mode[121].

In the foregoing discussion, a carbon-sulfur double bond was assumed to exist in complexes of xanthates and dithiocarbamates. This would imply that a carbon-sulfur single bond must also exist. The assignment of these bands, as well as the metal-sulfur bands, is the subject of some debate. The dependence of the carbon-sulfur stretching frequency on bond

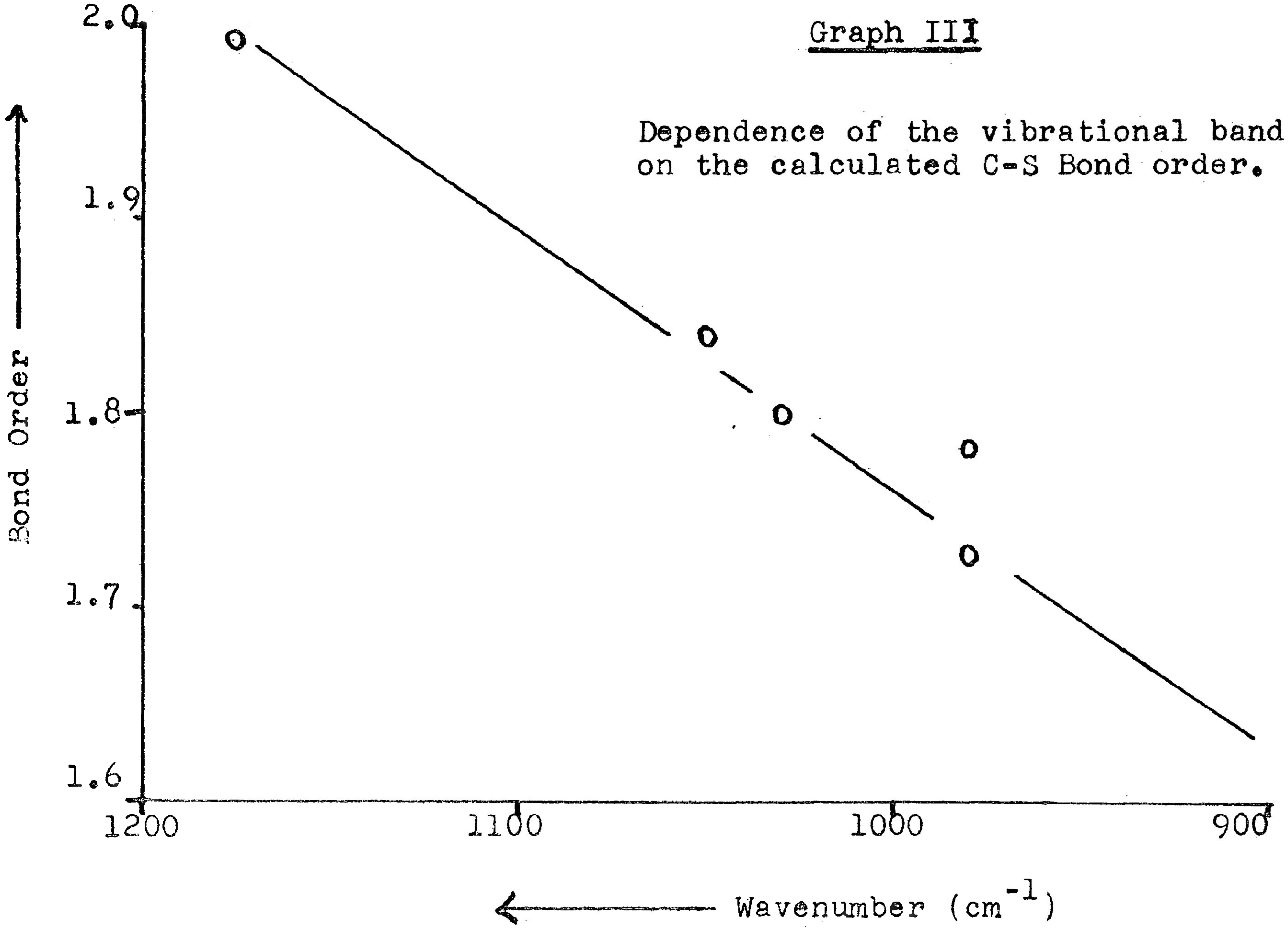


Graph II

Dependence of ν^2 on Bond Order for C-O and C-N Bonds.

order has been suggested[68] to be approximately linear for bond order between 1.7 and 2.0 (see Graph III). Bellamy[122] suggests that a carbon-sulfur single bond has a stretching frequency close to 650 cm^{-1}. Table 5 lists some postulated carbon-sulfur (single bond) and metal-sulfur stretching frequencies. If the band between 900 cm^{-1} and 1170 cm^{-1} for the compounds in group B (Table 5) is assumed to be the result of a carbon-sulfur double bond, it appears likely that there is usually one or two metal-sulfur bands between 300 cm^{-1} and 450 cm^{-1} and a carbon-sulfur band between 550 cm^{-1} and 600 cm^{-1} (only slightly below that suggested by Bellamy). Symmetric and assymetric modes may result in more than one band being observed in this region. Substitution of the sulfur atoms in some dithiocarbamate complexes in group D of Table 5 by selenium atoms[126] results in a carbon-selenium stretching frequency between 444 cm^{-1} and 461 cm^{-1}. These assignments are supported by two other publications[72,128]. It has also been suggested[129] that there may be several metal-sulfur bands between 400 cm^{-1} and 150 cm^{-1}.

It would seem likely, however, that many complexes of nickel and zinc, possess two similar carbon-sulfur bonds. On the basis of the preceding discussion, one might expect to observe these bands

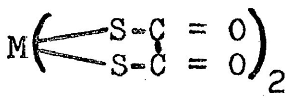
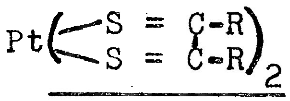


Graph III

Dependence of the vibrational band on the calculated C-S Bond order.

Table 5

Some M-S and C-S stretching frequencies.

Group	Compound	(M-S) cm^{-1}	(C-S) cm^{-1}	Reference
A	 M = Ni(II), Pd(II), Pt(II) and Co(II)	$420 \xrightarrow{322} 435$	$560 \rightarrow 575$	123
B		$310 \rightarrow 375$ $400 \rightarrow 435$	$560 \rightarrow 575$ $(900 \rightarrow 1170)$	124
C	$Ni(S_2P(OR)_2)_2 \cdot (N\text{-base})$	$325 \rightarrow 350$	-	125
D	$M(R_2dtc)_n$ $R = CH_3$ or C_2H_5 M = Co(III), Ni(II), Cu(II), Zn(II), or Cd(II)	-	$560 \rightarrow 580$	126
E	$Au(R_2dtc)_n$	380	-	127

somewhere between 700 cm^{-1} and 850 cm^{-1}. Alternatively, it has been suggested[130] that a carbon-sulfur single bond can absorb radiation as high as 835 cm^{-1}. It has also been suggested[131] that a band for a (C=S) species might be near 1250 cm^{-1}. Indeed, Graph III suggests[68] that such a species could give a band at 1200 cm^{-1} or greater. Finally, many studies of carbon-sulfur double bonds have involved xanthates or species of the type $(RO)_2C=S$ where electron resonance may easily lower the bond order from two. On this basis, it is possible that an absorption band due to two equivalent carbon-sulfur bonds could be found near 1050 cm^{-1}. A band in this region for many xanthate complexes [68,116,117] can thus be tentatively assigned as being the result (at least in part[115]) of such bonds.

It is not certain, therefore, whether Figure XX(a) or XX(b) makes the greater contribution to the structure of complexes of ethylxanthate. Since potassium ethylxanthate is reported to have carbon-sulfur bond distances corresponding to bond orders of 1.15, 1.33, 1.5 and 1.66 its infra-red spectrum might provide some interesting information[107].

The position of the metal-nitrogen stretching frequency is also the subject of some dispute. Table 6 lists several assigned metal-nitrogen frequencies for various complexes. There is apparently a great tendency to assign these frequencies between

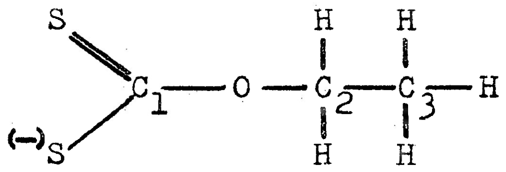


Figure XIX

(a)

(b)

Figure XX

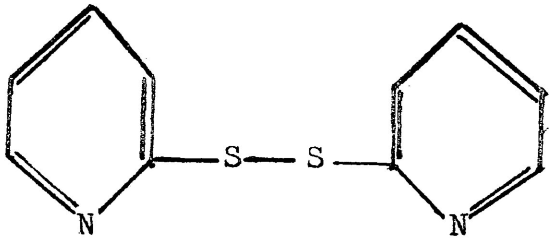


Figure XXI

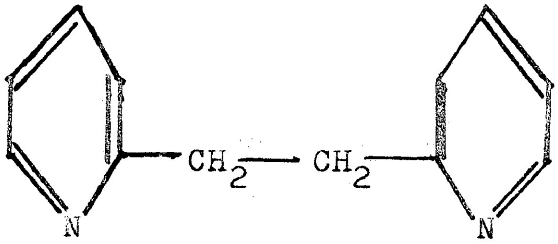


Figure XXII

Table 6

Some M-N vibrational frequencies.

Compound	ν(M-N) (cm^{-1}) L = Pyr	 L = bipy	 L = phen	References
$(FeL_3)^{2+}$		423	530	132
$(CoL_3)^{2+}$		264	288	
$(NiL_3)^{2+}$		286	294	
$(CuL_3)^{2+}$		297	300	
$(ZnL_3)^{2+}$		280	288	
$(FeL_3)^{2+}$			298,525	133
$(FeL_2)^{2+}$			285	
Cu/L	220			134
Co/L	240			
$(Cu(OH)L)_2^{2+}$		$265 \rightarrow 278$	$291 \rightarrow 303$	135

Table 6, cont'd.

ν(M-N) (cm^{-1})

Compound	L = Pyr	L = bipy	L = phen	References
$CuL_2(ClO_4)_2$		316		136
$(Cu(OH)L(NO_3))_2$		271;246		
$(Cu(OH)L(NO_3))$		278;256		
ML_3		< 200		137
SnL_x		$\lesssim 200$		138

200 cm^{-1} and 300 cm^{-1} with the exception of iron complexes in which they are assigned in the 400 cm^{-1} to 550 cm^{-1} region. Very recently, studies[139] on cobalt, nickel, zinc and mercury complexes of the ligands shown in Figures XXI and XXII revealed bands in this region which have been assigned to metal-nitrogen stretching frequencies. The occurance of two bands in some species may be due to symmetric and asymmetric modes as with the metal-sulfur bands. Clark and Williams[137], however, point out that since 1)an increase in oxidation state of the metal increases the metal-ligand stretching frequency and 2)there are no bands above, <u>ca</u>. 250 cm^{-1}, in trivalent metal-bipyridyl complexes, then the bands between 200 cm^{-1} and 300 cm^{-1} are probably not due to metal-nitrogen stretching frequencies. Also, since 1)the band in the 400 cm^{-1} to 500 cm^{-1} region is known to be due to an out-of-plane ring deformation, 2)the band in this region is independent of the oxidation state and stereochemistry of the metal and 3)prominent peaks appear in this region for pure 2,2'-bipyridyl and 1,10-phenanthroline, this peak also should not be assigned to the metal-nitrogen stretching mode[137]. It is further suggested that, since the metal-nitrogen stretching frequency is in the 200 cm^{-1} to 300 cm^{-1} region for ammonia complexes, it would be necessary for the

force constants of 2,2'-bipyridyl and 1,10-phenanthroline complexes to be much greater (due to the increased mass) if the metal-nitrogen mode was to remain in this region[137]. Since such an increase in force constant is not likely, it is suggested that the metal-nitrogen stretching frequency lies below 200 cm^{-1} in these complexes. Probably a normal coordinate analysis of a complex of 2,2'-bipyridyl or 1,10-phenanthroline, in the 50 cm^{-1} to 650 cm^{-1} region will be necessary to resolve the dispute.

1.7-Summary:

From the foregoing discussion, it is apparent that the inability to prepare tris(diethyldithiocarbamato)metalate(II) anions warrants some verification. Also, the tendency of ethylxanthate and diethyldithiocarbamate to oxidize or reduce various divalent transition metal halides, and of 2,2'-bipyridyl and 1,10-phenanthroline as well as various solvents to stabilize the divalent species, requires further study. Finally, a careful study of the infra-red bands of many dithiolato complexes (and their adducts) may augment the current knowledge regarding the frequencies of the carbon-nitrogen, carbon-oxygen, carbon-sulfur, sulfur-metal and metal-nitrogen stretching modes.

In an attempt to obtain some of this information, syntheses and properties of the following complexes were studied:

1) tris(diethyldithiocarbamato)metalate(II) complexes with first row transition metals,

2) tris(ethylxanthato)metalate(II) and bis(ethylxanthato)metal(II) species of as many first row transition metals as possible*, and

3) adducts of the type $ML_2 \cdot nB$, where:

M = a first row transition metal,
L = (Xan^-) or (dtc^-)**,
n = a number to be determined, and
B = bipy or phen.

Also, visible and near infra-red spectra, as well as the magnetic moments, were studied to ascertain the electronic state of the metal atom. Finally, unexpected structural properties in the bis(ethylxanthato)2,2'-bipyridylmetal(II) series prompted electrical conductivity and molecular weight studies of this series as well as the similar bis(ethylxanthato)1,10-phenanthrolinemetal(II) series in the hope of gleaning more relevant information.

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*A preliminary investigation of this work was executed as a project leading to a Bachelor of Science(Hon.) degree.

**My appreciation is expressed to Dr. D. G. Holah for first isolating the bis(diethyldithiocarbamato)-2,2'-bipyridylmetal(II) series and the analogous 1,10-phenanthroline complexes of manganese, iron, cobalt and zinc. Attempts to prepare similar complexes with copper, resulted in the precipitation of bis(diethyldithiocarbamato)copper(II). Attempts to prepare the 2,2'-bipyridyl adduct of nickel also resulted in the synthesis of the bis complex, whereas attempts to prepare the 1,10-phenanthroline adduct led to the tris(1,10-phenanthroline)nickel(II) diethyldithiocarbamate complex.

2. EXPERIMENTAL

Reagent grade chemicals were used without further purification in all the syntheses and were usually at least 98% pure. The hydrated chromium(II) chloride was obtained[140] from the action of concentrated, oxygen-free hydrochloric acid on chromium metal in a nitrogen atmosphere. The precipitate was filtered, dried *in vacuo* and stored in a stoppered flask under a nitrogen atmosphere. All preparations involved approximately 500 - 1500 mg of crude product from a total solvent volume of approximately 5 - 15 mls.

Due to the oxygen sensitivity of some of the complexes, various portions of their preparations were executed in a glove box which was continually flushed with dry, oxygen-free nitrogen. When not in use, the glove box was maintained at a positive pressure to reduce the inward diffusion of air. The solvents were degassed with oxygen-free nitrogen and stored in the glove box over molecular sieves.

2.1-Attempts to prepare tetraethylammonium tris(diethyldithiocarbamato)metalate(II) complexes:

The following attempts were made to prepare the tetraethylammonium tris(diethyldithiocarbamato)metalate (II) complexes of nickel, copper and zinc. Equimolar amounts of tetraethylammonium chloride and the metal chloride were dissolved in either water or ethanol. To this, a solution of sodium diethydithiocarbamate (in the same solvent) was added until the tetraethylammonium chloride:metal chloride:dithiocarbamate mole ratio was 1:1:3. The resultant mixture was often refluxed for as much as 18 hours. Alternatively, the bis(diethyldithiocarbamato)metal(II) complex was dissolved in ethanol to which equimolar quantities of tetraethylammonium chloride (first) and then sodium diethyldithiocarbamate were added. In no case was any of the tris complex obtained, the only products being the bis complex and starting materials.

The aqueous reaction with cobalt(II) chloride resulted in the oxidation of the cobalt and the formation of the well known, dark green tris(diethyldithiocarbamato)cobalt~~ate~~(III) complex[31,90,101]. The product was also obtained when the tetraethylammonium chloride was omitted. This same product was obtained by following exactly the procedure described by D'Ascenzo and Wendlandt[32] for the synthesis of a complex claimed to be sodium tris(diethyldithiocarbamato)cobaltate(II). The product obtained by following this procedure[32] was characterized as tris(diethyldithiocarbamato)cobalt(III) by visible spectroscopy, mass spectrometry and the fact that it is x-ray isomorphous with the product[141] obtained by reacting iron(III) chloride with sodium diethyldithiocarbamate in a 1:3 molar ratio, namely tris(diethyldithiocarbamato)iron(III)[142].

2.2-Attempts to prepare bis(ethylxanthato)metal(II) complexes:

2.2.1-Manganese-

An aqueous solution of potassium ethylxanthate was added to one of manganese(II) chloride until the mole ratio was 2:1, respectively. The resultant yellow solid is appreciably soluble in water and therefore the potassium chloride could not be removed by repeated washing with water. An acetonitrile solution of the yellow precipitate, which had been dried *in vacuo* and transferred to the glove box, moved rapidly down an alumina chromatography column (deactivated with ethylacetate), effectively removing all the potassium chloride. The liquor was then concentrated *in vacuo*, and pure crystals obtained by adding either benzene or ether. The solid decomposes in air within several hours, while solutions in organic solvents are oxidized immediately when exposed to oxygen. (Calculated for $Mn(S_2COC_2H_5)_2$: Mn = 18.5%, C = 24.2%, H = 3.4%. Found : Mn = 18.5%, C = 22.9%, H = 3.5%.)

2.2.2-Iron-

An oxygen-free aqueous solution of potassium ethylxanthate was added to one of iron(II) chloride, in a nitrogen atmosphere, until the mole ratio was 2:1 respectively. The red product was purified in the same manner as the x-ray isomorphous manganese complex. Both the solid and organic solutions are extremely sensitive to oxygen. The bright red solid begins to darken, even when stored in a stoppered tube under nitrogen, within twenty-four hours, becoming completely black within five days. (Calculated for $Fe(S_2COC_2H_5)_2$: C = 24.2%, H = 3.4%. Found : C = 23.7%, H = 3.4%.)

2.2.3-Cobalt-

The addition of an ethanolic solution of potassium ethylxanthate to one of cobalt(II) chloride, in a nitrogen atmosphere, resulted in the immediate oxidation of the cobalt. The same product (tris(ethylxanthato)cobalt(III)) was obtained from an oxygen-free sulfuric acid (1:10) solution, following the same procedure as with organic solvent and was identical in all respects with an authentic sample prepared by literature methods[143].

2.2.4-Nickel-

This complex was synthesized by a method similar to that reported in the literature[43]. (Calculated for $Ni(S_2COC_2H_5)_2$: Ni = 19.5%. Found : Ni = 18.8%.)

2.2.5-Copper-

Adding an aqueous solution of copper(II) chloride to one of potassium ethylxanthate (mole ratio 1:2, respectively) resulted in reduction of the copper and the formation of copper(I) xanthate along with dixanthogen. The same products were obtained in dilute ammonium hydroxide solution (at an approximate pH value of 11). This yellow product was identical and x-ray isomorphous with an authentic sample of copper(I) ethylxanthate obtained from the aqueous reaction of copper(I) chloride with potassium ethylxanthate.

2.2.6-Zinc-

This was prepared following literature methods[44]. (Calculated for $Zn(S_2COC_2H_5)_2$: Zn = 21.3%. Found : Zn = 21.5%.)

2.3-Attempts to prepare tetraethylammonium tris(ethylxanthato)metalate(II) complexes:

2.3.1-Chromium-

Addition of an ethanolic solution of potassium ethylxanthate to one of tetraethylammonium chloride and chromium(II) chloride hydrate in the glove box, resulted in a black residue, indicative of oxidation of the chromium.

2.3.2-Manganese-

The oily product, obtained by adding an aqueous solution of potassium ethylxanthate to one of manganese(II) chloride and tetraethylammonium chloride until the mole ratio was 3:1:1 respectively, was found to solidify upon scratching. After drying, in vacuo, the yellow complex was transferred to a glove box and recrystallized with ether, first from methylene chloride (to remove the potassium chloride), and then from acetonitrile. (Calculated for $(N(C_2H_5)_4)(Mn(S_2COC_2H_5)_3)$: Mn = 10.0%., C = 37.2%, H = 6.4%. Found : Mn = 10.4%, C = 37.4%, H = 6.4%.)

2.3.3-Iron-

The red complex was prepared in the glove box using oxygen-free water, by a method similar to that used for the preparation of the analgous manganese(II) complex. (Calculated for $(N(C_2H_5)_4)$ $(Fe(S_2COC_2H_5)_3)$: Fe = 10.2%. Found : Fe = 10.0%.)

2.3.4-Cobalt-

The addition of an ethanolic solution of potassium ethylxanthate to one of cobalt(II) chloride and tetraethylammonium chloride in the glove box such that the mole ratio was 3:1:1, respectively, resulted in oxidation of the cobalt. The same product (tris(ethylxanthato)cobalt(III)) was obtained from an oxygen-free sulfuric acid solvent (1:10), following the same procedure as with the organic solvent.

2.3.5-Nickel-

This complex which is x-ray isomorphous with the analogous iron complex was synthesized following the method described in the literature[45]. (Calculated for $(N(C_2H_5)_4)(Ni(S_2COC_2H_5)_3)$: Ni = 10.6%. Found : Ni = 9.9%.)

2.3.6-Copper-

Addition of potassium ethylxanthate to tetraethylammonium chloride and copper(II) chloride in dilute ammonium hydroxide (at an approximate pH value of 11 and a mole ratio of 3:1:1, respectively) gave a red "gummy" product which, upon scratching, became a yellow precipitate. This product was x-ray isomorphous with the product obtained from the attempted synthesis of bis(ethylxanthato)copper(II).

In aqueous solution, a brown oil was obtained which would not solidify. Likewise, the aqueous reaction of potassium ethylxanthate with tetraphenylarsonium chloride and copper(II) chloride (mole ratio 3:1:1, respectively) gave a reddish-brown syrup which would not solidify, even under a vacuum of 10^{-6} torr.

2.3.7-Zinc-

The crude product was obtained in a manner identical to that for the analgous manganese(II) complex. The recystallization from acetonitrile was critically dependent on the acetonitrile:ether ratio, an insufficient amount of the pure white complex being obtained for a metal analysis.

Several attempts to resynthesize this complex, both in water and in ethanol, resulted in oily products. No suitable solvent system was found to solidify the oils.

2.4-Attempts to prepare bis(ethylxanthato)2,2'-bipyridylmetal(II) complexes:

The syntheses of these complexes are interesting in that two phases (α and β) were obtained for the complexes of iron, cobalt and nickel. Whereas none of the β-phases were x-ray isomorphous with each other, the α-phases were all x-ray isomorphous with the manganese complex. Also, the bis(ethylxanthato)-2,2'-bipyridylzinc(II) complex was not x-ray isomorphous with any other phase, hence it was arbitrarily labelled a β-phase.

It is curious that low yields (<u>ca</u>: between 25% and 40%) were obtained for most of the reactions. It is also true that the procedures outlined below, although usually satisfactory, did on occasion yield unexpected products which were not reproducable. The reason for the low yields and unexpected products is not fully understood, although decomposition to unidentified and often amorphous products is suspected to be a heavily contributing factor. Indeed, many of the solid complexes, particularly with bipyridyl, are even unstable after they have been isolated and, in most cases, it proved impossible to store the compounds for any length of time. Samples for organic microanalysis were sealed under vacuum and were analyzed by F. Pascher, Bonn, West Germany. All samples were returned for a purity check (x-ray powder photograph and/or infra-red spectrum) after the analyses, and in some cases, decomposition had clearly occurred. Considerable effort was made to analyze the complexes for metal ions both gravimetrically and volumetrically, but no consistency was obtained, presumably because of the interference of sulfur or organic residues still present even after extensive treatment of the complexes with concentrated acids. Much use, therefore, has been made of x-ray powder photographs in the identification of various products.

2.4.1-Chromium-

The addition of potassium ethylxanthate to an ethanolic solution of 2,2'-bipyridyl and chromium(II) chloride gave a bluish precipitate whose reflectance spectrum (Appendix IV) suggested the presence of some octahedral chromium(II) ions. As attempts at isolating and purifying this species were unsuccessful, its presence could not be verified.

2.4.2-α-Manganese-

A crude precipitate was obtained by adding an aqueous potassium ethylxanthate solution to one of manganese(II) chloride and 2,2'-bipyridyl (mole ratio = 2:1:1, respectively). After drying *in vacuo*, bright yellow crystals were obtained by adding ether to a methylene chloride solution of the complex. The fact that several recrystallizations were often necessary to obtain a pure product, probably reflects some decomposition in solution. Indeed, the solid was found to decompose within hours in the atmosphere, resulting in an amorphous phase, but more slowly (several days) when stored under nitrogen. Two organic micro-analyses on different samples gave the following results: C = (38.2%, 39.4%), H = (3.6%, 3.8%), N = (5.3%, 5.4%), whereas the theoretical results for $Mn(S_2COC_2H_5)_2 \cdot bipy$ are: C = 42.5%, H = 4.0%, N = 6.2%. The low and inconsistent values found for this species suggest it had decomposed prior to analysis (although it had been stored for only a few days under vacuum). This suggestion is augmented by the fact that the sample was x-ray isomorphous with the α-$Co(Xan)_2 \cdot bipy$ complex, for which a good analysis was obtained.

2.4.3-β-Iron-

A crude red precipitate was obtained in the same manner as the crude precipitate of the analogous manganese(II) complex. Washing with water often removed most of the impurities, but no suitable method was found for recrystallization. Most organic solvents resulted in either oxidation of the iron or transformation of the complex to the α-phase. Although addition of acetonitrile resulted in a bright red solution, it was not possible to recover a crystalline solid. Column chromatography, using ethyl-acetate-deactivated alumina also proved inadequate as the β-phase could not be recovered from solution. (Calculated for $Fe(S_2COC_2H_5)_2\cdot bipy$: C = 42.4%, H = 4.0% and N = 6.2%. Found : C = 42.0%, H = 3.8% and N = 6.37%.)

2.4.4-α-Iron-

A pure brown solid was obtained by recrystallizing a deep blue methylene chloride solution of of the β-phase with ether. The solid was found to become red and amorphous after several days. Also, on a few occasions, a dark green methylene chloride solution was obtained which did not yield a consistent phase upon addition of the ether. Column chromatography of the deep blue solution, when obtained, did not result in any phase other than the α-phase.

The analysis was inferred from the x-ray isomorphous cobalt(II) complex.

2.4.5-α-Cobalt-

Potassium ethylxanthate was added in a glove box to a mixture of hexa(aquo)cobalt(II) chloride and 2,2'-bipyridyl in acetone, such that the mole ratio was 2:1:1, respectively. The resultant mixture was centrifuged and the liquor was decanted from the insoluble potassium chloride. Removing the acetone *in vacuo* gave olive-brown crystals which could be recrystallized from methylene chloride with ether. (Calculated for $Co(S_2COC_2H_5)_2 \cdot bipy$: C = 42.0%, H = 3.9%, N = 6.1%. Found : C = 42.7%, H = 4.5%, N = 6.2%.)

2.4.6-β-Cobalt-

The crude product was obtained in a manner identical to that of the analogous manganese(II) complex. Recrystallization was effected in the glove box with high boiling petroleum ether from benzene to give a brown product. (Calculated for $Co(S_2COC_2H_5)_2 \cdot bipy$: C = 42%, H = 3.9%, N = 6.1%. Found : C = 41.0%, H = 3.7%, N = 5.4%.)

2.4.7-β-Nickel-

This brown complex was prepared and purified in a manner similar to the analogous manganese(II) complex. The aqueous mixture of the crude product was allowed to stand for several days before being dried and recrystallized,as this resulted in substantially increased yields of product. An obnoxious odour (similar to hydrogen sulfide) suggested some decomposition to sulfur-containing side products. (Calculated for $Ni(S_2COC_2H_5)_2 \cdot bipy$: C = 42.0%, H = 4.0%, N = 6.1%. Found : C = 41.3%, H = 3.9%, N = 6.1%.)

2.4.8-α-Nickel-

A methylene chloride solution of the β -phase was run down an alumina chromatography column (deactivated with ethylacetate). Ether was added to the resultant green solution, but since no solid appeared at this point, the solvents were removed *in vacuo*, giving olive-brown crystals. Occasionally, however, a brown layer was obtained in addition to the green layer. Crystals of the β -phase were precipitated, when ether was added to a concentrated solution of this brown layer. The analysis of the α-phase was inferred from the x-ray isomorphous cobalt-(II) complex.

2.4.9-Copper-

Addition of potassium ethylxanthate to a solution of 2,2'-bipyridyl and copper(II) chloride, in either water or dilute ammonium hydroxide (with a pH value of 11, approximately), such that the mole ratio was 2:1:1, respectively, resulted in a red precipitate, which yielded yellow copper(I) ethylxanthate in organic solvents. The production of this yellow complex and infra-red evidence suggests the reaction results in oxidation of the ethylxanthate ions by the copper(II) ions.

2.4.10-β-Zinc-

This white complex was synthesized in a manner strictly identical to the preparation of the manganese(II) complex. (Calculated for $Zn(S_2COC_2H_5)_2 \cdot$ bipy : C = 41.5%, H = 3.9%, N = 6.0%. Found : C = 42.0%, H = 3.7%, N = 6.2%.)

A second phase was often obtained whose infra-red spectrum suggests the presence of 2,2'-bipyridyl and, perhaps, ethylxanthate. Insolubility prevented NMR, electrical conductivity, and molecular weight studies, while the chemical analysis (40.3%C, 3.5%H and 7.5%N) is difficult to interpret, in any reasonable way.

2.5-Attempts to prepare the bis(ethylxanthato)1,10-phenanthrolinemetal(II) complexes:

Although these preparations are somewhat more reliable than those of the 2,2'-bipyridyl adducts, the occurrence of low yields (less than 50%) again suggests some decomposition or side reactions.

2.5.1-Chromium-

The addition of potassium ethylxanthate to an oxygen-free ethanol solution of chromium(II) chloride and 1,10-phenanthroline resulted in the oxidation of chromium(II) to chromium(III).

2.5.2-Manganese-

An aqueous solution of potassium ethylxanthate was added to one of manganese(II) chloride and 1,10-phenanthroline, so that the resultant mole ratio was 2:1:1, respectively. After drying *in vacuo*, pure yellow crystals were obtained by adding ether to a methylene chloride solution of the complex. (Calculated for $Mn(S_2COC_2H_5)_2 \cdot phen$: C = 45.3%, H = 3.8%, N = 5.9%. Found : C = 45.3%, H = 3.8%, N = 6.0%.)

2.5.3-Iron-

This red-blue solid was synthesized in a manner identical to that for the analogous manganese(II) complex. The occurrence of a deep blue methylene chloride solution, suggests that this species is similar to α-bis(ethylxanthato)2,2'-bipyridyliron(II). (Calculated for $Fe(S_2COC_2H_5)_2 \cdot phen$: C = 42.5%, H = 3.8%, N = 5.9%. Found : C = 46.0%, H = 3.9%, N = 6.2%.)

2.5.4-Cobalt-

This brown complex was prepared in a manner similar to that for the analogous manganese(II) complex, the recrystallization being executed in a glove box. This product appeared to be stable indefinitely in the absence of oxygen. (Calculated for $Co(S_2COC_2H_5)_2 \cdot phen$: C = 44.9%, H = 3.8%, N = 5.8%. Found : C = 45.3%, H = 3.6%, N = 6.0%.)

2.5.5-Nickel-

This brown complex was synthesized in a manner identical to the preparation of the analogous manganese(II) complex. The original "gummy" product obtained upon adding ether to the methylene chloride solution, solidified if allowed to stand for a few minutes after vigorous scratching. Occasionally, the solid was found to be either amorphous or only slightly crystalline. The analysis was inferred from the x-ray isomorphous cobalt(II) complex.

2.5.6-Copper-

Attempts to prepare this adduct in the same fashion as the attempted preparation of the 2,2'-bipyridyl adduct, also resulted in a red precipitate, suspected to contain copper(I). An identical, x-ray isomorphous product was obtained by the addition of potassium ethylxanthate to a solution of copper(I) chloride and 1,10-phenantholine (in a 1:1:1 molar ratio). Again, copper(I) ethylxanthate was obtained upon adding an organic solvent to the red product. The theoretical analysis (C = 44.5%; H = 3.7%; N = 5.8%) of a mixture of $Cu(S_2COC_2H_5)\cdot$phen and dixanthogen (molar ratio = 2:1) closely approximates the analysis obtained on the product obtained from the reaction with copper(II) chloride (C =42.2%; H = 3.9%; N = 6.5%). This and infra-red evidence strongly suggests the oxidation of ethylxanthate by copper(II) in this reaction.

2.5.7-Zinc-

Potassium ethylxanthate was added to a suspension of zinc chloride and 1,10-phenanthroline in methylene chloride such that the mole ratio was 2:1:1, respectively. The solution was decanted from the insoluble potassium chloride and the white complex precipitated in good yield by addition of ether. (Calculated for $Zn(S_2COC_2H_5)_2\cdot$phen : C = 44.4%, H = 3.7%, N = 5.7%. Found : C = 44.6%, H = 3.5%, N = 5.8%.)

2.6-Physical Measurements:

2.6.1-X-ray Powder Photographs-

Samples of finely ground complexes were sealed in Lindemann capillaries and the powder photograph measured on a 114.83 millimeter diameter Debye-Scherrer camera. The air sensitive samples were packed in a glove box, the top of the capillary sealed with vacuum grease, and the capillary then sealed in a flame outside the glove box. The films were exposed on a Philips PW 1010 x-ray generator for one hour at 40 kV and 20 mA, using a nickel-filtered copper-K-αradiation source.

2.6.2-Infra-Red Spectra-

The infra-red spectra were recorded on a Beckman IR 12 spectrophotometer, calibrated periodically with polyethylene. Nujol mulls of the samples were spread between potassium bromide plates for the 4000 cm^{-1} to 400 cm^{-1} region and between polyethylene plates for the 650 cm^{-1} to 200 cm^{-1} region.

Also, hexachlorobutadiene mulls of the dithiocarbamate complexes were used between potassium bromide plates in the 1300 cm^{-1} to 1600 cm^{-1} region to obtain the carbon-nitrogen stretching frequency which occurred near 1500 cm^{-1} and was, therefore, masked by a nujol band.

2.6.3-Visible and Near-Infra-Red Spectra-

A Cary 14 recording spectrophotometer was used to measure the d-d transitions in the 30,000 cm^{-1} to 5,000 cm^{-1} region. A reflectance attachment was used to obtain spectra of the complexes in the solid state, the samples being contained in a circular brass cell with a quartz window. Tightening the quartz window against a rubber o-ring (which was inserted between the window and the brass sample compartment) and covering the o-ring with vacuum grease rendered the cell air-tight. The spectra were recorded against a magnesium carbonate reference.

Solution spectra were recorded in carefully balanced infrasil cells with a path length of one centimeter and volumes of 2.5 millilters. Carefully removing the solvent, in vacuo, from the cells enabled the weight of the solute to be determined, and hence the molar extinction coefficient. Either acetonitrile or methylene chloride was used as a solvent.

2.6.4-Magnetic Measurements-

The magnetic susceptibilities were measured on a Gouy balance constructed at this institute, using a Mettler H 20 semi-micro balance and a water-cooled, Varian V-4005 electromagnet (requiring one kilowatt per coil). A Varian V-2900 power supply with less than 5 PPM current instability (giving a field ripple of less than 10 mG) was used in conjunction with the electromagnet. A double-ended pyrex glass Gouy tube was also constructed at this institute, and calibrated with mercuri tetra(thiocyanato)cobaltate(II), tris(ethylenediamine)-nickel(II) thiosulfate and copper(II) sulfate penta-hydrate. A more complete description of the apparatus and its use is contained in Appendix I. The calibration and subsequent susceptibilities were calculated at fields of 5.8 kG and 6.9 kG and the average value used in calculations, along with a (T+θ) value of 300 degrees (equation (7) in Appendix I). The diamagnetic corrections used were those listed in Lewis and Wilkins[144].

2.6.5-Electrical Conductivities-

The conductivities were measured in nitromethane, at four different concentrations, on a YSI model 31 conductivity bridge. The cell, which could be made air-tight, was calibrated using a standard potassium iodide solution.

2.6.6-Molecular Weight Studies-

Molecular weight studies were attempted via the boiling-point-elevation method, using a Gallenkamp ebulliometer, thermistor bridge and galvanometer. Portions (about 50 milligrams to 100 milligrams) were weighed into the ebulliometer, which held 10 milliliters of methylene chloride, and the change in resistance of a thermistor was noted after the system had reached equilibrium. The ebulliometer was calibrated with tetraphenylcyclopentadienone (molecular weight = 348.5) and the cell constant calculated from equation (1):

$$(MW)(\Delta R) = K(wt) \text{------} (1)$$

where: (MW) = molecular weight of the sample,

(ΔR) = total change in resistance,

K = cell constant, and

(wt) = total weight of sample added.

Knowing the cell constant, equation (1) permits the calculation of the molecular weights of unknown samples.

The ebulliometer could be fitted with a rubber sleeve, making it air-tight. Oxygen-sensitive samples could then be admitted to the ebulliometer in a glove box, and the resistance change measured in the laboratory atmosphere.

2.6.7-Mass Spectra-

The mass spectra were recorded on a Hitachi Perkin Elmer RMU7 double focusing mass spectrometer.

3. RESULTS AND DISCUSSION

3.1-Complex Stability:

3.1.1-Significant Reactions-

The increased stability of bis(diethyldithiocarbamato)metal(II) complexes over bis(ethylxanthato)metal(II) complexes was verified by the inability to prepare tris complexes with the former ligand, whereas tris complexes with ethylxanthate with divalent metals were quite readily prepared when the metal was stable towards oxidation or reduction.

It is instructive to compare the syntheses of the bis(ethylxanthato)2,2'-bipyridylmetal(II) and the bis(ethylxanthato)1,10-phenanthrolinemetal(II) complexes, with those of the analogous diethyldithiocarbamato complexes, prepared by Dr. Holah. Whereas the ethylxanthate adducts required only one mole of nitrogen-base for each mole of metal halide, the analogous diethyldithiocarbamato complexes would not form unless the tris complex of the nitrogen-base was first prepared, to which sodium diethyldithiocarbamate was added until the mole ratio of metal:adduct:dithiolate was 1:3:2, respectively. If the mole ratio of metal:adduct:dithiolate was the same as for the ethylxanthato complexes (i.e: 1:1:2), the bis(diethyldithiocarbamato)metal(II) complex would form. This apparently reflects the necessity of having a large excess of the base present to overcome the tendency to form the stable bis complex.

The aqueous reaction of sodium diethyldithiocarbamate with tris(1,10-phenanthroline)nickel(II) chloride is interesting in that it results in the precipitation of the insoluble tris(1,10-phenanthroline)nickel(II) diethyldithiocarbamate complex ($Ni(phen)_3dtc_2$) rather than one analogous to the manganese(II), iron(II), cobalt(II) and zinc(II) complexes ($M(dtc)_2 \cdot phen$). An analogous pink tris(1,10-phenanthroline)nickel(II) diethyldithiophosphate is reported[133] to form when 1,10-phenanthroline is added to bis(diethyldithiophosphato)nickel(II). It seems likely that the inability of the diethyldithiocarbamate ion to break any of the metal-nitrogen bonds reflects the strength of the phenanthroline complex. The displacement of the chloride ions by diethyldithiocarbamate ions is attributed to the insolubility of the product. It is to be expected that the displacement of the diethyldithiocarbamate ions by chloride ions (<u>i. e</u>: the reaction of a solute with a precipitate) is much slower than the chloride displacement by diethyldithiocarbamate (the reaction of a solute with a solute). The red product was found to be soluble in methylene chloride, releasing the dithiocarbamate ion which is then able to attack the solvent, forming the soluble di(diethyldithiocarbamato)methane ($CH_2(dtc)_2$) and insoluble tris(1,10-phenanthroline)nickel(II) chloride as a by-product, i. e:

$$(Ni(phen)_3)\,dtc_2 + CH_2Cl_2 \xrightarrow{fast}$$
$$(Ni(phen)_3)\,Cl_2 + (dtc)_2CH_2.$$

The reaction appeared complete within about five seconds as the red color was discharged and the yellow precipitate appeared. It was found, upon analysis, that two solvent molecules were present for every molecule of the nickel complex, i. e: $Ni(phen)_3Cl_2(CH_2Cl_2)_2$. Also, recrystallization of the material from ethanol with ether resulted in the displacement of the methylene chloride by ethanol. Since the x-ray powder patterns of the last two complexes revealed both species to be isomorphous, it is believed that the solvent molecules are trapped in the interstices of the lattice. The dimer was previously prepared by refluxing a mixture of sodium diethyldithiocarbamate in methylene chloride for several hours[145]. The necessity of these vigorous conditions probably is due to the insolubility of sodium diethyldithiocarbamate.

Upon addition of sodium diethyldithiocarbamate to the analogous tris(2,2'-bipyridyl)nickel(II) chloride, the insoluble bis(diethyldithiocarbamato)nickel(II) immediately precipitates. Important factors in this anomolous reaction are likely to be the weakness of the 2,2'-bipyridyl chelates as opposed to 1,10-phenanthroline chelates and the stability of the square planar bis(diethyldithiocarbamato)nickel(II) complex.

3.1.2-Isomorphism-

From a crystallographic study of the bis(diethyldithiocarbamato)metal(II) series, and a knowledge of the great tendency to form these species, one might arrive at the fortuitous conclusion that isomorphism within a dithiolate series is governed by the stability of the species. Indeed, the d-spacings of the analogous species with the weaker ethylxanthate chelate (which are listed in Appendix II along with those of the other xanthate complexes studied in this thesis) indicate a lesser tendency for this series to exhibit isomorphism. Although x-ray isomorphism has repeatedly been found for only the iron and nickel components of the tetraethylammonium tris(ethylxanthato)metalate(II) series, the powder pattern of the manganese compound is very similar. It would not be unreasonable, therefore, to expect similar structures for these three compounds.

An application of the above reasoning to the α-bis(ethylxanthato)2,2'-bipyridylmetal(II) series, would suggest that these species are quite stable. This suggestion, however, appears to be erroneous. Not only have these species been found to decompose, but a second phase of the (presumably) same compound has been isolated for iron, cobalt and nickel. Also, the bis(ethylxanthato)1,10-phenanthrolinemetal(II) series displays isomorphism for only the cobalt and nickel members, despite the fact that 1,10-phenanthroline complexes are more stable than similar 2,2'-bipyridyl complexes[82]. Finally, the bis(diethyldithiocarbamato)1,10-phenanthrolinemetal-(II) complexes of iron and cobalt (in which the dithiocarbamate forms more stable complexes than the xanthate and the phenanthroline forms more stable complexes than the bipyridyl) have been found to be non-isomorphous with the manganese species. Hence it appears very unlikely that isomorphism within a dithiolate series can (in general) be related to the complex stability. Perhaps such factors as electronegativities, ionic radii and lattice energies play a more important role in determining isomorphism.

The fact that two phases were isolated for most of the bis(ethylxanthato)2,2'-bipyridylmetal(II) species is somewhat intriguing. Just as the manganese complex tends to become amorphous (as was mentioned in section 2.4.2) so does the α-iron phase decompose to an amorphous red phase. Perhaps the different phases, and decomposition therein, reflect the ability of the bipyridyl to adopt both a trans (through polymerization) and a cis arrangement (or arrangements intermediate to these extremes).

Lastly, two independent studies[75,76] which include a bis(ethylxanthato)2,2'-bipyridylnickel(II) complex make no mention of the species forming two different phases. This is attributed to the fact that the studies involved spectrophotometric titrations and the pure, crystalline complexes were, presumably, not isolated.

3.2-Oxidation-Reduction Properties:

Bis and tris complexes of manganese(II) and iron(II) with ethylxanthate have been found to be stable for short periods of time in the absence of oxygen. Once prepared, the tris complexes of manganese and iron even exhibit some stability in the presence of oxygen. Cobalt(II), however, is so readily oxidized by the ligand that even with the strict exclusion of oxygen, the bis and tris complex could not be isolated. Repeated attempts at the preparation in the presence of sulfuric acid and absence of oxygen demonstrated that this medium, suggested by Zagyanskii[55], is not adequate for the prevention of the oxidation by all xanthates.

It is curious that manganese(II) and iron(II) complexes with ethylxanthate have increased stability toward oxidation when a basic adduct is incorporated into the species. Indeed, the ability to form basic adducts of ethylxanthate complexes of cobalt(II), combined with the fact that the crude product can be prepared in the presence of oxygen, is dramatic testimony to the stabilizing effect of 2,2'-bipyridyl and 1,10-phenanthroline. This stabilizing effect may be due, in part, to the presence of an electron donor adjacent to the metal atom. It is noted that the electron-donating sulfur-atom of ethylxanthate does not cause the same stabilizing effect with regard to oxidation (in the tris complexes) as do the basic adducts. This may be due to the greater ability of the sulfur-atom to accept electrons from the metal atom (into an empty 3d orbital) than the nitrogen-atoms. Thus, although both sulfur and nitrogen atoms are able to donate electron density toward the metal atom, only the sulfur atom can accept electron density from the metal, reducing the tendency of the xanthate species to hinder metal oxidation.

The stabilizing effect of nitrogen-bases is also shown to be adequate for the diethyldithiocarbamate ligand by the isolation of bis(diethyldithiocarbamato)2,2'-bipyridylcobalt(II) along with the previously reported, analogous 1,10-phenanthroline species[67].

The recent report of sodium tris(diethyldithiocarbamato)cobaltate(II), i.e: $Na(Co(dtc)_3)$, by D'Ascenzo and Wendlandt[32] contradicts, as mentioned in the introduction to this thesis, the observation[31,33] that cobalt oxidizes spontaneously in the presence of diethyldithiocarbamate. This prompted a reinvestigation of the system and it was found that the same dark green product was obtained from several reactions between cobalt(II) chloride and sodium diethyldithiocarbamate, in different solvents, including the reaction described by D'Ascenzo and Wendlandt. This product is identical in all respects with the well-known tris(diethyldithiocarbamato)cobalt(III) complex. A band at 15,500 cm^{-1} with a molar extinction coefficient near 600 and a higher energy shoulder near 20,800 cm^{-1} corresponds with the visible spectrum of the tris complex[38]. Its mass spectrum (direct inlet, 220 C, 80 eV.) shows very strong peaks at m/e 503, which is the base peak and which corresponds to the molecular ion ($Co(dtc)_3^+$), and at 355 and 207 which correspond to the loss of one and two dithiocarbamate units respectively, together with a large number of smaller peaks below m/e 200. The species was also found to be x-ray isomorphous with the black precipitate of tris(diethyldithiocarbamato)iron(III), i. e: $Fe(dtc)_3$ formed according to the literature method[142] by adding sodium diethyldithiocarbamate to iron(III) chloride in a mole ratio of 3:1, respectively. Finally, the published analysis for the supposed cobalt(II) complex agrees very closely with the theoretical value for the tris complex of cobalt(III). Similarly, it is suggested that the previous report by Bhatt, et al.,[64] of bis(diethyldithiocarbamato)-cobalt(II), for which the synthesis was not described is erroneous. The magnetic susceptibility which these authors report for this bis complex (2669 x 10^{-6} Bohr Magnetons) is rather difficult to interpret in terms of a cobalt(II) species.

The increased stability of 2,2'-bipyridyl and 1,10-phenanthroline adducts of manganese(II) and iron(II) complexes of diethyldithiocarbamate towards oxygen was also noted.

In a study[118,56] of several metal xanthates, Little, et al., showed that since the addition of alkali xanthate to copper(II) chloride, in aqueous medium, results in the co-precipitation of one-half mole of the corresponding dixanthogen for every mole of the copper(I) xanthate, <u>i. e</u>:

$$Cu^{++} + 2\ RXan^{-} \longrightarrow CuRXan + \tfrac{1}{2}(RXan)_2,$$

the percentage of copper in the precipitate will be the same as the percentage of copper in bis(xanthato)-copper(II). Hence, unless the dixanthogen is extracted from the precipitate by an organic solvent, analysis of the precipitate will indicate, falsely, the presence of bis(xanthato)copper(II).

In this study, an infra-red spectrum of an ether-extracted product from the yellow precipitate of the reaction intended to produce bis(ethylxanthato)copper(II) was identical to that published for diethyldixanthogen and the infra-red spectrum of the crude precipitate was identical to that published for a mixture of copper(I) ethylxanthate and diethyldixanthogen[118] Repetition of this reaction in both water and dilute ammonium hydroxide (at an approximate pH value of 11) resulted in the same products. Neither were 2,2'-bipyridyl nor 1,10-phenanthroline able to stabilize the copper in a divalent state when ethylxanthate was added (in either aqueous or basic medium). This was attested by the diamagnetic nature of the product and the fact that washing with organic solvent removed the red coloration and resulted in a yellow solid remaining which was x-ray isomorphous with copper(I) xanthate. Also the infra-red spectrum of the red product indicated the presence of diethyldixanthogen. The mass spectrum (direct inlet, 80 °C, 16 eV) of the 1,10-phenanthroline adduct showed no peak at m/e 366, which would correspond to a $(Cu(Xan)\cdot phen^+)$ ion, nor at m/e 242, which would correspond to a $((Xan)_2^+)$ ion. This is attributed to decomposition of both species under these conditions (the red mixture was found to become a black liquid at this temperature). Several peaks around m/e 180, m/e 121 and m/e 64 may correspond to ions of $(phen^+)$, (Xan^+) and (Cu^+), respectively. However, these assignments are probably fortuitous as many other peaks are observed, suggesting fragmentation of the organic species.

The inability of the basic adducts to stabilize a divalent copper complex is not surprising since the potential for the reduction of bis(2,2'-bipyridyl)copper(II) is similar to that for the reduction of the copper(II) ion. The fact that the reaction with tetraethylammonium chloride in dilute ammonium hydroxide (at a pH value of about 11) gave copper(I) xanthate suggests, that the reddish-brown oils obtained from the aqueous reaction also contained the monovalent species.

Since bis(diethyldithiocarbamato)copper(II) forms readily, it may be that the potential for the oxidation of sodium diethyldithiocarbamate to tetraethylthiuram disulfide (see Figure XXIII) is -0.15 volts, or less, making the reduction unfavorable.

3.3-Infra-Red Spectra:

The infra-red spectra of all complexes studied in this project, as well as those of potassium ethylxanthate, sodium diethyldithiocarbamate, diethyldixanthogen, di(diethyldithiocarbamato)methane, tetraethylammonium chloride, 2,2'-bipyridyl and 1,10-phenanthroline, are shown in Appendix III.

3.3.1-M-N and M-S frequencies-

It has been illustrated in the introduction to this thesis that the exact position of the M-N stretching frequency (near 200 cm^{-1}) is the subject of some debate. It has also been shown[123,124,-125, 127,129] that M-S vibrations may be found between 150 cm^{-1} and 450 cm^{-1}. It is to be expected, then, that some ambiguity in the assignment of bands in the spectra of these complexes will occur.

It is readily apparent from Figure XXIV that the spectra of many of the complexes show a rapidly rising absorption near 200 cm^{-1} which probably indicates the presence of a strong band just below 200 cm^{-1}. With this in mind it is noted that most species exhibit a strong band in the 200 cm^{-1} to 250 cm^{-1} region (care must be taken not to confuse the 250 cm^{-1} peak in 1,10-phenanthroline itself with a M-N or M-S frequency in any of the complexes containing this species). As this band is present in all the bis and tris complexes, except $Ni(Xan)_2$, it is assigned to a M-S mode rather than a M-N mode. Similarly a strong band near 350 cm^{-1} in most of these complexes (with the possibility of a shift to higher energy in the bis(ethylxanthato)nickel-(II) complex is assigned to a M-S mode). The absence of both these bands in the tris(phenanthroline)nickel-(II) cation supports these assignments.

A strong band near 300 cm^{-1} for all the species containing the $(Ni(phen)_3^{++})$ cation is in agreement with several assignments[132,133,134,135,136,159] of M-N modes. These assignments, however, contradict work by Clark and Williams[137], which renders the assignment of bands in this region ambiguous. Also, it is noted that there are no corresponding bands in the

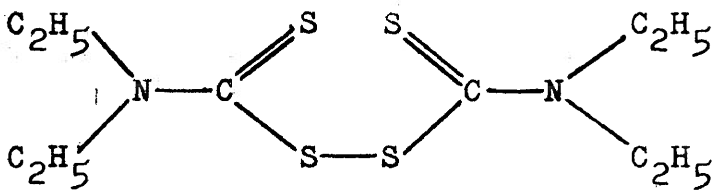


Figure XXIII

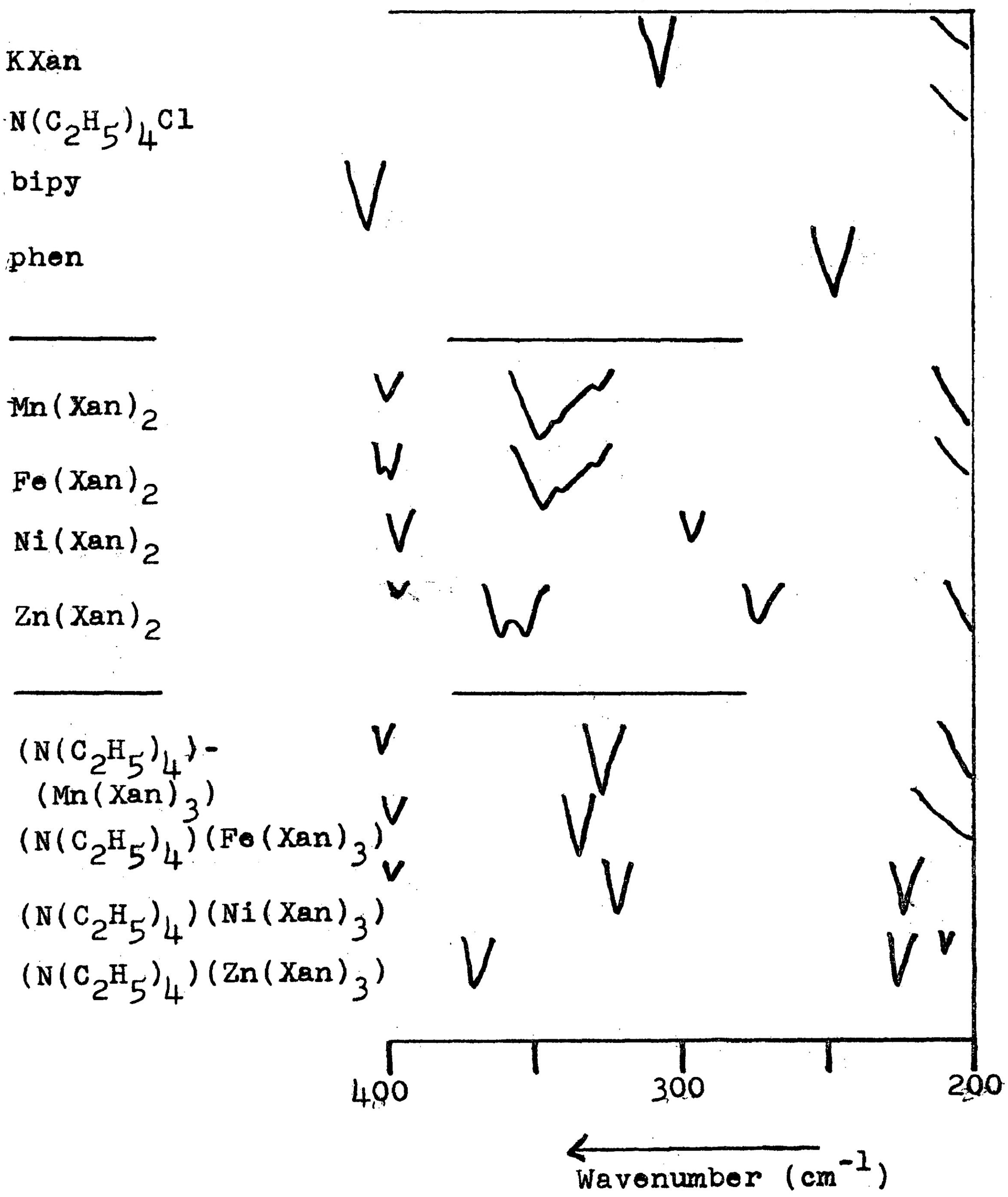

KXan
$N(C_2H_5)_4Cl$
bipy
phen
$Mn(Xan)_2$
$Fe(Xan)_2$
$Ni(Xan)_2$
$Zn(Xan)_2$
$(N(C_2H_5)_4)$-
$(Mn(Xan)_3)$
$(N(C_2H_5)_4)(Fe(Xan)_3)$
$(N(C_2H_5)_4)(Ni(Xan)_3)$
$(N(C_2H_5)_4)(Zn(Xan)_3)$
400
300
200
Wavenumber (cm^{-1})

Figure XXIV

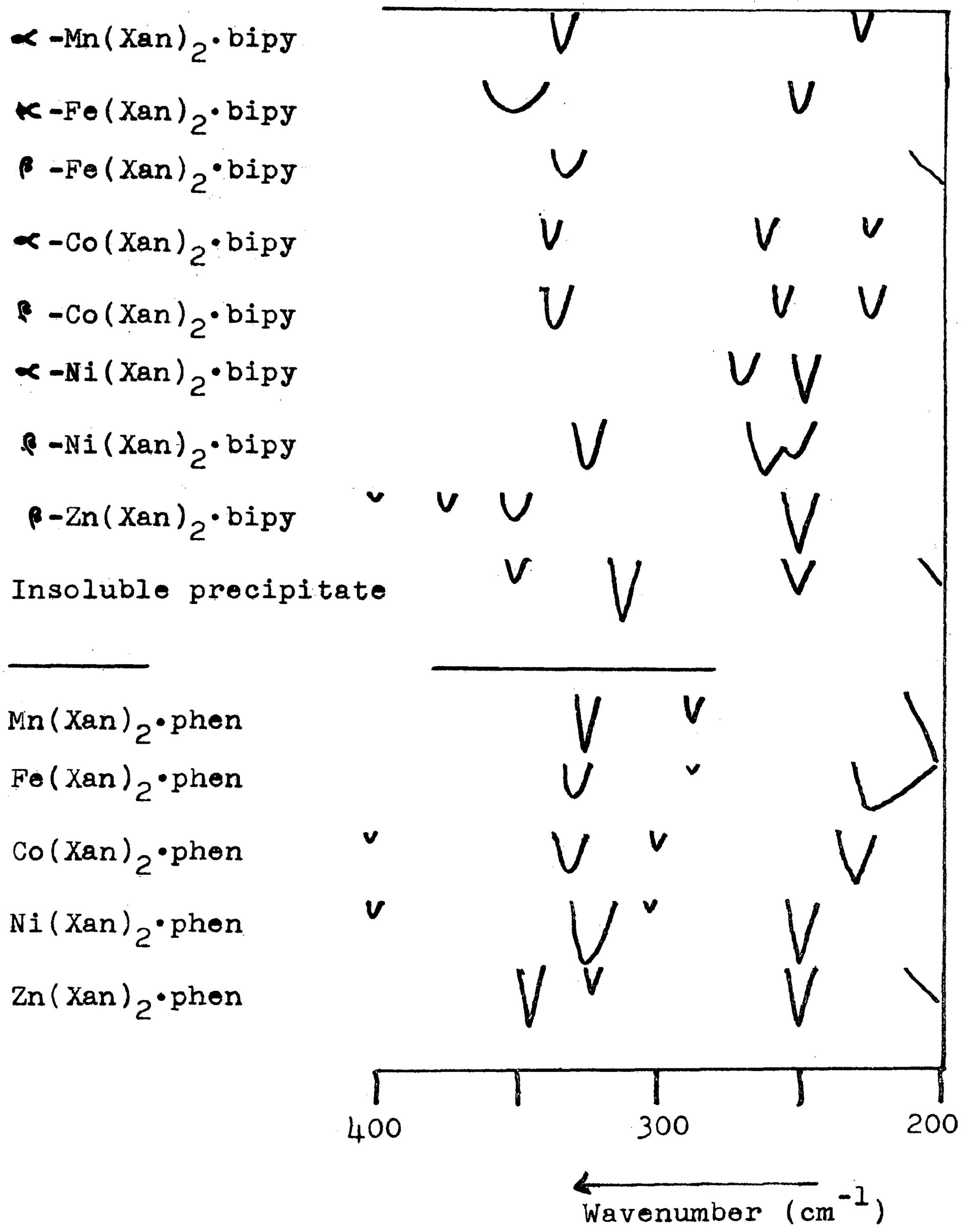

α-Mn(Xan)$_2$·bipy
α-Fe(Xan)$_2$·bipy
β-Fe(Xan)$_2$·bipy
α-Co(Xan)$_2$·bipy
β-Co(Xan)$_2$·bipy
α-Ni(Xan)$_2$·bipy
β-Ni(Xan)$_2$·bipy
β-Zn(Xan)$_2$·bipy
Insoluble precipitate
Mn(Xan)$_2$·phen
Fe(Xan)$_2$·phen
Co(Xan)$_2$·phen
Ni(Xan)$_2$·phen
Zn(Xan)$_2$·phen
400
300
200
Wavenumber (cm^{-1})

Figure XXIV

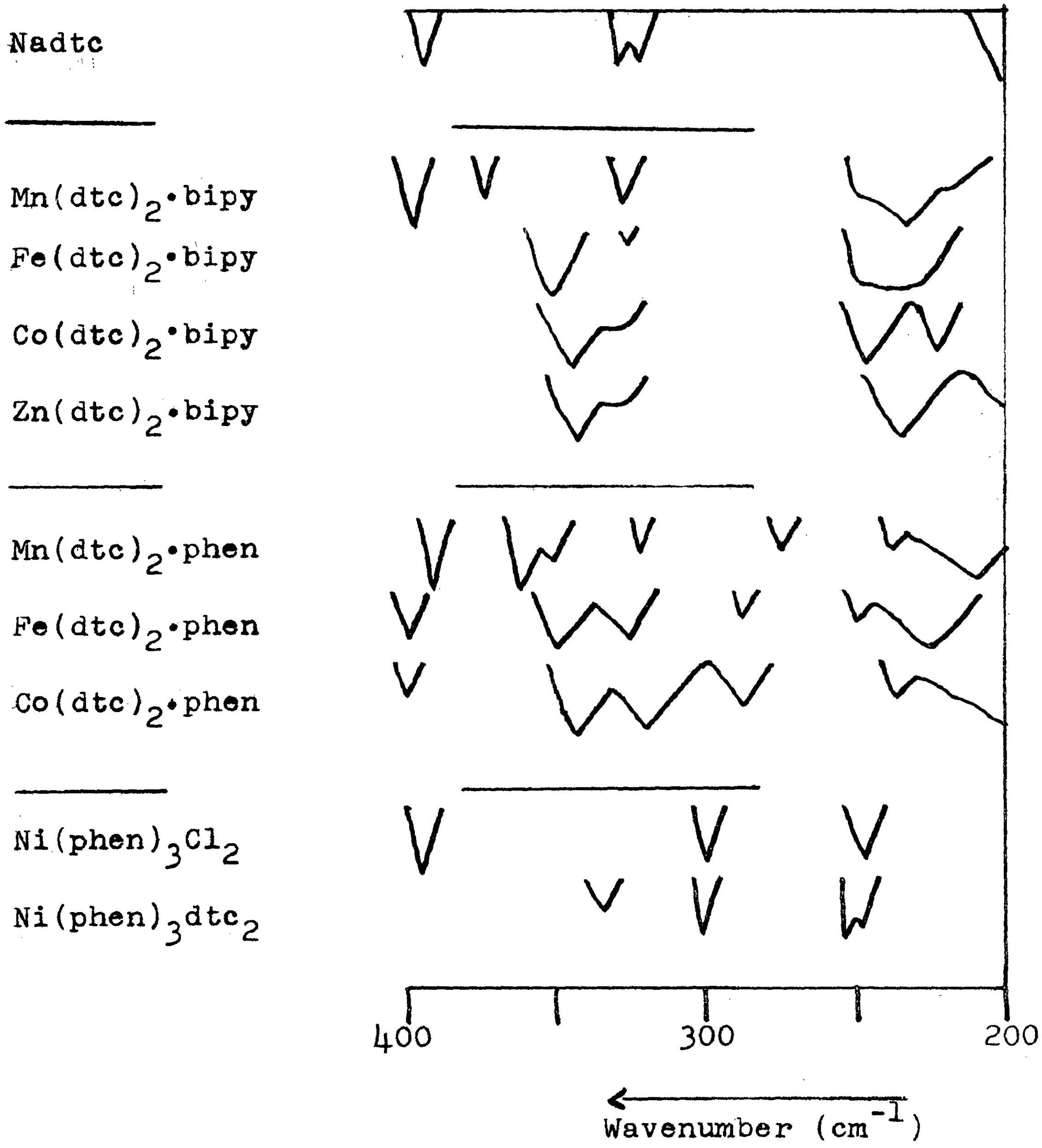

Nadtc
Mn(dtc)$_2$·bipy
Fe(dtc)$_2$·bipy
Co(dtc)$_2$·bipy
Zn(dtc)$_2$·bipy
Mn(dtc)$_2$·phen
Fe(dtc)$_2$·phen
Co(dtc)$_2$·phen
Ni(phen)$_3$Cl$_2$
Ni(phen)$_3$dtc$_2$
400
300
200
Wavenumber (cm^{-1})

Figure XXIV

2,2'-bipyridyl adducts which can be assigned to M-N vibrational modes. This lack of a band in the 2,2'-bipyridyl adducts and the thorough examination of the problem by Clark and Williams (see the introduction to this thesis), renders the assignment of the band near 300 cm^{-1} in the 1,10-phenanthroline adducts somewhat doubtful.

3.3.2-C-S frequencies-

The assignment of this band in these complexes is made difficult by various conflicting reports which quote the C-S stretching frequency as occurring over the very wide range of 550 cm^{-1} to 900 cm^{-1} (see Table 5). It is, therefore, difficult to make an empirical assignment which will be independent of a specific reference or group of references. Perhaps the most important purpose of assigning this band is to determine whether there could be two bands, corresponding to unequal C-S bonds or one band, indicative of equivalent C-S bonds.

There is much evidence[68,117,118,119] to suggest that a $C\overset{\cdots}{—}S$ bond (of bond order 1.8 or greater) absorbs radiation near 1050 cm^{-1}. All the xanthate complexes exhibit a broad band in this region of which one component may well be the $C\overset{\cdots}{—}S$ mode (despite the fact that bands are found in this region in tetraethylammonium chloride, 2,2'-bipyridyl and 1,10-

phenanthroline). It becomes necessary, therefore, to determine whether a band corresponding to a $C\overset{\cdots}{-}S$ bond with bond order 1.2 or less can be assigned in each spectrum.

Warranting immediate attention is a band at 450 cm^{-1} for all complexes. Although this may suggest a C-S single bond, it is surprising that such a band, which is also present in potassium ethylxanthate, should appear totally insensitive to the ionic character of the species. It is also noted that this band lies somewhat below the values of 550 cm^{-1} to 600 cm^{-1} postulated for other C-S single bonds (Table 5). It seems unlikely, therefore, that this band represents a C-S single bond. The bis complexes of manganese and iron both exhibit strong bands at 485 cm^{-1} and 805 cm^{-1}, the weak band at 850 cm^{-1} being disregarded. If the lower energy band is assigned to the C-S bond, its complete disappearance (or the unreasonably large shift of 175 cm^{-1} to higher energy) in bis(ethylxanthato)zinc(II), as well as the tris complexes, is difficult to explain. Since the higher energy peak is also observable in the bis complexes of nickel and zinc, it may be considered as one possibility for the missing C-S frequency. Although this peak is of little consequence in the tris complexes of manganese, iron and nickel, peaks at 780 cm^{-1} to 795 cm^{-1} may well be analogous to the 805 cm^{-1} peaks in the bis complexes. The 865 cm^{-1} peak in tetraethylammonium tris(ethylxanthato)zincate(II) is regarded as being too inconsistantly present in the complexes to represent a C-S bond, leaving a peak at 785 cm^{-1} which appears analogous to the 805 cm^{-1} peak in the bis complexes. Such a postulate receives some support from Fackler and Coucouvanis who assign a peak between 800 cm^{-1} and 850 cm^{-1} in metal complexes of trithiocarbonates as due to a C-S stretching frequency[130]. It is also to be remembered that if a C-S stretching frequency is found near 650 cm^{-1}, as suggested by Bellamy[122], a peak at 800 cm^{-1} may, alternatively, reflect two equivalent C-S bonds, each of about 1.2 to 1.4 bond order.

The spectra of $M(Xan)_2 \cdot bipy$ complexes show that the only peak between 450 cm^{-1} and 1000 cm^{-1} occurs at 702 cm^{-1} (for the α-$M(Xan)_2 \cdot bipy$ complexes of manganese, iron, cobalt and nickel) and at 690 cm^{-1} (for β-$Co(Xan)_2 \cdot bipy$). The absence of this peak in all the β-species except β-$Co(Xan)_2 \cdot bipy$, in which it is exceptionally strong, is inherently interesting. It may be that the symmetry of all the β-species is such that it renders this peak infra-red inactive, except with cobalt, in which the symmetry may permit infra-red activity. Since all the α-species show the peak to have medium intensity, it follows that their symmetry may be such as to permit some infra-red activity. The assignment of such a band to a C-S mode would be sheer speculation. A study of the Raman spectra in this region would be of some interest.

The only peaks between 400 cm^{-1} and 1000 cm^{-1} in M(Xan)$_2$·phen complexes which cannot be assigned to 1,10-phenanthroline modes, occur at 810 cm^{-1} and between 890 cm^{-1} and 910 cm^{-1}. The weakness of these bands makes their assignment to C-S modes somewhat doubtful.

As there is no reasonably consistant peak below 1000 cm^{-1} in all the complexes which can be assigned to a C-S stretching mode, it seems worthwhile to study the possibility of the 1050 cm^{-1} peak being representative of two equivalent $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ bonds. It was shown in the introduction of this thesis that if a C=S (double bond) absorbs energy between 1200 cm^{-1} and 1250 cm^{-1} and a C-S (single bond) absorbs energy around 850 cm^{-1}, then the peak near 1050 cm^{-1} may well represent two equal $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ bonds. A peak at 1260 cm^{-1} for diethyldixanthogen and at 1220 cm^{-1} for di(diethyldithiocarbamato),methane in which there should be a C=S double bond, may represent its stretching frequency. Since there is little electron-donation by the oxygen atom, it is quite possible that the 1050 cm^{-1} peak represents a bond order close to 1.5.

All the species which contain diethyldithiocarbamate exhibit a strong band between 990 cm^{-1} and 1000 cm^{-1}, which may represent a $C\overset{\cdots}{-}S$ mode. The fact that this band is of lower energy than the corresponding band in ethylxanthate complexes probably reflects the increased donor ability of the nitrogen-atom over the oxygen-atom. The lack of this peak in the tris(1,10-phenanthroline)nickel-(II) chloride complexes lends some credance to this hypothesis. It is to be remembered that the 800 cm^{-1} to 1400 cm^{-1} region has been said to display combination bands[146]. Hence this probably accounts for the difficulty in assigning bands in this region to pure vibrational modes (*i. e*: the band attributed to the C-S mode is likely composed partly, of some other vibration).

3.3.3-C-O frequency-

Articles discussed in the introduction to this thesis suggest that the C-O stretching frequency is in the 1200 cm^{-1} to 1250 cm^{-1} region. The spectra of the bis complexes of manganese and iron show bands at 1260 cm^{-1} and a broad band at 1200 cm^{-1}, either of which may be due to the C-O stretching mode. The absence of a band at 1200 cm^{-1} in bis(ethylxanthato)nickel(II) suggests that the C-O stretching mode in these three complexes is at 1260 cm^{-1}. In bis(ethylxanthato)zinc(II), either the bands at 1195 cm^{-1} or 1210 cm^{-1} may be the C-O stretching mode. Its decrease in energy likely reflects the filled d-orbitals' inability to accept as much electron density as the analogous manganese, iron and nickel complexes. The tris complexes exhibit only weak peaks at 1260 cm^{-1} for manganese, iron and nickel and no peak for zinc. A broad band about 1200 cm^{-1} may well mask the C-O stretching frequency at this energy. A decrease in energy over the bis complexes can be explained in terms of an increased electron density about the metal atom, which would restrict electron donation by the oxygen-atom. A band near 1200 cm^{-1} in all the adducts likely is due to the C-O stretching frequency, its decrease in energy over the bis complexes of manganese, iron and nickel, again reflecting the increased electron density about the metal atom.

3.3.4-<u>C-N frequency</u>-

A peak at 1480 cm^{-1} in all the complexes which contained diethyldithiocarbamate can be assigned to the $C\overset{\cdots}{-}N$ stretching frequency, and is in agreement with previous work (*e.g*: Table 4).

3.3.5-Conclusions-

The infra-red spectra of these complexes have been interpreted in terms of 1)the M-N stretching modes occurring below 200 cm^{-1}, 2)several M-S stretching modes occurring between 200 cm^{-1} and 400 cm^{-1}, 3)a C-S stretching frequency corresponding to two equivalent $C\overset{\cdots}{-}S$ bonds, occurring near 1050 cm^{-1} for xanthate complexes and between 990 cm^{-1} and 1000 cm^{-1} for species containing diethyldithiocarbamate; 4)the C-O stretching frequency occurring at 1260 cm^{-1} for bis complexes of manganese, iron and nickel and near 1200 cm^{-1} for all other complexes, and 5)the C-N stretching frequency occurring at 1480 cm^{-1} for all the basic adducts of the dithiocarbamate complexes studied and for tris(1,10-phenanthroline)nickel(II) diethyldithiocarbamate. This is in keeping with greater electron donation by the nitrogen-atom (of dithiocarbamate) than by the oxygen-atom (of xanthate).

3.4-Electronic Structure of the Metal Atom:

3.4.1-Visible and Near Infra-Red Spectra-

The visible and near infra-red spectra of all the complexes studied, excluding the d^{10} systems, are given in Appendix IV. The bands, with shoulders indicated in parentheses, and their molar extinction coefficients (ϵ) are listed in Table 7, along with the assignments of these transitions.

The solution spectra of all the manganese complexes showed no observable bands. This is attributed to the weakness of the spin-forbidden transitions only being observable in a more concentrated solution or in a cell with a greater path length than 1.0 cm. The reflectance spectra of the bis and tris complexes, and of the 2,2'-bipyridyl and 1,10-phenanthroline adducts of the bis complexes all displayed a shoulder at the base of the charge transfer band. If all the complexes are assumed to be approximately octahedral, this band is in keeping with a $^6A_{1g} \longrightarrow {}^4T_{1g}$ transition. The assumption of an octahedral species for the bis complex implies that the species is polymeric in the solid state, with an octahedron of sulfur atoms about the manganese.

The similarity between the band observed in acetonitrile solution for bis(ethylxanthato)iron(II) and the $^5T_{2g} \longrightarrow {}^5E_g$ transition of the octahedral iron(II) complexes with ethylxanthate suggests that this complex interacts with the solvent to form a pseudo-octahedral species. The broadness of this band (indeed a shoulder or second band is often observed) is attributed to splitting of the excited

Table 7

The near infra-red and visible bands and their extinction coefficients (when attainable) for the compounds studied in this thesis.

Compound	Band (cm^{-1})	ε	Assignment
$Mn(Xan)_2$	(15,900)	-	$^6A_{1g} \rightarrow {}^4T_{1g}$
	18,800		Charge Transfer
$Fe(Xan)_2$	8,560	8.8	$^5T_{2g} \rightarrow {}^5E_g$
$Ni(Xan)_2$	15,900	69	$^1A_{1g} \rightarrow {}^1B_{1g}$
$(N(C_2H_5)_4)(Mn(Xan)_3)$	(14,700)	-	$^6A_{1g} \rightarrow {}^4T_{1g}$
	(22,200)		Charge Transfer
$(N(C_2H_5)_4)(Fe(Xan)_3)$	(7,150)	11.7	$^5T_{2g} \rightarrow {}^5E_g$
	8,500		
$(N(C_2H_5)_4)(Ni(Xan)_3)$	(8,440)	7.2	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^1E_g$
	9,500		
	14,940	10.4	$^3A_{2g} \rightarrow {}^3T_{1g}$
α-$Mn(Xan)_2 \cdot bipy$	(14,700)	-	$^6A_{1g} \rightarrow {}^4T_{1g}$
	(20,000)		Charge Transfer
α-$Fe(Xan)_2 \cdot bipy$	8,700	-	$^5T_{2g} \rightarrow {}^5E_g$
	(11,500)		
	(16,400)	695	$t_{2g} \rightarrow \pi^*$
	18,200	740	$\pi \rightarrow e_g^*$
β-$Fe(Xan)_2 \cdot bipy$	8,600	-	$^5T_{2g} \rightarrow {}^5E_g$
	(18,900)	450	$t_{2g} \rightarrow \pi^*$
	20,800	400	$\pi \rightarrow e_g^*$
α-$Co(Xan)_2 \cdot bipy$	8,700	7.9	$^4T_{1g} \rightarrow {}^4T_{2g}$
	18,200	12.6	$^4T_{1g} \rightarrow {}^4A_{2g}$ **
β-$Co(Xan)_2 \cdot bipy$	8,700	4.8	$^4T_{1g} \rightarrow {}^4T_{2g}$
	(18,180)	-	$^4T_{1g} \rightarrow {}^4A_{2g}$ **
	(20,000)	-	$^4T_{1g} \rightarrow {}^4T_{1g}$ **

Table 7, cont'd.

Compound	Band (cm^{-1})	ε	Assignment
α-Ni(Xan)$_2$·bipy	(9,350) 10,400	19	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^1E_g$
	(16,700)	-	$^3A_{2g} \rightarrow {}^3T_{1g}$
β-Ni(Xan)$_2$·bipy	(9,250) 10,400	21	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^1E_g$
	16,700	24	$^3A_{2g} \rightarrow {}^3T_{1g}$
Mn(Xan)$_2$·phen	(15,400)	-	$^6A_{1g} \rightarrow {}^4T_{1g}$
Fe(Xan)$_2$·phen	8,600 (11,500)	-	$^5T_{2g} \rightarrow {}^5E_g$
	(16,700)	100	$\sigma \rightarrow \pi^*$
	18,900	100	$\pi \rightarrow \sigma^*$
Co(Xan)$_2$·phen	8,600	5.6	$^4T_{1g} \rightarrow {}^4T_{2g}$
Ni(Xan)$_2$·phen	9,350 (11,500)	14.8	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^1E_g$
	(15,400)	20	$^3A_{2g} \rightarrow {}^3T_{1g}$
Mn(dtc)$_2$·bipy	22,200	-	$^6A_{1g} \rightarrow {}^4T_{1g}$
Fe(dtc)$_2$·bipy	(9,500)	-	$^5T_{2g} \rightarrow {}^5E_g$
	16,400	-	Charge Transfer
Co(dtc)$_2$·bipy	8,700	-	$^4T_{1g} \rightarrow {}^4T_{2g}$
Mn(dtc)$_2$·phen	(20,000)	-	$^6A_{1g} \rightarrow {}^4T_{1g}$
Fe(dtc)$_2$·phen	(8,900)	-	$^5T_{2g} \rightarrow {}^5E_g$
	15,800	-	Charge Transfer
Co(dtc)$_2$·phen	8,750	-	$^4T_{1g} \rightarrow {}^4T_{2g}$
	(14,500)	-	***

Table 7, cont'd.

Compound	Band (cm^{-1})	ε	Assignment
	(19,200)	-	$^4T_{1g} \rightarrow {}^4A_{2g}$**
	(21,300)	-	$^4T_{1g} \rightarrow {}^4T_{1g}$**
$Ni(phen)_3(dtc)_2$	(11,100) 12,700	-	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^1E_g$
$Ni(phen)_3Cl_2 2(CH_2Cl_2)$	(11,100) 12,700	-	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^1E_g$
$Ni(phen)_3Cl_2 2(EtOH)$	(11,100) 12,700	-	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^1E_g$
	18,500	-	$^3A_{2g} \rightarrow {}^3T_{1g}$

**The excited state may be either $^4A_{2g}$ or $^4T_{1g}$, depending on the strength of the ligands.

***Possibly indicative of some oxidation to Co(III).

^5E_g state (Jahn-Teller distortion) as has been suggested by others[147]. This transition for the 2,2'-bipyridyl adduct was not observed in solution, due to the large extinction coefficient (ca: 700) of the charge transfer bands. This prevented a determination of the extinction coefficient for the $^5T_{2g} \longrightarrow {}^5E_g$ transition. The reflectance spectrum of this compound, however, did show the charge transfer band to be about fifteen times more intense than the d-d transition. The charge transfer bands are in accord with the $t_{2g} \longrightarrow \pi^*$ and $\pi \longrightarrow e_g^*$ transitions between 17,000 cm^{-1} and 20,000 cm^{-1} (ε = 1000), respectively, reported for 2,2'-bipyridyl complexes of iron(II) with bromide, iodide or chloride ions[148]. Similar charge transfer bands hindered the calculation of the extinction coefficients for the 1,10-phenanthroline adduct. Again the reflectance spectrum showed the charge transfer band to be much more intense (ca: ten times) than the $^5T_{2g} \longrightarrow {}^5E_g$ transition. The charge transfer bands agree well with a band reported at 18,500 cm^{-1} to 19,000 cm^{-1} (ε = 500) with a low energy shoulder at 16,500 cm^{-1} to 17,000 cm^{-1} for $Fe(phen)_2 \circ X_2$ species, where X is a chloride, bromide or thiocyanate ion[149]. The broadness of the d-d transition suggests splitting of the excited ^5E_g state, similar to the tris complex.

The three bands observed in the reflectance spectrum of β-Co(Xan)$_2$·bipy can be assigned with some certainty to the three spin-allowed transitions predicted by ligand-field theory for octahedral cobalt(II), while in methylene chloride the two higher energy transitions are obscured by charge transfer bands. Similarly, the two observed bands for α-Co(Xan)$_2$·bipy are assigned as ${}^4T_{1g} \longrightarrow {}^4T_{2g}$ and ${}^4T_{1g} \longrightarrow {}^4A_{2g}$ transitions and the only band in Co(Xan)$_2$·phen to the ${}^4T_{1g} \longrightarrow {}^4T_{2g}$ transition. Presumably, the unobserved transitions in these complexes are hidden beneath the charge transfer bands.

The 15,900 cm^{-1} band for bis(ethylxanthate)nickel(II), which verifies the previously published band[43] at 16,000 cm^{-1}, is indicative of a square planar species, the band being the result of an ${}^1A_{1g} \longrightarrow {}^1B_{1g}$ transition (or ${}^1B_{2g} \longrightarrow {}^1B_{1g}$ if the ligand field causes such large splitting of the E_g and T_{2g} states that the energy of the d_{z^2} orbital becomes less than that of the d_{xy} orbital) (Figure XXV). An assignment of the band to a ${}^1A_{1g} \longrightarrow {}^1B_{1g}$ transition would be in keeping with assignments of similar bands in other square planar nickel(II) series[2,38]. The spectrum of α-Ni(Xan)$_2$·bipy is indicative of an octahedral d^8 system whose highest

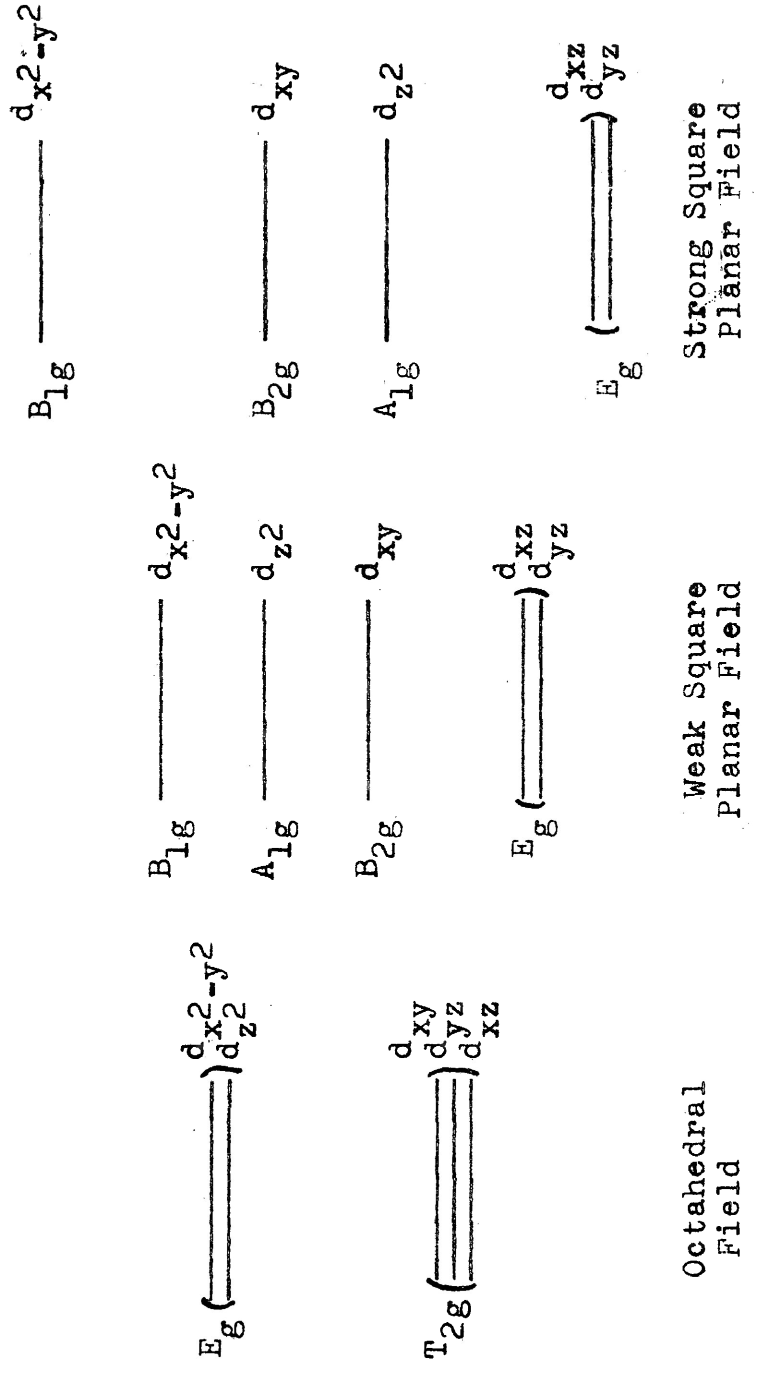

B_{1g}
$d_{x^2-y^2}$
B_{2g}
d_{xy}
A_{1g}
d_{z^2}
E_g
d_{xz}
d_{yz}
Strong Square Planar Field
B_{1g}
$d_{x^2-y^2}$
A_{1g}
d_{z^2}
B_{2g}
d_{xy}
E_g
d_{xz}
d_{yz}
Weak Square Planar Field
E_g
$d_{x^2-y^2}$
d_{z^2}
T_{2g}
d_{xy}
d_{yz}
d_{xz}
Octahedral Field

Figure XXV

energy transition is hidden beneath a charge transfer band. It is also analogous to bands at 8,900 cm^{-1} and 15,000 cm^{-1} (with splitting of the lower energy band analogous to previous results[45]) for bis(diethyldithiophosphato)2,2'-bipyridylnickel(II)[150]. The extinction coefficient of the $^3A_{2g} \longrightarrow {}^3T_{1g}$ transition is probably inaccurate, as it is observed on the low energy side of a charge transfer band. The bands of the β-phase, which are analogous to those of the α-phase, are also assigned in accord with those predicted by ligand-field theory for octahedral nickel(II). The spectrum of $Ni(Xan)_2 \cdot phen$ which is analogous to the $Ni(Xan)_2 \cdot bipy$ spectra is similar to that published for $Ni(dtp)_2 \cdot phen$[150].

The similarity of the reflectance spectra of $Mn(dtc)_2 \cdot bipy$, $Fe(dtc)_2 \cdot bipy$, $Co(dtc)_2 \cdot bipy$, $Mn(dtc)_2 \cdot phen$, $Fe(dtc)_2 \cdot phen$ and $Co(dtc)_2 \cdot phen$ to the analogous xanthate complexes indicates that these complexes, also, are probably all high spin species with $^6A_{1g}$, $^5T_{2g}$ and $^4T_{1g}$ ground states for Mn(II), Fe(II) and Co(II), respectively.

The superimposability of the lowest energy transitions for both $(Ni(phen)_3)Cl_2$ and $(Ni(phen)_3)(dtc)_2$ is further evidence that the ligand field about the nickel atom is identical in both species.

The lowering of the energy of the charge transfer band in $(Ni(phen)_3)Cl_2 2(CH_2Cl_2)$ as compared with $(Ni(phen)_3)Cl_2 2(EtOH)$ may reflect the molecules of solvent which are believed to be trapped in the lattice (as was suggested by the analysis).

3.4.2-Magnetic Studies-

From the preceding discussion it is to be expected that all the complexes will display magnetic moments indicative of high spin metal atoms, except for bis(ethylxanthato)nickel(II) as square planar nickel(II) species are usually low spin. From Table 8, which lists the various magnetic susceptibilities and moments, it is seen that this is true except for the bis xanthato complexes of Mn(II) and Fe(II) and β-$Fe(Xan)_2 \cdot bipy$ which yielded low values. The low value for β-$Fe(Xan)_2 \cdot bipy$ was known to arise from potassium chloride contamination. All attempts at isolating a large enough quantity of the pure species for magnetic studies were unsuccessful. It is not known whether the low values for $Mn(Xan)_2$ and $Fe(Xan)_2$ which were reproduced by measurements on different samples, arise from metal-metal interaction in a polymer (or dimer) or some other mechanism.

The large magnetic moment obtained for tetraethylammonium tris(ethylxanthato)iron(II) may re-

Table 8

Magnetic susceptibilities and magnetic moments for the complexes studied.

Series	M = Mn(II)		M = Fe(II)		M = Co(II)		M = Ni(II)	
	$\chi_M^{corr} \times 10^6$	μ(B.M.)	$\chi_M^{corr} \times 10^6$	μ(B.M.)	$\chi_M^{corr} \times 10^6$	μ(B.M.)	$\chi_M^{corr} \times 10^6$	μ(B.M.)
$\mathrm{M(Xan)_2}$	9,300	4.8	7,800	4.4	-	-	Diam.	-
$\mathrm{(N(C_2H_5)_4)}$-$\mathrm{(M(Xan)_3)}$	15,150	6.0	12,510	5.5	-	-	5,510	3.4
α-$\mathrm{M(Xan)_2}$-·bipy	12,800	5.6	9,540	4.8	8040	4.4	4050	3.1
β-$\mathrm{M(Xan)_2}$-·bipy	-	-	<7,300	<4.2	8070	4.6	3740	3.0
$\mathrm{M(Xan)_2}$·phen	14,770	6.0	10,670	5.1	9300	4.8	3780	3.0
$\mathrm{M(dtc)_2}$·bipy	15,070	6.0	-	-	10,130	5.0	-	-
$\mathrm{M(dtc)_2}$·phen	14,910	6.0	-	-	~10,200*	5.1*	-	-

*previously published[75]

flect considerable orbital contribution or, alternatively, some oxidation to iron(III). Only a small amount of oxidation would be required to increase the moment to this value, and indeed, no decomposition was detected by an x-ray powder photograph of this sample. The adducts of the dithiocarbamate complexes of iron(II) (i.e: $Fe(dtc)_2 \cdot bipy$ and $Fe(dtc)_2 \cdot phen$) were not studied as a method of purifying a sufficiently large sample has not yet been found.

Perhaps a study of many of these complexes over a temperature range would reveal some interesting features.

3.5-Structural Features:

3.5.1-Ionic Character-

The dependence of the equivalent conductivity on the square root of the concentration (in normality) of each species dissolved in nitromethane, is given in Appendix V. The studies were done for all the xanthate series, except β-$Fe(Xan)_2 \cdot bipy$ from which the potassium chloride contamination could not be removed in a sufficiently large quantity, and the bis and tris complexes of Mn(II) and Fe(II), due to their extreme air-sensitivity.

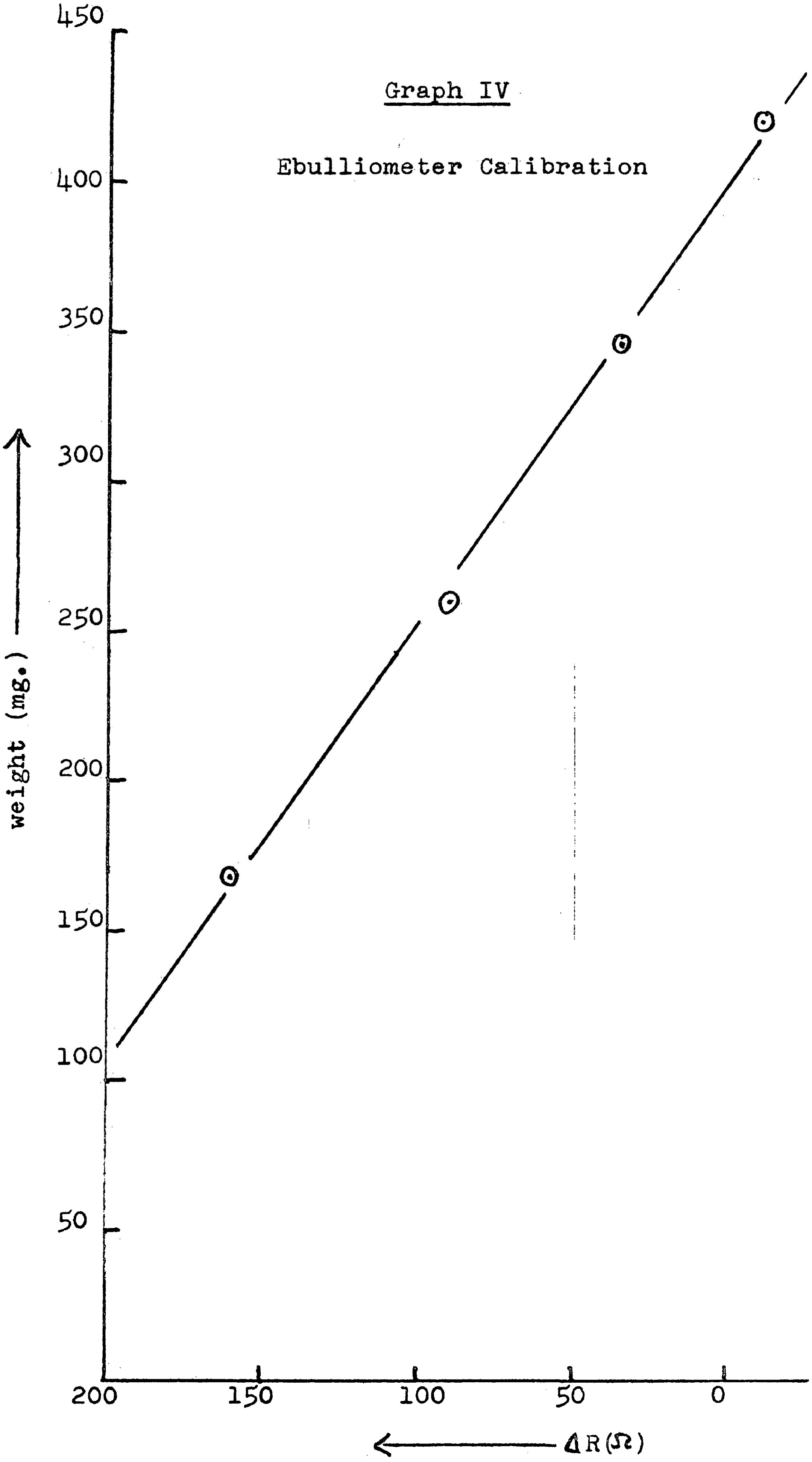
A cursory glance at these graphs indicates that the complexes all behave as weak electrolytes (even the presumably "ionic" tris complexes) in this solvent. A striking feature is that all the 1,10-phenanthroline complexes display a slightly greater equivalent conductivity at the (relatively) high concentrations than do the 2,2'-bipyridyl complexes. Indeed, $Ni(Xan)_2$•phen is as good a conductor at concentrations of 2.5 x 10^{-3} N, or greater , as is $(N(C_2H_5)_4)(Ni(Xan)_3)$, probably reflecting the weak dissociation of the tris complex, rather than the strong dissociation of the adduct in this solvent. If the increased ligand strength of the 1,10-phenanthroline over 2,2'-bipyridyl can be related to the increased ability of the former species to donate electrons to the metal atom, it is possible that the $M(Xan)L^+$ cation is more stable with L = 1,10-phenanthroline than with L = 2,2'-bipyridyl.

The increased equivalent conductivity of β -Ni-$(Xan)_2$•bipy over α-$Ni(Xan)_2$•bipy, at (relatively) high concentration, suggests that the α-species possesses a more stable orientation of chelates about the nickel atoms. It is not surprising that at (relatively) low concentration the two phases become identical solutes, hence the similarity of the curves below 10^{-3} normality.

Finally, changes in equivalent conductivities within each series have not been found to be related to changes in electronegativities of the metal atoms. This is not surprising if the metal-ligand bonds are assumed to be mainly covalent, as opposed to ionic.

3.5.2-<u>Molecular Weight Studies</u>-

The average (of three) calibration constants was (-440)±5%. A typical dependence of (MW)(ΔR) on the total weight added (see equation (1)), in milligrams, is given in Graph IV. Using this value a molecular weight of 420 was calculated for $Mn(Xan)_2$·phen. Although this may be indicative of a monomer, an amorphous residue which formed in the ebulliometer suggests the occurrence of decomposition, introducing the likelihood of considerable error in this value. A similar amorphous residue for $Fe(Xan)_2$·phen, $Co(Xan)_2$·phen, $Ni(Xan)_2$·phen and $Zn(Xan)_2$·phen and a constant resistance when a weight of solute is increased from 60 mg to 250 mg suggests such studies on this series are not feasible. Although changes in the resistance were measured when up to 450 mg of α-$Mn(Xan)_2$·bipy, α-$Co(Xan)_2$·bipy or β-$Zn(Xan)_2$·bipy were introduced to the ebulliometer, the formation, again, of amorphous phases renders molecular weights of 675, 370 and 1070, respectively, meaningless. Due to the instability of these complexes, under these rather vigorous conditions (<u>i. e</u>: boiling methylene chlor-


Graph IV
Ebulliometer Calibration
weight (mg.)
450
400
350
300
250
200
150
100
50
200
150
100
50
0
ΔR(Ω)

ide), further species were not studied.

Molecular weight studies[151] on the triphenylphosphine adduct of copper(I) diethyldithiocarbamate and its silver(I) analogue have also given unusual results (30% to 50% low). It was suggested that these species, which exhibit low conductivities in chloroform and in nitrobenzene, dissociate into $((Ph_3P)_2M^+)$ and the diethyldithiocarbamate anion. Similar dissociation in the xanthate series studied may result in the amorphous residue, either by interaction with the solvent or by recombining as an amorphous phase.

3.6-Summary:

The reactions of some of the first row transition metals with potassium ethylxanthate and sodium diethyldithiocarbamate and the formation of mixed chelates containing one of these ligands as well as either 2,2'-bipyridyl or 1,10-phenanthroline have been discussed in terms of the increased stability of dithiocarbamate complexes over xanthate complexes and of 1,10-phenanthroline adducts over 2,2'-bipyridyl adducts. This has been shown to be inadequate in explaining isomorphism in the various series which were studied.

The ability to stabilize the divalent states of manganese, iron and cobalt by forming adducts with nitrogen-bases has been demonstrated. Also demonstrated was the inability to form certain divalent complexes of cobalt (with diethyldithiocarbamate) and copper (with ethylxanthate).

A study of the infra-red spectra resulted in the empirical assignment of M-S bands (between 200 cm^{-1} and 400 cm^{-1}), C-S bands (between 990 cm^{-1} and 1050 cm^{-1}), C-O bands (near 1200 cm^{-1} or 1260 cm^{-1}) and C-N bands (at 1480 cm^{-1}). Further evidence is added to the controversial assignment of the M-N vibrational bands (which are suggested to be below 200 cm^{-1}).

All visible and near infra-red spectra, except that of bis(ethylxanthato)nickel(II), in solution, have been in agreement with an octahedral arrangement of ligands about the metal atom. This suggests the occurrence of polymers for bis(ethylxanthato)manganese(II) and bis(ethylxanthato)iron(II) in the solid state. Magnetic moments of all basic adducts and tris complexes are consistent with high spin electronic states for the metal atom. Although five and four unpaired electrons are apparent for bis(ethylxanthato)manganese(II) and bis(ethylxanthato)iron(II), respectively, the mechanism by which the moments are lowered below those found for similar high spin species is not yet understood.

All complexes studied have been found to be weak electrolytes, except bis(ethylxanthato)nickel(II) which is a non-electrolyte. It has been shown that replacing the 2,2'-bipyridyl species by 1,10-phenanthroline, in the basic adducts, increases the conductivity of the species, perhaps a result of the formation of somewhat more stable species upon dissociation.

3.7-Future Work:

Although considerable light has been shed on the chemistry of ethylxanthate and diethyldithiocarbamate compounds, the following studies would probably increase current knowledge in these areas even further.

Detailed crystallographic studies of either bis(ethylxanthato)manganese(II) or bis(ethylxanthato)-iron(II) are required to verify the suggestion of an octahedral arrangement of sulfur atoms about the metal atom. Also, the α-bis(ethylxanthato)2,2'-bipyridylmetal(II) species, which are all x-ray isomorphous, warrant a detailed structural study. Perhaps a study of thermodynamic properties would reveal a consistent trend for the ability or inability of a series to display x-ray isomorphism.

The blue precipitate obtained from the attempted synthesis of $Cr(Xan)_2 \cdot bipy$, and suspected to contain chromium(II), requires considerable further study. Prior to this, a method for purifying the product must be found.

It would be of considerable interest to determine the organic by-products of ethylxanthate and diethyldithiocarbamate formed during the oxidation of a metal ion and the potential for the half-reaction leading to their formation. Presumably this information would enable some accurate predictions to be made regarding the likelihood of stabilizing these metals in their lower oxidation states.

The insoluble white product formed during the preparation of β-$Zn(Xan)_2 \cdot bipy$ warrants further investigation. Perhaps an analysis of the amount of zinc present in the complex would assist in determining its chemical composition.

A study of the ability to form copper(II) complexes with ethylxanthate in benzene in also necessary as bis(ethylxanthato)copper(II) has already been reported[63] to form in this medium.

Although the M-N stretching frequency is suggested to be below 200 cm^{-1} in these complexes, the dispute has not been settled. Perhaps a study of some analogous O-ethyldiselenocarbonate and diethyldiselenocarbamate complexes or of some pyridyl adducts would be more instructive. Alternatively, normal coordinate analyses of some of these complexes would probably be instructive.

Since the boiling-point-elevation technique has been found inadequate for determining the molecular weights of the species, the freezing-point-depression technique might prove more useful. Another method of obtaining these values might be to study their mass spectra under very mild conditions (room temperature, low eV) to reduce the probability of decomposition of the xanthate ligand.

APPENDIX (I)

Magnetic Studies at Low Temperatures

It has already been suggested[2] that a study of the magnetic properties of bis(diethyldithiocarbamato)1,10-phenanthrolinecobalt(II) as a function of temperature may lead to interesting results. This suggestion applies equally to the other complexes prepared in this study and particularly to bis(ethylxanthato)manganese(II) and bis(ethylxanthato)-iron(II) which show very interesting room temperature magnetic moments. A cryostat was therefore constructed and used in conjunction with the magnet and balance described in section 2.2.4. It was hoped to utilize this apparatus to study the magnetic properties of a variety of complexes at temperatures ranging from 90°K to 300°K in an attempt to gain more detailed information about the electronic structure of the particular metal ions.

Description of the Cryostat

The basic design of the cryostat was modelled after one described by Colton[152] (see Figure XXVI). However, several major modifications were made which are now described.

The diameter of the cryostat tail was reduced

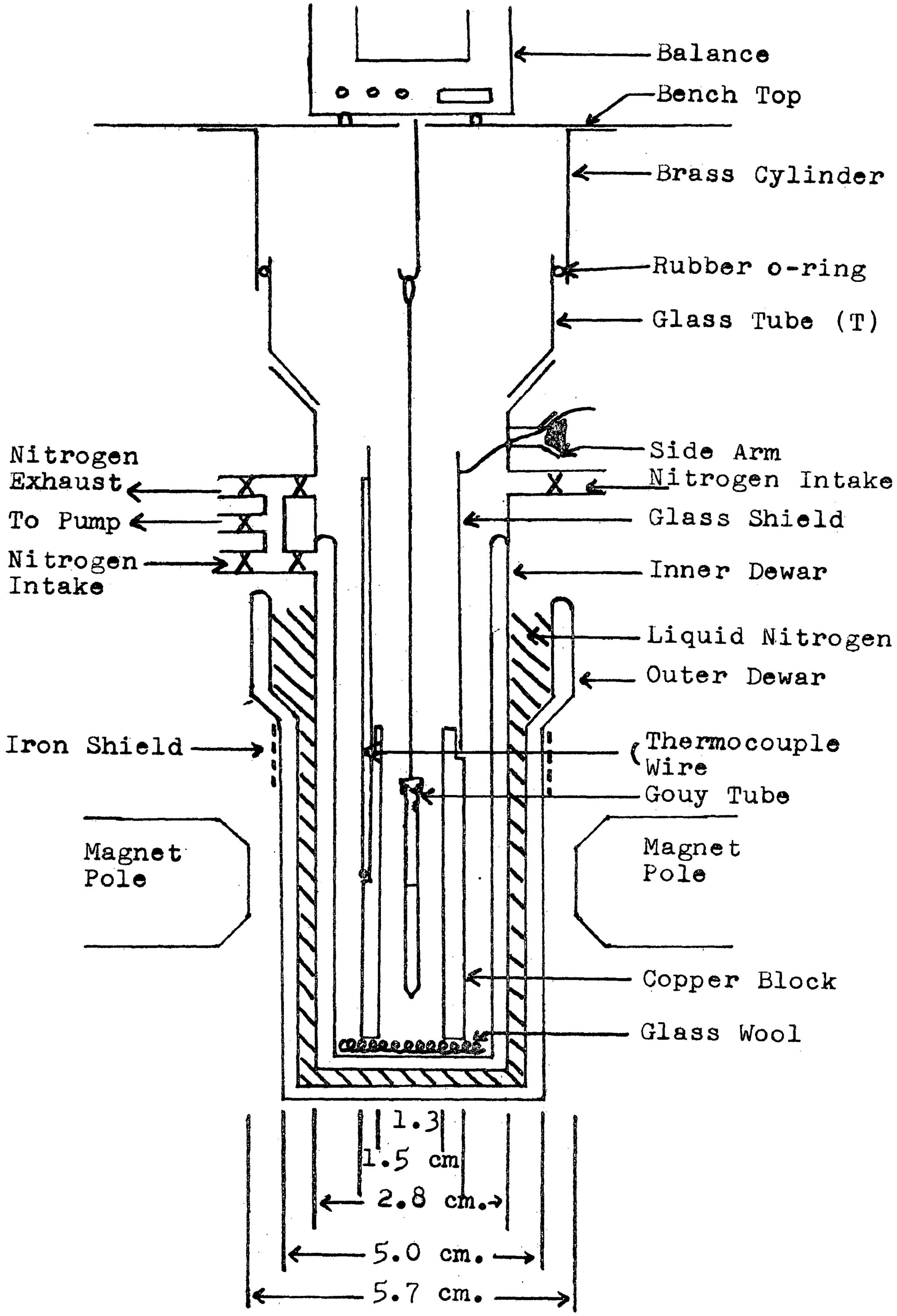

Balance
Bench Top
Brass Cylinder
Rubber o-ring
Glass Tube (T)
Side Arm
Nitrogen Intake
Glass Shield
Inner Dewar
Liquid Nitrogen
Outer Dewar
Thermocouple Wire
Gouy Tube
Magnet Pole
Copper Block
Glass Wool
Nitrogen Exhaust
To Pump
Nitrogen Intake
Iron Shield
Magnet Pole
1.3
1.5 cm
2.8 cm.
5.0 cm.
5.7 cm.

Figure XXVI

from that of the Colton model (7 cm.) to 5 cm., resulting in a greater field strength to which the sample was exposed. The magnet pole pieces were tapered from a diameter of 10 cm. to a diameter of 5 cm. to provide an optimum area of constant field gradient (dH/dx).

The overall length of the cryostat tail was increased so that the somewhat longer heating block (21.5 cm.) permitted the use of a double ended Gouy tube. This led to a more stable arrangement when weighing paramagnetic samples in a relatively high field, as there was less tendency for the tube to be attracted over to the side than with a single ended tube. It also eliminated the necessity of introducing a correction factor for the susceptibility of air. The copper block, (or tube), which had an outer diameter of 1.5 cm. and an inner diameter of 1.3 cm. was cut with four separate spiralling grooves. The grooves were started ninety degrees from each other at one end of the copper block and were cut on a lathe such that each had two windings <u>per</u> centimeter. Finally, a vertical groove was cut in the block so that a thermocouple (and the thermocouple wires) could be inserted in good thermal contact with the block.

Having cut the grooves, the block was coated with a soft epoxy (Copron 90-238-EA215) supplied by Bapco and the copper-constantan thermocouple (supplied by Leeds and Northrup Company and specified to be accurate to within one part in a thousand) was inserted in the vertical groove. A further coating of the soft epoxy and then one of a hard epoxy (clear epoxy finish) was then applied. A platinum wire (183 cm. long and 0.013 cm. diameter), used as a temperature regulator, was then wound down one set of grooves, wrapped around a pin and wound back up an adjacent set of grooves. After more application of the hard epoxy, the nichrome heating wire (135 cm., 35Ω resistance) was wound on the block in a similar manner to that of the platinum wire. To eliminate a potential being set up in the platinum wire over the temperature gradient, a gold wire was brazed at the top of the copper block to the ends of the platinum wire, and also to a copper wire at the control box. The nichrome, gold and thermocouple wires were then transferred up the outside of a glass shield (Figure XXVII) and removed from the system through a side arm.

The use of the platinum wire to regulate the temperature is of some interest. At a certain temperature (T), the resistance of the wire which was part of an electronically balanced system, was a

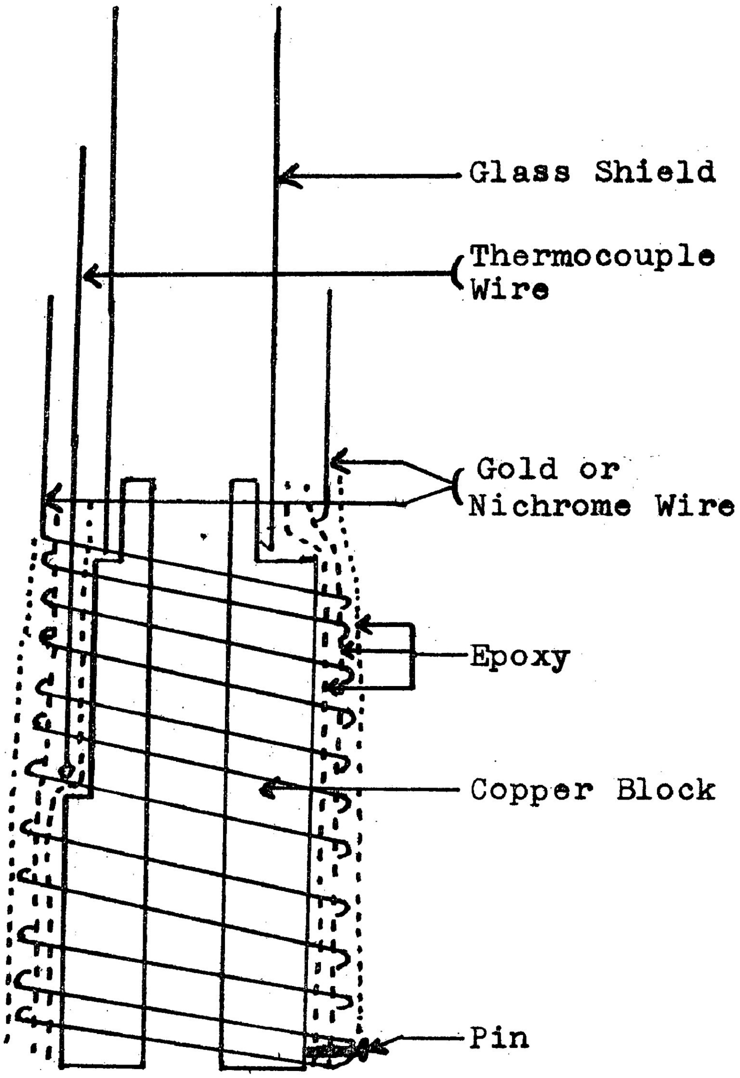


Figure XXVII

constant. As the temperature of the block (and therefore, that of the platinum wire) increased, so did the resistance of the wire. At some temperature (T+t) the increased resistance created such an imbalance in the system, that the heater current automatically switched off. As the temperature lowered, the resistance decreased until at some temperature (T-t') an opposite imbalance existed in the system and the heater current once again switched on.

Use of the Cryostat

The sample specimen could be cooled by introducing liquid nitrogen into the vessel indicated (with the inner dewar containing a vacuum or dry nitrogen and the sample surrounded by nitrogen gas). Temperatures between liquid nitrogen temperature and room temperatures were attained by adjusting an external resistance with which the platinum wire must remain balanced. To maintain a constant level of liquid nitrogen, the coolant was siphoned under pressure into the vessel at a rate equal to that at which it was being boiled away. Due to the close proximity of the liquid nitrogen to the heating coil, and to the narrow vacuum jacket of the outermost dewar, large losses (about 10 liters an hour) were encountered. This was unavoidable as an increase in the dimensions of the cryostat would have had the undesirable effect of decreasing the magnetic field to which the sample would be exposed.

An iron shield assured the reduction of the magnetic field to zero over the length of the sample.

Operational Procedure

Figure XXVI also shows how the sample tube is admitted and suspended. The glass tube (T) slides, on an o-ring, up the brass pipe, which is fitted to the balance table. A stopper is then placed in the ground glass joint allowing the sample chamber to be successively evacuated and filled with dry, oxygen-free nitrogen several times. All exit valves were then closed and a small positive pressure of nitrogen allowed to build up inside the sample compartment. The stopper could then be removed and a small constant flow of nitrogen was maintained to prevent the diffusion of oxygen and water vapour into the compartment. The Gouy tube could then be admitted and hung, using a nylon line, from the metal suspension as shown in Figure XXVI. The Gouy tube was weighed at room temperature at 0 kG, 5.8 kG (microdial = 780), and 6.9 kG (microdial = 925) field strengths (as determined _via_ a Hall probe). This was repeated until the readings for each current strength were all within 0.1 milligrams of each other. With the inner dewar filled with nitrogen gas, to aid cooling, liquid nitrogen was then introduced to the outer dewar and the system allowed to cool until the thermocouple indicated the temperature was below 90°K. A small amount of current was then passed through the heating coil so that the temperature raised 5° or 10°K. Once the thermocouple indicated a constant temperature (about 95°K), the system was permitted to come to thermal equilibrium (about 30 to 45 minutes). The sample was then reweighed at field strengths of 0 kG, 5.8 kG and 6.9 kG, until the weight at each current strength became constant (within 0.1 milligrams). The current flowing through the heating coil was then increased, so that the temperature raised 25° or 30°K, the system was allowed to equilibrate again and the sample reweighed as before. This process was repeated until the sample chamber had returned to room temperature, for which the weighings were repeated. All measurements between 100°K and 300°K were taken with the inner dewar under vacuum to reduce liquid nitrogen loss due to the heating coil.

Calibration

A double ended Gouy tube, the lower end under vacuum, was used, eliminating the necessity of introducing the atmospheric correction factor, α, see equation (2),

$$\chi = \left(\frac{\alpha + \beta F}{wt}\right) \cdot 10^{-6} \text{------} (2)$$

where:

χ = the magnetic susceptibility,

α = a constant which takes the displaced air by the sample into account,

β = tube calibration constant,

F = force exerted on the sample due to the magnet (expressed in mg.), and

wt = the weight of the sample (in grams).

Hence equation (2) becomes:

$$(10^6)\chi = \frac{\beta F}{wt} \text{------} (3)$$

As the tube was constructed from pyrex glass, it was necessary to determine its "apparent" weight at all the appropriate temperatures and field strengths to eliminate errors due to its inherent diamagnetism and the paramagnetic impurities. The weight of the sample at zero field strength and temperature (T) is given by equation (4):

$$(wt)_T = (S)_T^o - (E)_T^o \text{------} (4)$$

where:

$(wt)_T$ = the weight of the sample at some temperature (T),

$(S)_T^o$ = the weight of the Gouy tube plus the sample at zero field strength and temperature (T), and

$(E)_T^o$ = the weight of the empty tube at zero field strength and temperature (T),

and the force which the field (H) exerts on the sample at the same temperature (T) is given by equation (5):

$$F_T^H = (S)_T^H - (E)_T^H - (wt)_T \text{ ------(5)}$$

where:

F_T^H = the force exerted on the sample at temperature (T) by the magnetic field (H),

$(S)_T^H$ = the apparent weight of the Gouy tube plus the sample at temperature (T) and field strength (H), and

$(E)_T^H$ = the apparent weight of the empty Gouy tube at field strength (H) and temperature (T).

Substituting equations (4) and (5) into equation (3), we have:

$$(10^6)\chi = \frac{((S)_T^H + (E)_T^o - (S)_T^o - (E)_T^H)}{(S)_T^o - (E)_T^o} \text{ ------(6)}$$

Since the calibrant was mercuri tetra(thiocyanato)cobaltate(II), χ was known[144] to be (16.44 x

10^{-6}). Substituting this value into equation (6), and determining $(S)_T^H$, $(S)_T^o$, $(E)_T^H$, and $(E)_T^o$, it was possible to determine β at room temperature. This was done three times for both field strengths, and found to be (0.431, 0.431 and 0.424) at a field strength of 5.8 kG and (0.322, 0.319 and 0.314) at a field strength of 6.9 kG. For subsequent calculations, constants of 0.43 and 0.32, respectively, were used.

Having determined β , χ was determined over a range of temperatures, at both field strengths, on three different occasions. The average molar susceptibility (of the two valves obtained at different field strengths), its reciprocal and the temperature at which these were determined are listed in Table 9, for the three different trials. The dependence of $1/\chi$ on the temperature was essentially identical for all trials (Graph V), with a value of 9° being obtained for θ. This agrees very well with the value ($\theta = 10^\circ$) reported in the literature[153].

Using the appropriate values for β , the magnetic susceptibilities of tris(ethylenediamino)nickel(II) thiosulphate and penta(aquo)copper(II) sulphate were calculated at both field strengths and found to be 10.93×10^{-6} and 6.06×10^{-6}, respective-

Table 9

The dependence of $\frac{1}{\chi}$ on the temperature for $Hg(Co(SCN)_4)$

(a)

Temperature (°K)	Weight (gm.)	Force (mg.) 5.8 kG	Force (mg.) 6.9 kG	χ_{AVER}	$\frac{1}{\chi_{AVER}} \times 10^3$
94.2	0.56740	64.84	86.17	48.9	20.45
118.9	0.56766	52.87	70.80	40.0	25.00
144.2	0.56776	44.34	59.92	33.7	29.67
169.4	0.56779	37.65	51.15	28.65	34.90
199.1	0.56776	32.09	43.85	24.5	40.82
227.6	0.56765	28.25	38.37	21.5	46.51
255.8	0.56774	25.25	34.38	19.25	51.95
295.0	0.56732	21.99	29.69	16.44	60.83

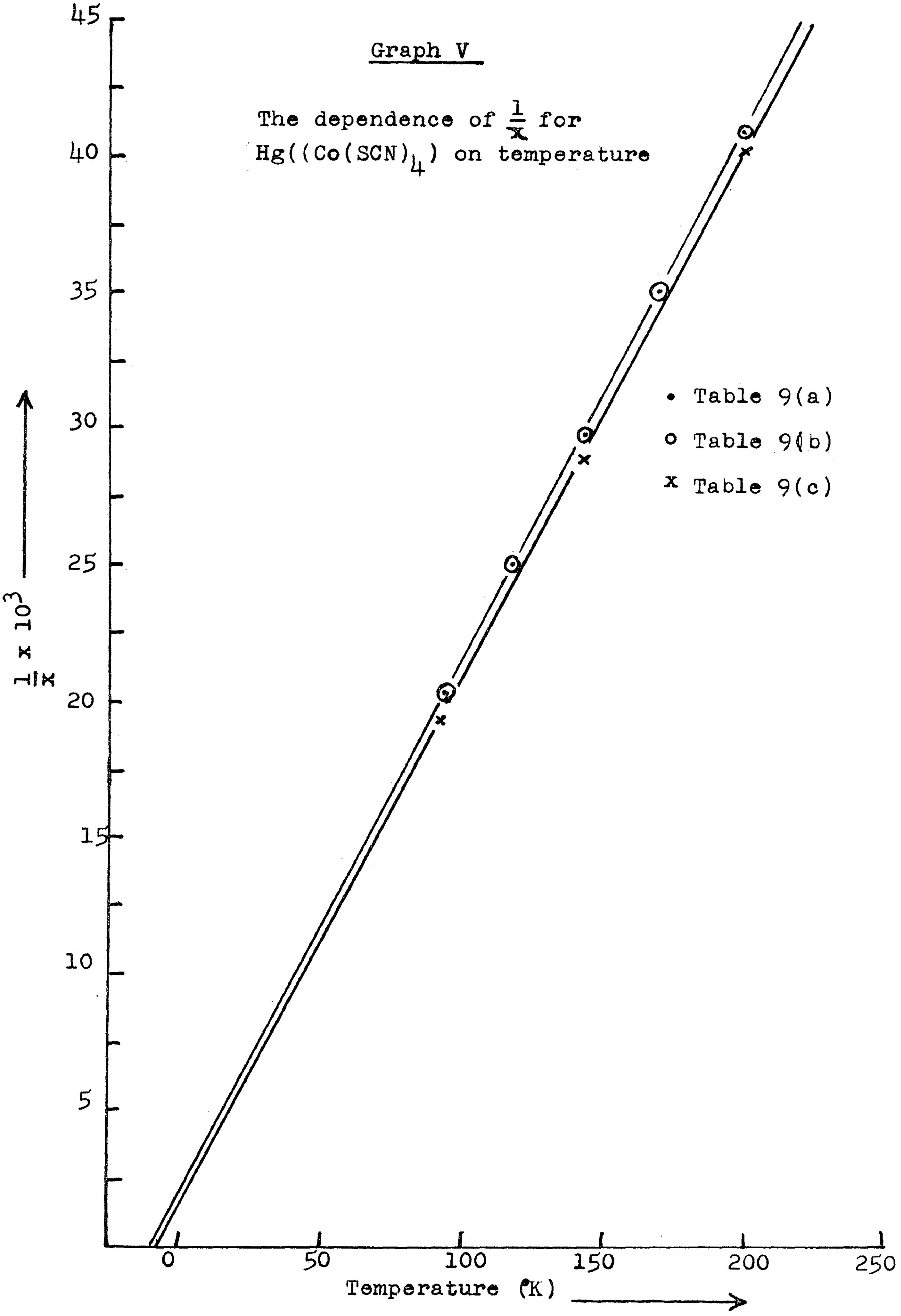
Table 9, cont'd.

(b)

Temperature (°K)	Weight (gm.)	Force (mg.)		χ_{AVER}	$\frac{1}{\chi_{AVER}} \times 10^3$
		5.8 kG	6.9 kG		
94.7	0.57845	67.04	89.94	49.80	20.08
144.1	0.57848	45.47	60.44	33.65	29.72
199.6	0.57853	33.01	45.79	24.58	40.70
255.0	0.57853	25.97	35.01	19.37	51.62
295.7	0.57899	22.08	29.81	16.44	60.83

(c)

Temperature (°K)	Weight (gm.)	Force (mg.)		χ_{AVER}	$\frac{1}{\chi_{AVER}} \times 10^3$
		5.8 kG	6.9 kG		
92.1	0.59962	72.46	99.78	52.10	19.19
144.6	0.59982	48.84	65.00	34.85	28.69
199.8	0.59974	34.83	46.68	24.93	40.12
255.4	0.60023	27.68	37.13	19.82	54.42
295.8	0.59822	22.79	30.49	16.44	60.83



Graph V

The dependence of $\frac{1}{x}$ for $Hg((Co(SCN)_4)$ on temperature ly, at room temperature. These agreed, within 1% and 0.2%, with the published values[154,155] of 10.82 x 10^{-6} and 6.05 x 10^{-6}, respectively.

Difficulties

A difficulty already mentioned is the large loss of liquid nitrogen. Although not hampering the ease with which the studies could be conducted, it did make them rather expensive (sixty to eighty dollars for each study).

A more severe difficulty was encountered with static electricity. It was often found that the tube was pulled so strongly to the glass jacket that it collided with the copper heating block, making reproducible weighings impossible. Indeed, the problem developed to such an extent that, when the copper block was removed from the cryostat, the sample tube often collided with the inner dewar of the cryostat. Under these conditions the tube could not be weighed although the effective diameter of the sample compartment had been increased to 1.9 cm. After some investigation, it was learned that the static was accumulating on the two large dewars of the cryostat. Although this static, which posed no problem during summer months, could be removed temporarily during winter months (by dismantling the cryostat and thoroughly grounding both walls of both dewars) it always returned within hours. This was attributed to the dryness of the atmosphere during the cold season. Indeed, it was found that much less ice formed at the top of the outer dewar during winter months than during the summer. Since dismantling the cryostat, removing the static electricity and realigning the vessels with the magnet and balance would have necessitated redetermining the constant after each dismantling process, it was not feasible to do this before each run. Attempts at coating the dewars with a gold ribbon, which could then be grounded, were also unsuccessful due to the inability of obtaining good ventiliation in such a long cylinder already sealed at one end. Various "anti-static" sprays were used in an attempt to remedy the problem, but none proved effective. Hence a new cryostat, the dewars of which will be gold plated, is currently under construction.

Static electricity was easily removed from the Gouy tube by grounding it with an acetone-soaked cloth. Similar problems with static electricity have been encountered elsewhere[156], but could often be overcome by adjusting the position of the balance to "pull" the Gouy tube from the copper block. The drier climate of this locale likely increases the effect of static to the point where such a remedy is no longer possible.

Another problem was encountered due to the expansion and contraction of the copper block with temperature. This eventually fractured the glass shield and severed the platinum wires at the copper-glass joint. Thereafter, the temperature was controlled by the cruder method of regulating the current via a variac. A new copper block is currently being constructed with a cellulose "buffer" at the copper-glass join.

Unknown Samples

Despite the above problems, which eventually made a continuation of these studies impossible, the molar susceptibilities of α-$Mn(Xan)_2 \cdot bipy$, β-$Fe(Xan)_2 \cdot bipy$ and β-$Co(Xan)_2 \cdot bipy$ as a function of temperature were determined. The results are listed in Table 10 and plotted on Graphs VI, VII and VIII, respectively. The manganese and iron complexes were studied a second time due to the tendency of the $\frac{1}{\chi}$ vs temperature plot of the former to deviate from a straight line above 230°K and the low value of the susceptibility obtained for the latter. These results are listed in Table 11 and plotted, again, on Graphs VI and VII. It is seen that the results were

Table 10

The dependence of $\frac{1}{\chi}$ on the temperature.

(a) - for α-Mn(Xan)$_2$•bipy

Temperature (°K)	Weight (gm.)	Force (mg.) 5.8 kG	Force (mg.) 6.9 kG	χ^{AVER}	$\frac{1}{\chi}^{AVER} \times 10^3$
94.1	0.18763	37.00	50.09	85.2	21.74
118.9	0.18771	29.69	40.27	68.40	14.62
143.8	0.18775	24.91	33.70	57.25	17.47
169.1	0.18768	21.34	28.75	49.0	20.41
199.6	0.18782	18.02	24.26	41.25	24.24
227.8	0.18774	18.85	21.42	36.4	27.47
255.5	0.18768	14.15	19.07	32.45	30.82
273.5	0.18781	13.21	17.86	30.3	33.00
295.1	0.18700	12.28	16.52	28.2	35.46

Table 10, cont'd.

(b) - for β-Fe(Xan)$_2$·bipy

Temperature (°K)	Weight (gm.)	Force (mg.) 5.8 kG	Force (mg.) 6.9 kG	χ^{AVER}	$\frac{1}{\chi^{AVER}} \times 10^3$
94.3	0.13724	14.06	18.94	44.0	22.73
119.6	0.13702	11.46	15.40	35.9	27.86
144.7	0.13703	9.67	13.04	30.4	32.89
169.5	0.13684	8.37	11.26	26.3	38.02
199.2	0.13693	7.10	9.50	22.25	44.94
227.4	0.13678	6.20	8.43	19.60	51.02
255.8	0.13666	5.59	7.58	17.65	56.66
273.3	0.13670	5.09	6.85	15.95	62.70
295.4	o.13593	4.86	6.49	15.33	65.25

Table 10, cont'd.

(c) - for β-Co(Xan)$_2$•bipy

Temperature (°K)	Weight (gm.)	Force (mg.) 5.8 kG	Force (mg.) 6.9 kG	χ^{AVER}	$\frac{1}{\chi^{AVER}} \times 10^3$
96.5	0.13969	12.68	17.05	43.8	22.83
120.1	0.13899	10.95	14.71	38.03	26.30
143.5	0.13871	9.48	12.73	32.95	30.35
168.9	0.13868	8.12	10.99	28.38	35.24
199.0	0.13854	7.12	9.56	24.80	40.32
227.1	0.13861	6.41	8.64	22.35	44.74
255.4	0.13857	5.72	7.69	19.95	50.12
273.2	0.13867	5.28	7.20	18.5	54.05
294.8	0.13818	4.90	6.59	17.11	58.49

Table 11

The dependence of $\frac{1}{\chi}$ on the temperature.

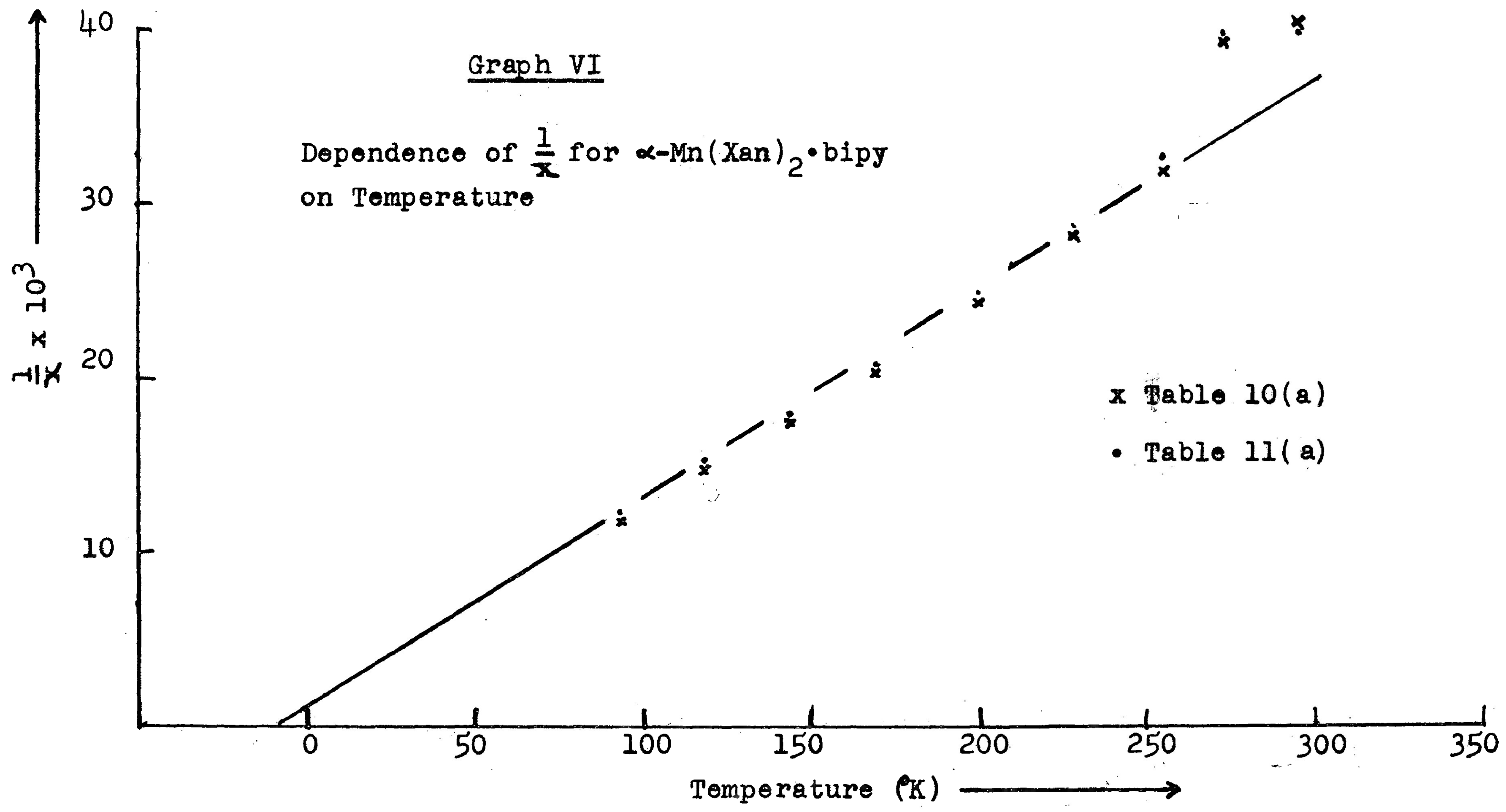
(a) - for α-Mn(Xan)$_2$·bipy

Temperature (°K)	Weight (gm.)	Force (mg.)		χ_{AVER}	$\frac{1}{\chi_{AVER}} \times 10^3$
		5.8 kG	6.9 kG		
94.2	0.16758	31.81	43.09	82.0	12.20
119.0	0.16409	25.09	34.29	66.3	15.08
144.2	0.16432	21.08	28.84	55.6	17.86
169.4	0.16417	17.99	24.79	47.7	20.96
199.9	0.16430	15.05	20.94	40.0	25.00
227.9	0.16427	12.99	18.29	34.8	28.74
255.2	0.16408	11.35	16.20	30.6	32.68
273.2	0.16426	10.45	14.96	27.7	36.10
295.7	0.16207	10.77	13.67	27.7	36.10

Table 11, cont'd.

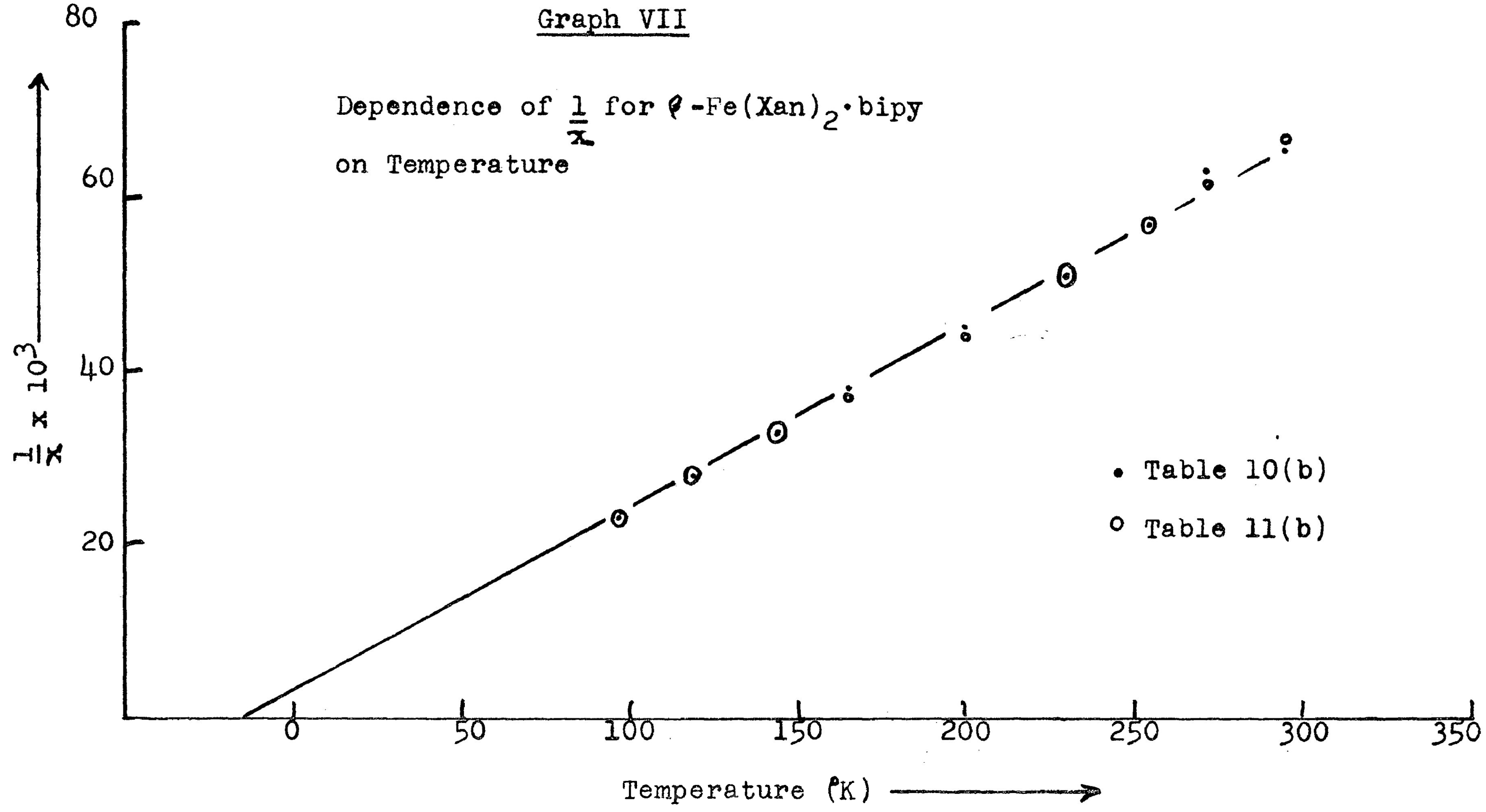
(b) - for β-Fe(Xan)$_2$·bipy

Temperature (°K)	Weight (gm.)	Force (mg.) 5.8 kG	Force (mg.) 6.9 kG	χ_{AVER}	$\frac{1}{\chi_{AVER}} \times 10^3$
93.6	0.13715	12.37	16.61	43.5	23.00
119.2	0.13695	10.21	13.70	35.95	27.82
143.8	0.13671	8.68	11.69	30.7	32.52
168.4	0.13664	7.64	10.21	26.9	37.17
198.9	0.13677	6.43	8.68	22.7	44.05
226.9	0.13653	5.65	7.70	20.1	49.75
257.4	0.13669	5.04	6.71	17.83	56.10
274.3	0.13700	4.59	6.20	16.2	61.73
295.8	0.13624	4.24	5.70	15.0	66.67



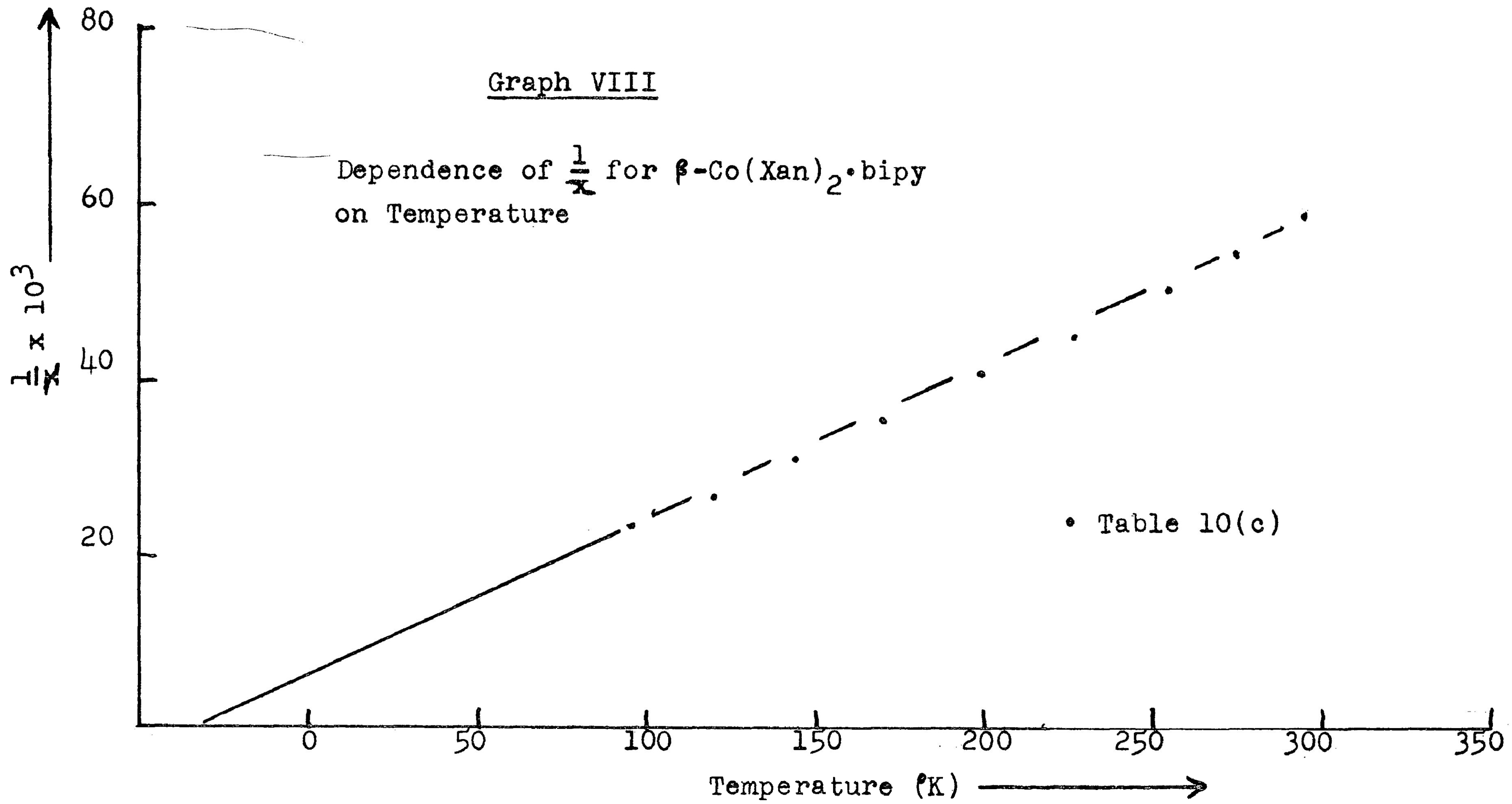
Graph VI

Dependence of $\frac{1}{\chi}$ for α-Mn(Xan)$_2$•bipy on Temperature



Graph VII

Dependence of $\frac{1}{\chi}$ for β-Fe(Xan)$_2$·bipy on Temperature



Graph VIII

Dependence of $\frac{1}{\chi}$ for β-Co(Xan)$_2$•bipy on Temperature essentially identical. The tendency to obtain rather high values for $\frac{1}{\chi}$ when approaching room temperature is suggested to reflect an unstable system i.e: the extremely fast rate of liquid nitrogen loss due to the (relatively) high temperature of the heating coil. As the reservoir of coolant is only about 0.5 cm. thick at the point adjacent the heating block, the vigorously boiling nitrogen results in the reservoir containing a mixture of nitrogen gas (the escaping bubbles) and liquid, hence lowering the cooling ability. This would result in a longer time being required to obtain thermal equilibrium. For this reason the magnetic susceptibility obtained at room temperature, prior to the introduction of liquid nitrogen to the system is considered to be more reliable than the value obtained at the end of the study when the heating coil was required to raise the temperature of the cold apparatus. The low value for β-Fe(Xan)$_2$·bipy was, as mentioned previously, the result of potassium chloride contamination.

From Graphs VI, VII and VIII, it is seen that the θ-values for α-Mn(Xan)$_2$·bipy, β-Fe(Xan)$_2$·bipy and β-Co(Xan)$_2$·bipy are 8.5°, 15° and 30°, respectively. Multiplying χ by the molecular weight (to obtain the molar susceptibility) and correcting for the diamagnetism inherent in the atoms[144], a corrected value for the molar susceptibility (χ_M^{corr}) was obtained. Substituting this value and "θ" into equation (7), where "μ" is the magnetic moment (in Bohr Magnetons)

$$\mu = 2.84\sqrt{\chi_M^{corr}(T+\theta)} \text{ ------(7)}$$

and "T" is the temperature (in degrees Kelvin), the magnetic moments for these compounds were found to be 5.6 B.M., 4.2 B.M. and 4.6 B.M., respectively.

Despite the low value for β-Fe(Xan)$_2$·bipy, these complexes have all been shown to exhibit normal Curie-Weiss behaviour.

APPENDIX II

d-spacings and approximate relative intensities for the xanthate complexes studied in this thesis:

$M(Xan)_2$

M = Mn or Fe		M = Ni		M = Zn	
d-spacing	Relative Intensity	d-spacing	Relative Intensity	d-spacing	Relative Intensity
10.9	8	10.45	10	9.0	10
8.7	1	5.06	5	5.5	4
7.8	8	4.67	5	5.1	1
7.3	10	4.22	6	4.8	1
5.9	6	3.78	6	4.6	-
5.4	4	3.69	-	4.36	-
4.7	3	3.55	-	4.12	-
4.45	3	3.46	2	3.94	-
4.10	1	3.30	2	3.78	-
4.00	1	3.14	2	3.68	3
3.89	-	3.01	1	3.51	1
3.59	1	2.82	1	3.32	-
3.35	-	2.76	-	3.14	6
3.22	-	2.60	-	3.04	-
3.08	-	2.55	1	2.97	-
2.95	-	2.46	1	2.83	-
2.86	-	2.33	1	2.76	-
2.77	2	2.28	-	2.70	-
2.71	1	2.25	-	2.61	-
2.60	2	2.22	2	2.54	-
2.49	-	2.11	-	2.40	-

$M(Xan)_2$

M = Mn or Fe		M = Ni		M = Zn	
d-spacing	Relative Intensity	d-spacing	Relative Intensity	d-spacing	Relative Intensity
2.44	1	2.06	-	2.35	-
2.30	-	2.04	-	3.30	-
2.24	1	1.86	-	2.23	4
2.09	-	1.81	-	1.81	1
2.05	-	1.78	-	1.57	1
1.96	-	1.65	-	-	-
1.69	-	1.63	-	-	-
1.67	-	1.59	-	-	-
1.63	-	1.51	-	-	-

$(N(C_2H_5)_4)(M(Xan)_3)$

M = Mn		M = Fe or Ni		M = Zn	
d-spacing	Relative Intensity	d-spacing	Relative Intensity	d-spacing	Relative Intensity
8.63	10	11.85	1	9.25	6
7.75	7	10.00	1	8.4	-
7.30	6	8.5	10	7.55	10
6.60	-	8.1	2	6.58	1
5.95	7	7.5	2	6.15	6
5.55	4	7.2	8	5.63	-
5.20	1	6.8	3	5.20	5
4.70	3	6.25	3	4.93	3
4.40	1	5.75	9	4.73	4
4.25	3	5.15	-	4.58	1
3.88	2	4.80	3	4.34	3
3.65	-	4.51	5	4.17	-
3.52	4	4.28	2	3.96	2
3.41	-	4.12	3	3.81	3
3.26	1	4.00	-	3.59	-
2.97	-	3.77	-	3.50	2
2.94	1	3.58	4	3.34	-
2.85	-	3.40	-	3.23	-
2.76	-	3.28	1	3.11	-
2.70	-	3.19	-	3.03	-
2.60	-	2.95	-	2.90	-
2.48	-	2.85	-	2.81	-
2.35	-	2.72	-	2.71	-
2.23	-	2.51	-	2.66	-
-	-	2.45	-	2.60	-

$(N(C_2H_5)_4)(M(Xan)_3)$

M = Mn		M = Fe or Ni		M = Zn	
d-spacing	Relative Intensity	d-spacing	Relative Intensity	d-spacing	Relative Intensity
-	-	2.36	-	2.46	1
-	-	2.25	-	2.36	-
-	-	2.20	-	2.27	-
-	-	2.15	-	2.24	-
-	-	2.10	-	2.21	-
-	-	2.06	-	2.16	-
-	-	1.99	-	2.09	-
-	-	-	-	1.89	-

α-M(Xan)$_2$•bipy M = Mn, Fe, Co or Ni		β-Fe(Xan)$_2$•bipy		β-Co(Xan)$_2$•bipy	
d-spacing	Relative Intensity	d-spacing	Relative Intensity	d-spacing	Relative Intensity
10.28	6	12.00	2	10.15	8
8.95	5	8.80	5	8.78	1
7.30	1	7.90	1	8.10	3
6.70	3	7.20	6	6.60	10
5.98	1	6.25	10	6.21	-
5.72	10	5.65	-	5.70	7
5.18	-	4.70	1	5.35	2
4.61	-	4.43	-	5.03	-
4.48	-	4.25	2	4.60	4
4.23	5	3.94	3	4.40	4
4.00	1	3.78	2	4.20	1
3.87	-	3.45	1	3.83	7
3.76	-	3.32	-	3.70	1
3.59	4	3.01	-	3.55	-
3.42	-	2.76	-	3.37	4
3.32	1	2.61	-	3.09	-
3.26	-	2.49	-	2.89	1
3.19	-	2.34	-	2.84	-
3.08	-	2.23	-	2.70	-
2.96	2	2.13	-	2.61	-
2.82	-	2.00	-	2.52	-
2.66	-	-	-	2.38	-
2.57	-	-	-	2.33	-
2.53	-	-	-	2.16	-
2.41	-	-	-	2.09	-
2.35	-	-	-	2.01	-
2.30	1	-	-	-	-
2.20	-	-	-	-	-
1.93	-	-	-	-	-

β-Ni(Xan)$_2\cdot$bipy		β-Zn(Xan)$_2\cdot$bipy	
d-spacing	Relative Intensity	d-spacing	Relative Intentsity
9.75	-	10.3	10
8.55	5	9.25	-
7.90	1	8.15	-
7.20	10	7.2	8
6.65	3	6.75	-
6.25	-	5.90	2
5.68	1	5.70	-
5.39	3	5.45	1
5.05	1	5.15	3
4.81	3	4.94	1
4.63	2	4.67	4
4.40	-	4.45	2
4.30	1	4.35	2
4.16	-	4.18	1
4.05	2	3.93	2
3.90	1	3.74	3
3.75	5	3.57	1
3.55	1	3.44	1
3.47	1	3.38	-
3.27	1	3.21	5
3.13	-	3.09	-
3.03	-	2.94	-
2.94	-	2.84	-
2.80	-	2.73	-
2.60	-	2.60	-
2.49	-	2.47	1
2.45	-	2.43	-
2.33	-	2.37	-
-	-	2.27	-
-	-	2.18	1

M(Xan)$_2$•phen

M = Mn		M = Fe		M = Co or Ni		M = Zn	
d-spacing	Relative Intensity	d-spacing	Relative Intensity	d-spacing	Relative Intensity	d-spacing	Relative Intensity
10.45	1	11.55	1	8.70	8	11.5	10
7.30	10	8.9	2	8.10	1	7.78	4
5.5	7	7.75	10	7.23	10	7.50	-
5.2	-	6.9	8	6.81	2	6.75	8
4.60	4	5.78	-	5.70	-	6.25	5
4.19	5	5.33	-	5.46	1	5.60	6
4.02	3	5.00	8	5.19	2	5.30	2
3.78	-	4.71	2	4.98	-	5.00	-
3.53	1	4.54	-	4.77	4	4.81	-
3.42	8	4.44	-	4.58	2	4.60	2
3.27	-	4.25	-	4.34	1	4.43	-
3.18	-	4.05	-	4.12	2	4.30	-
2.96	-	3.90	2	3.83	2	4.10	7
2.90	-	3.82	-	3.58	2	3.95	-
2.74	1	3.71	1	3.35	-	3.77	4
2.55	-	3.55	1	3.23	-	3,65	-
2.45	-	3.40	2	3.07	1	3.55	1
2.42	-	3.24	3	2.97	-	3.44	-
2.29	-	3.06	-	2.84	-	3.34	8
2.18	1	2.93	-	2.75	-	3.12	1
2.09	-	2.85	-	2.68	-	3.00	-
2.02	1	2.75	-	2.52	-	2.93	-
1.94	-	2.68	-	2.45	-	2.79	-
1.90	-	2.57	1	2.38	-	2.53	-
1.86	-	2.48	-	2.22	-	2.48	-
-	-	2.41	-	-	-	2.37	-
-	-	2.31	-	-	-	2.27	-
-	-	-	-	-	-	2.23	-
						2.00	-

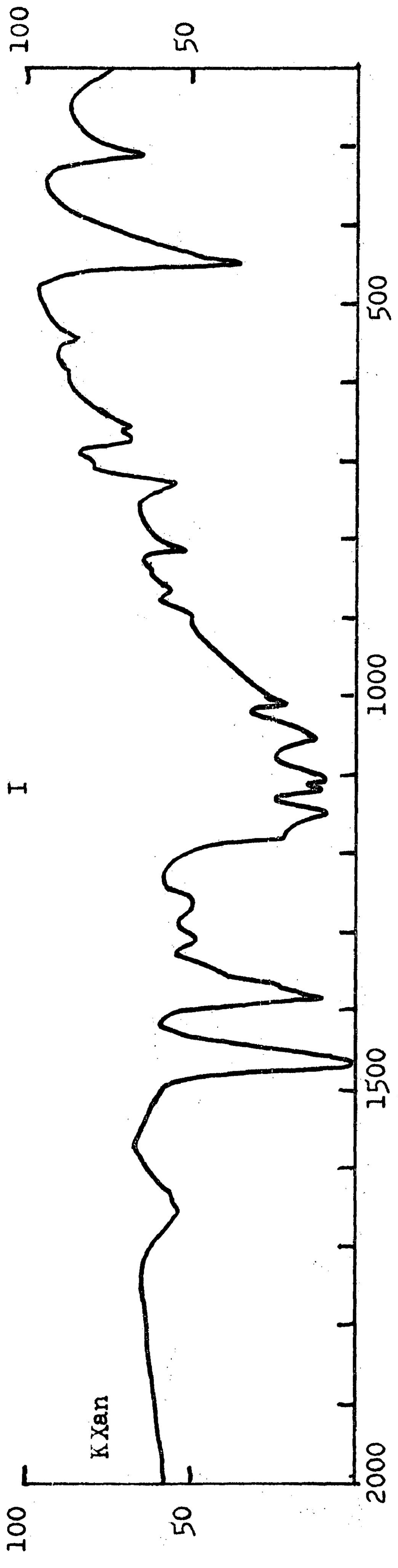
APPENDIX III

The infra-red spectra of the compounds studied in this thesis:

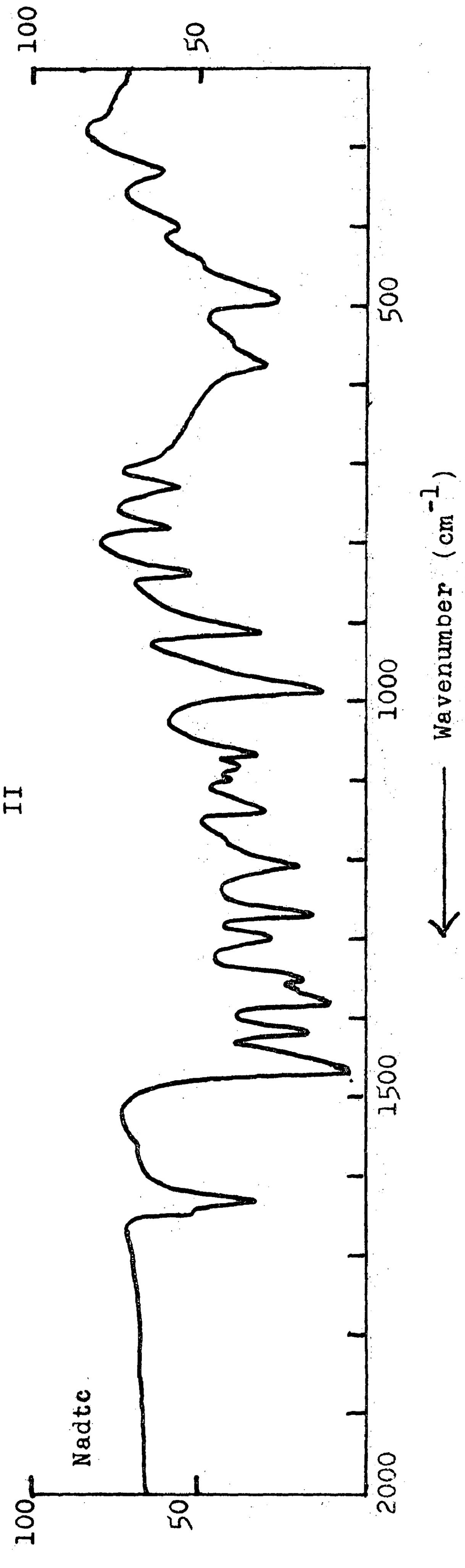
KXan	I
Nadtc	II
(N(C_2H_5)$_4$)Cl	III
2,2'-bipyridyl	IV
1,10-phenanthroline	V
(Xan)$_2$	VI
CH_2(dtc)$_2$	VII
Mn(Xan)$_2$	VIII
Fe(Xan)$_2$	IX
Ni(Xan)$_2$	X
Zn(Xan)$_2$	XI
(N(C_2H_5)$_4$)(Mn(Xan)$_3$)	XII
(N(C_2H_5)$_4$)(Fe(Xan)$_3$)	XIII
(N(C_2H_5)$_4$)(Ni(Xan)$_3$)	XIV
(N(C_2H_5)$_4$)(Zn(Xan)$_3$)	XV
α-Mn(Xan)$_2$·bipy	XVI
α-Fe(Xan)$_2$·bipy	XVII
β-Fe(Xan)$_2$·bipy	XVIII
α-Co(Xan)$_2$·bipy	XIX
β-Co(Xan)$_2$·bipy	XX
α-Ni(Xan)$_2$·bipy	XXI
β-Ni(Xan)$_2$·bipy	XXII

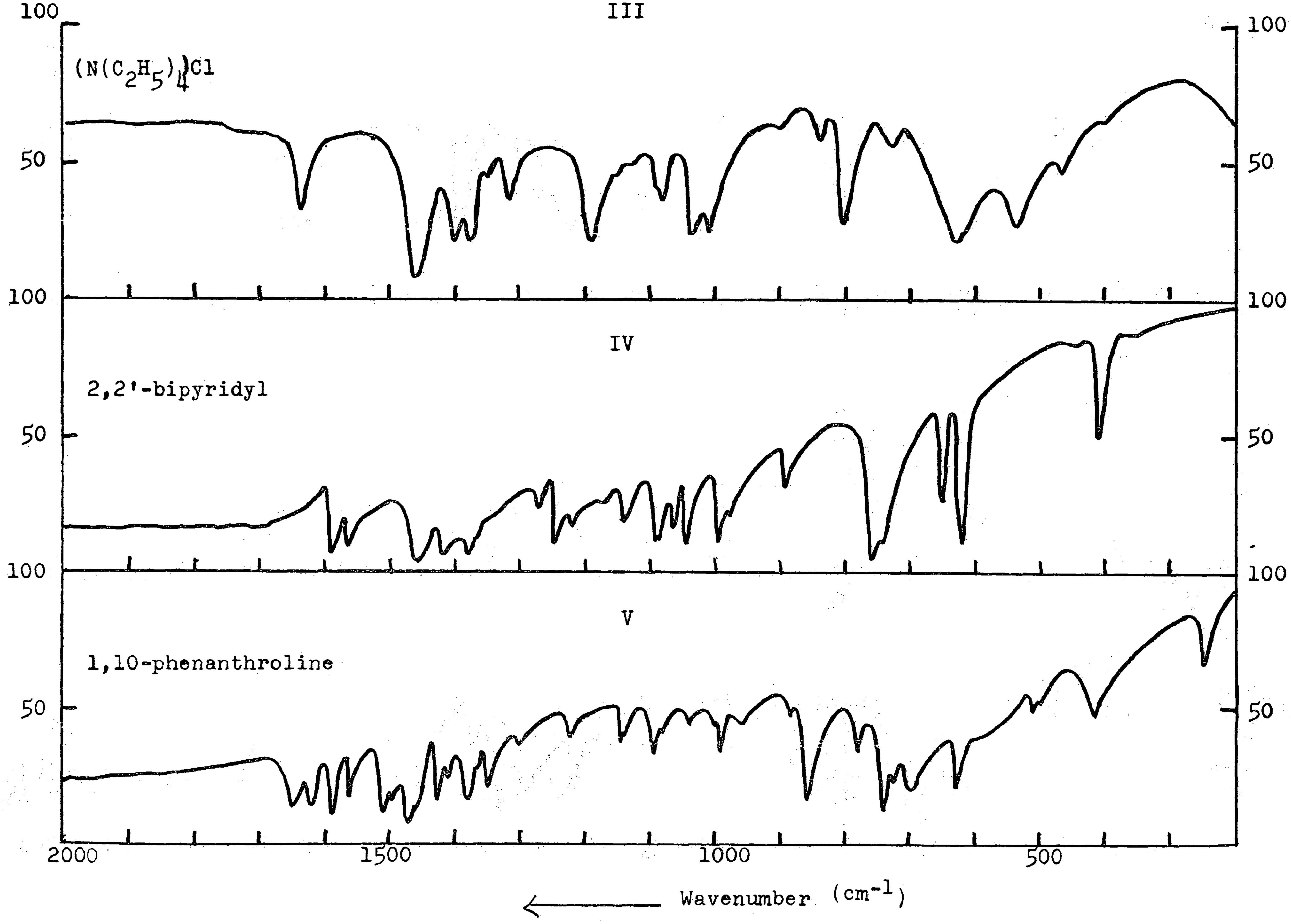
β -$Zn(Xan)_2 \cdot bipy$	XXIII
insoluble residue from the reaction to prepare β -$Zn(Xan)_2 \cdot bipy$	XXIV
$Mn(Xan)_2 \cdot phen$	XXV
$Fe(Xan)_2 \cdot phen$	XXVI
$Co(Xan)_2 \cdot phen$	XXVII
$Ni(Xan)_2 \cdot phen$	XXVIII
$Zn(Xan)_2 \cdot phen$	XXIX
$Mn(dtc)_2 \cdot bipy$	XXX
$Fe(dtc)_2 \cdot bipy$	XXXI
$Co(dtc)_2 \cdot bipy$	XXXII
$Zn(dtc)_2 \cdot bipy$	XXXIII
$Mn(dtc)_2 \cdot phen$	XXXIV
$Fe(dtc)_2 \cdot phen$	XXXV
$Co(dtc)_2 \cdot phen$	XXXVI
$Ni(phen)_3(dtc)_2$	XXXVII
$Ni(phen)_3Cl_2(CH_2Cl_2)_2$	XXXVIII
$Ni(phen)_3Cl_2(C_2H_5OH)_2$	XXXIX

I

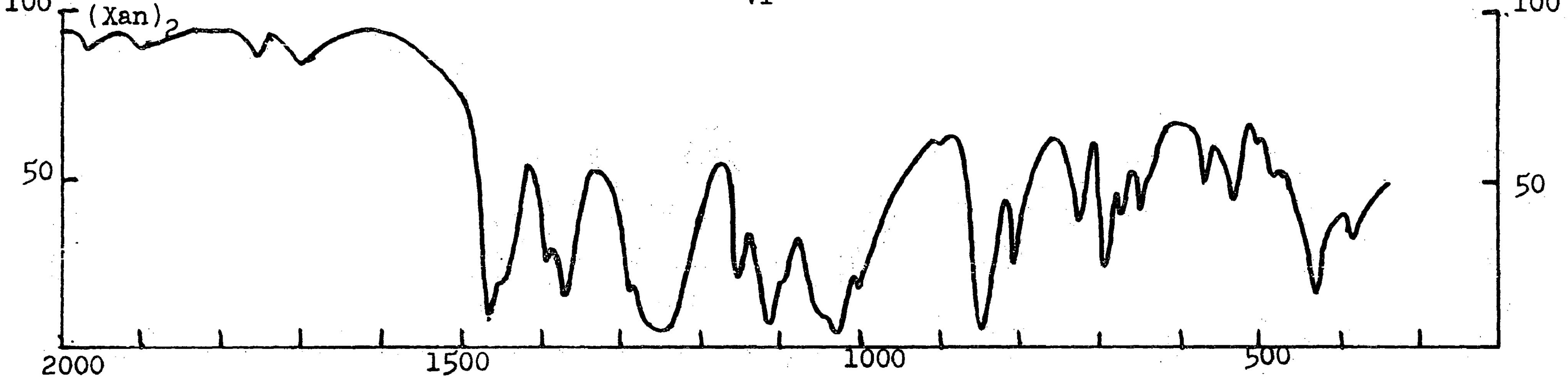

KXan
100
50
100
50
2000
1500
1000
500

II

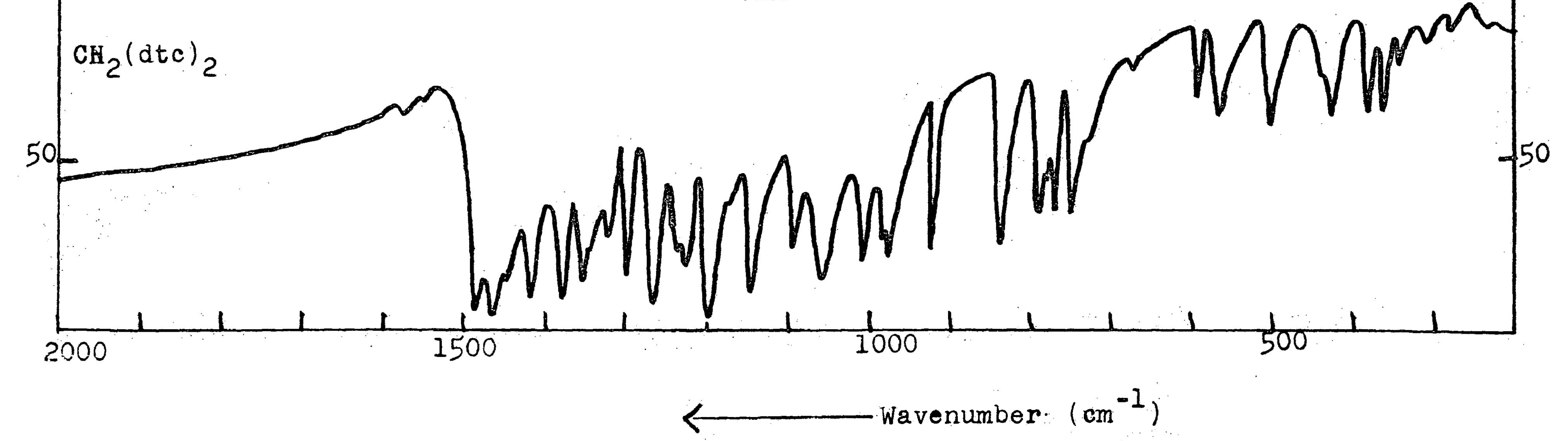

Nadtc
100
50
100
50
2000
1500
1000
500
Wavenumber (cm^{-1})


III
$(N(C_2H_5)_4)Cl$
IV
2,2'-bipyridyl
V
1,10-phenanthroline
100
50
100
50
100
50
2000
1500
1000
500
Wavenumber (cm^{-1})

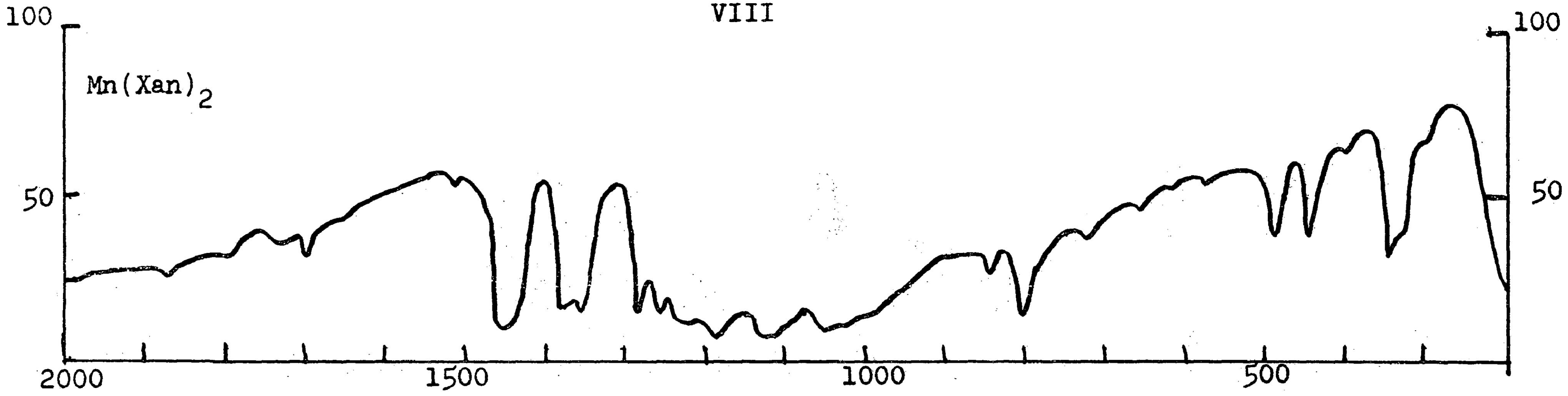
VI


(Xan)$_2$
100
50
100
50
2000
1500
1000
500

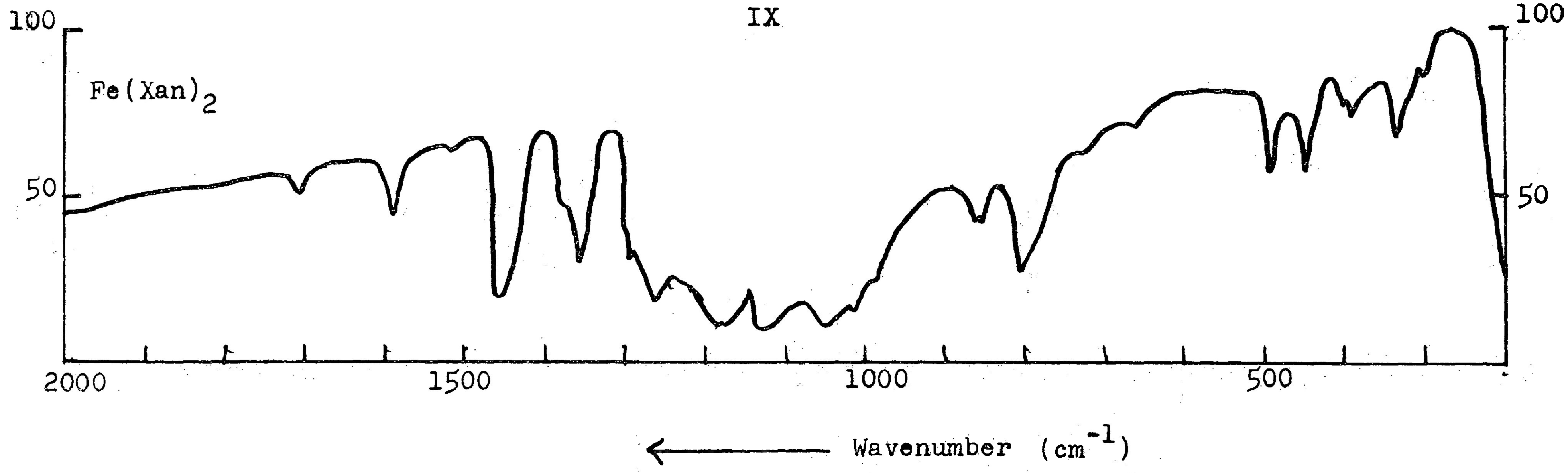
VII

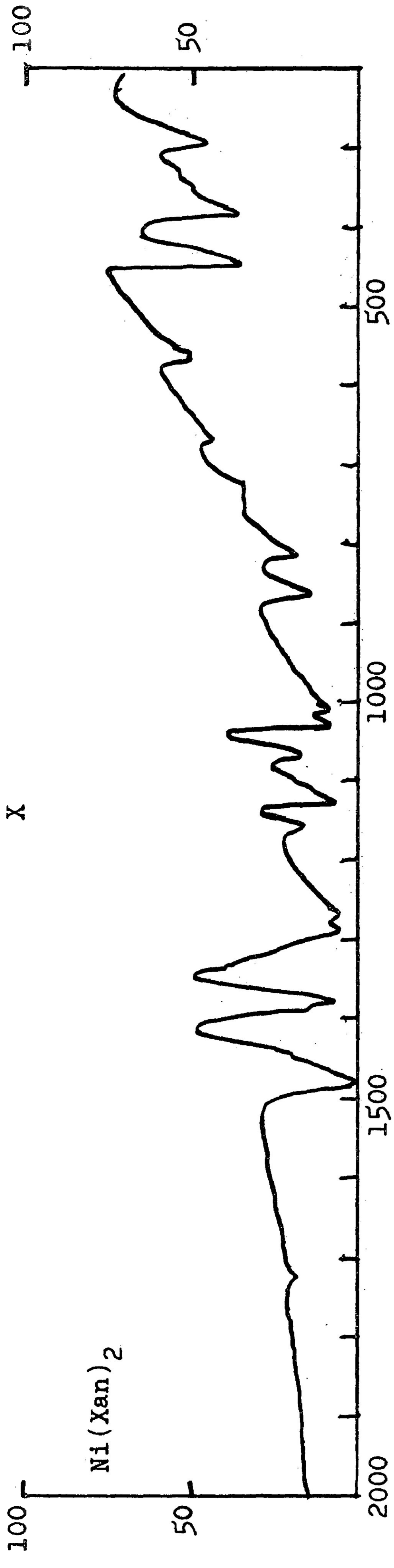

CH$_2$(dtc)$_2$
100
50
100
50
2000
1500
1000
500
Wavenumber (cm^{-1})

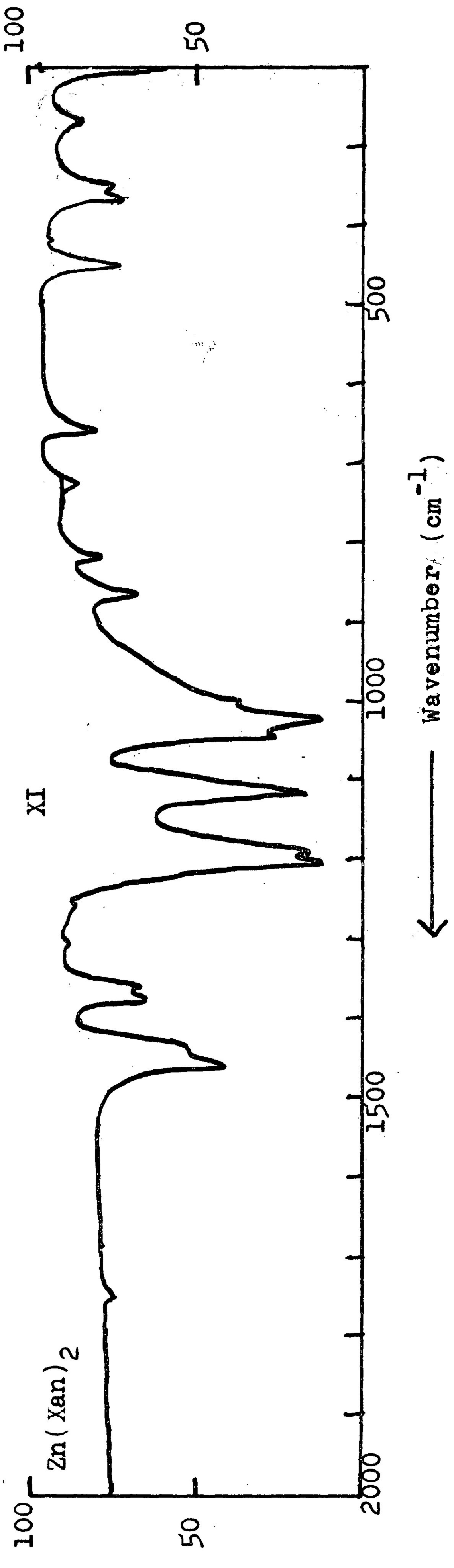
VIII


100
Mn(Xan)$_2$
50
2000
1500
1000
500
100
50

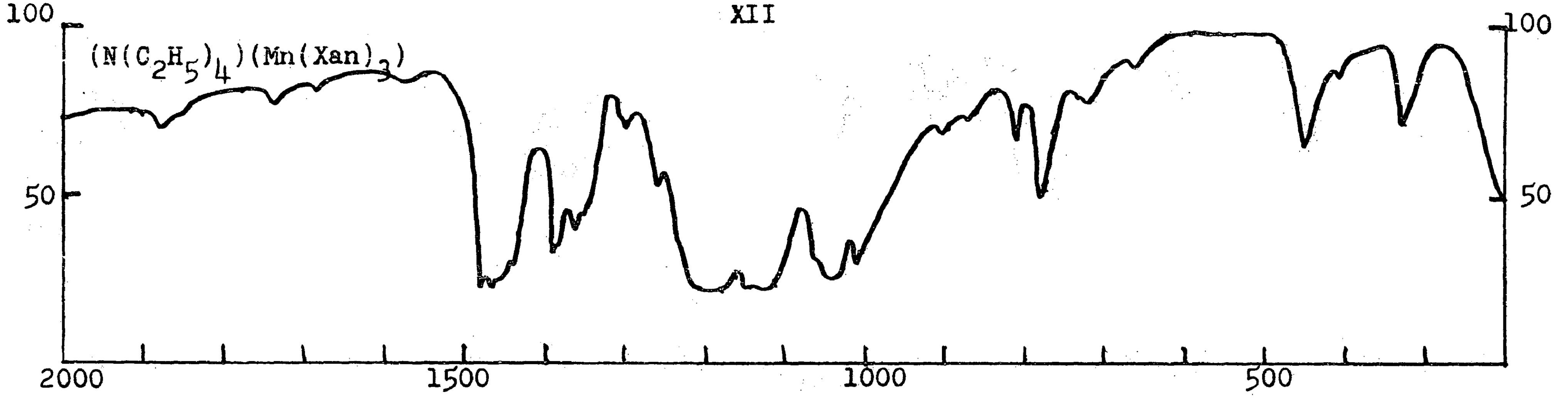
IX


100
Fe(Xan)$_2$
50
2000
1500
1000
500
100
50
Wavenumber (cm^{-1})

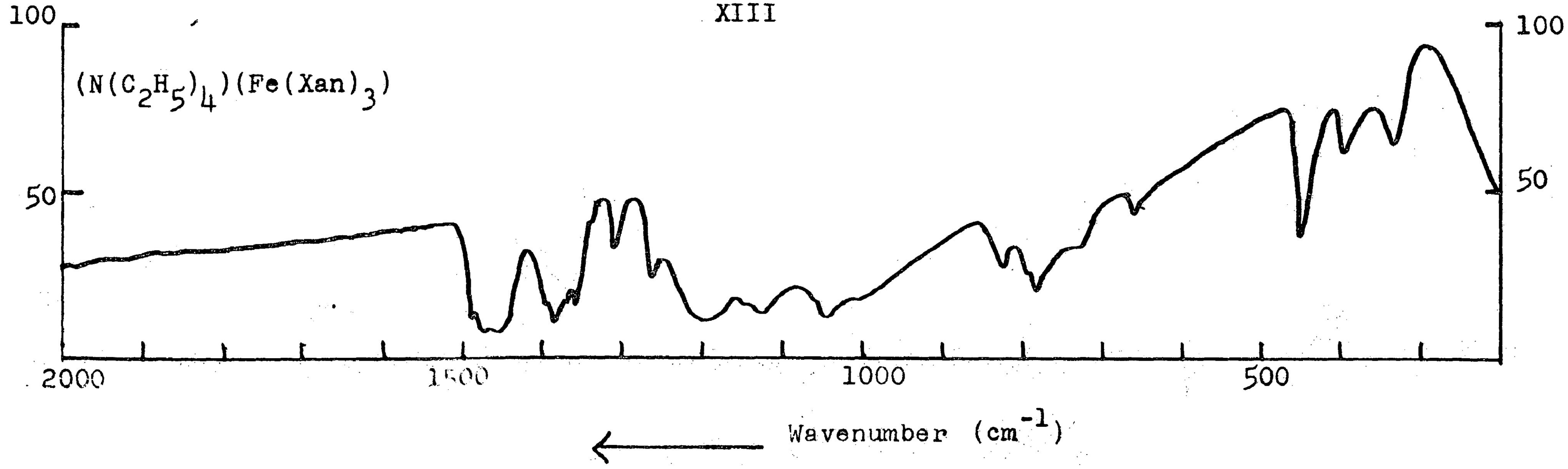

X
Ni(Xan)$_2$
100
50
100
50
500
1000
1500
2000


XI
Zn(Xan)$_2$
100
50
100
50
500
1000
1500
2000
Wavenumber (cm^{-1})

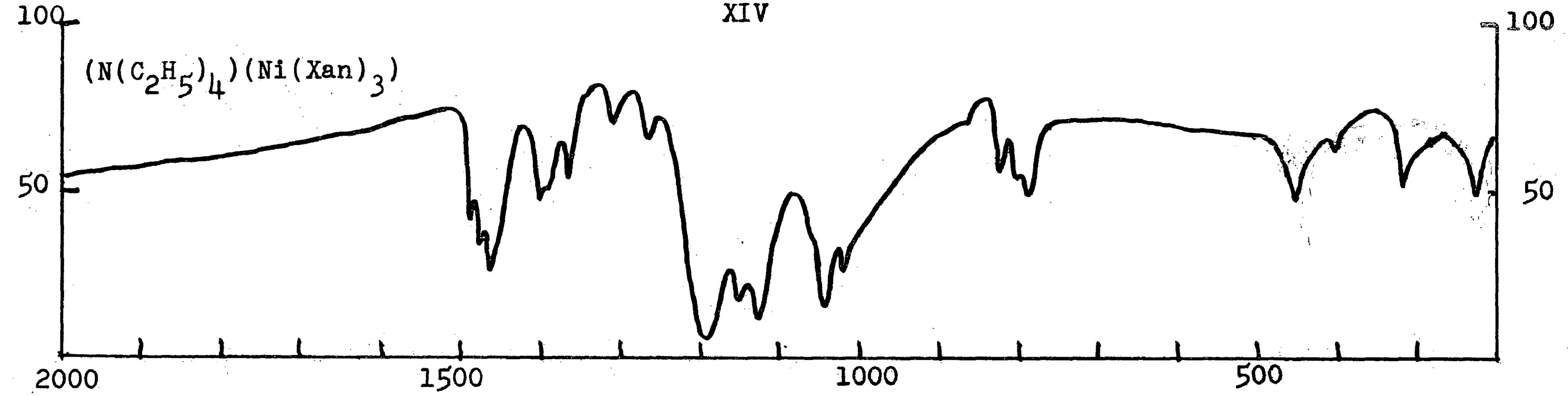
XII


(N(C2H5)4)(Mn(Xan)3)
100
50
100
50
2000
1500
1000
500

XIII

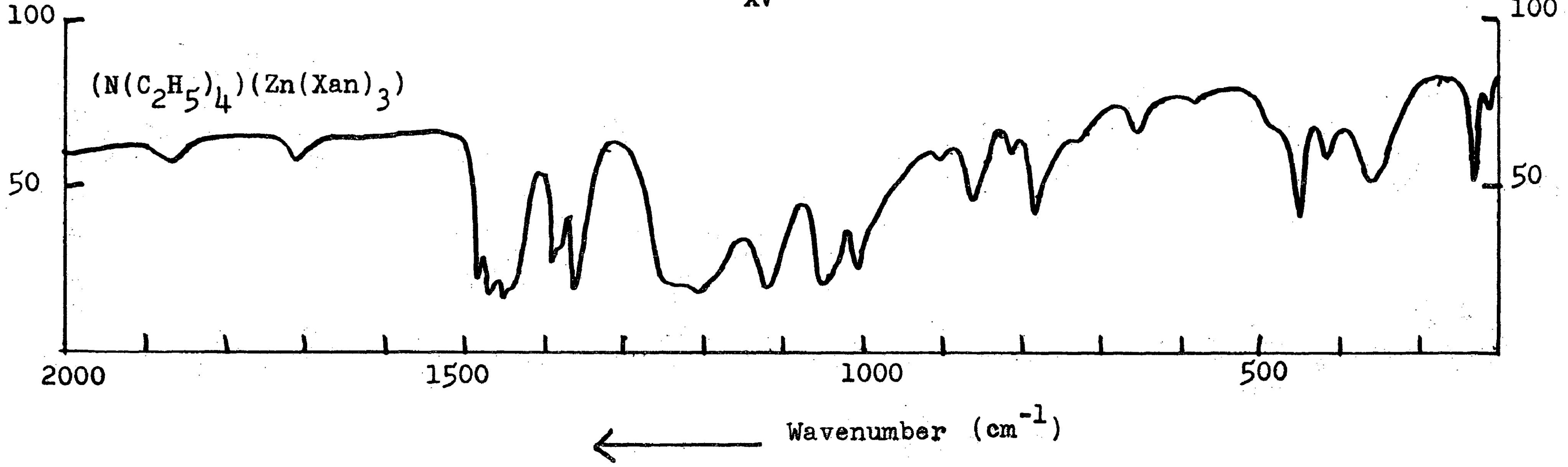

(N(C2H5)4)(Fe(Xan)3)
100
50
100
50
2000
1500
1000
500
Wavenumber (cm-1)

XIV

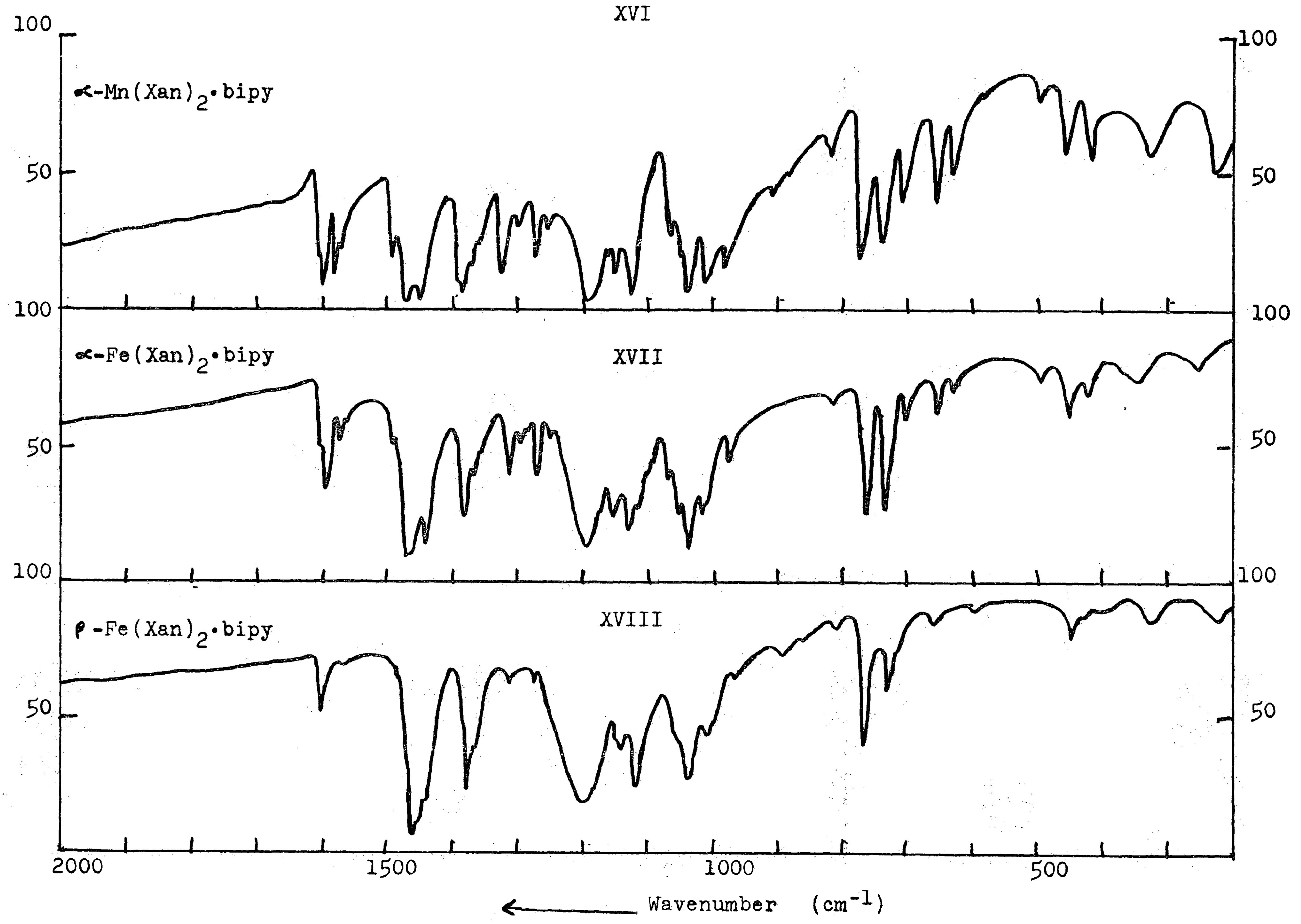


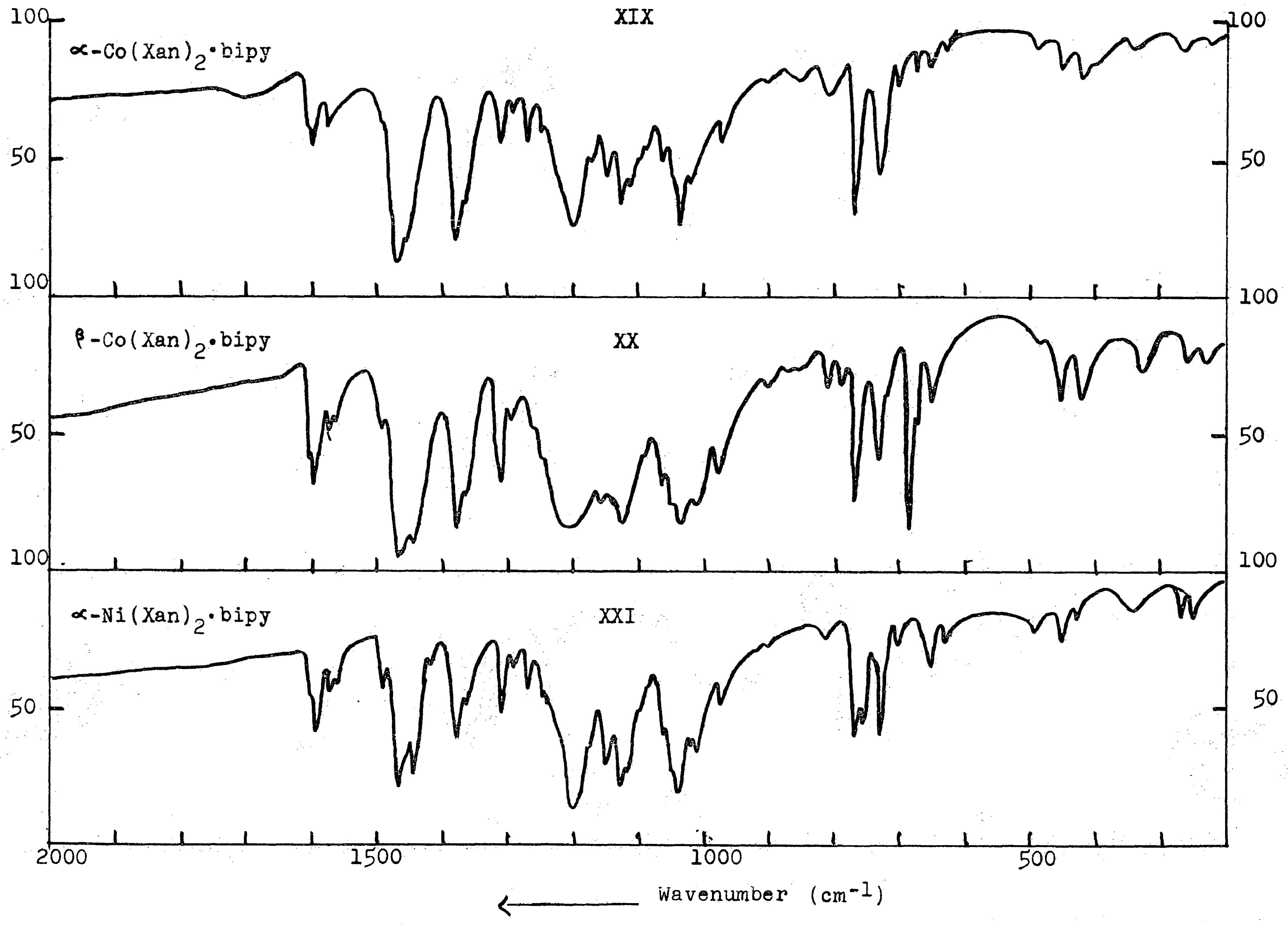
100
50
100
50
$(N(C_2H_5)_4)(Ni(Xan)_3)$
2000
1500
1000
500

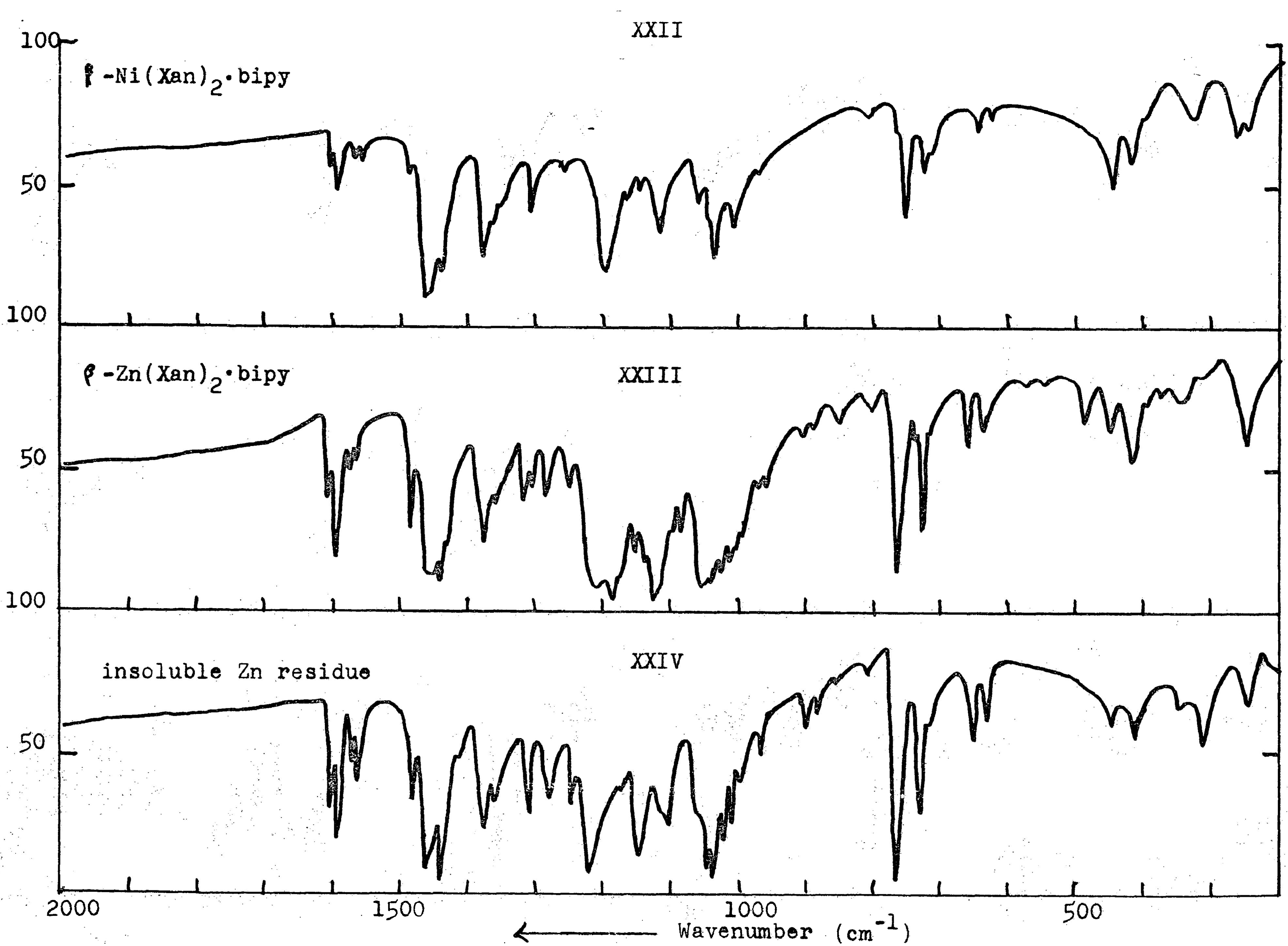
XV

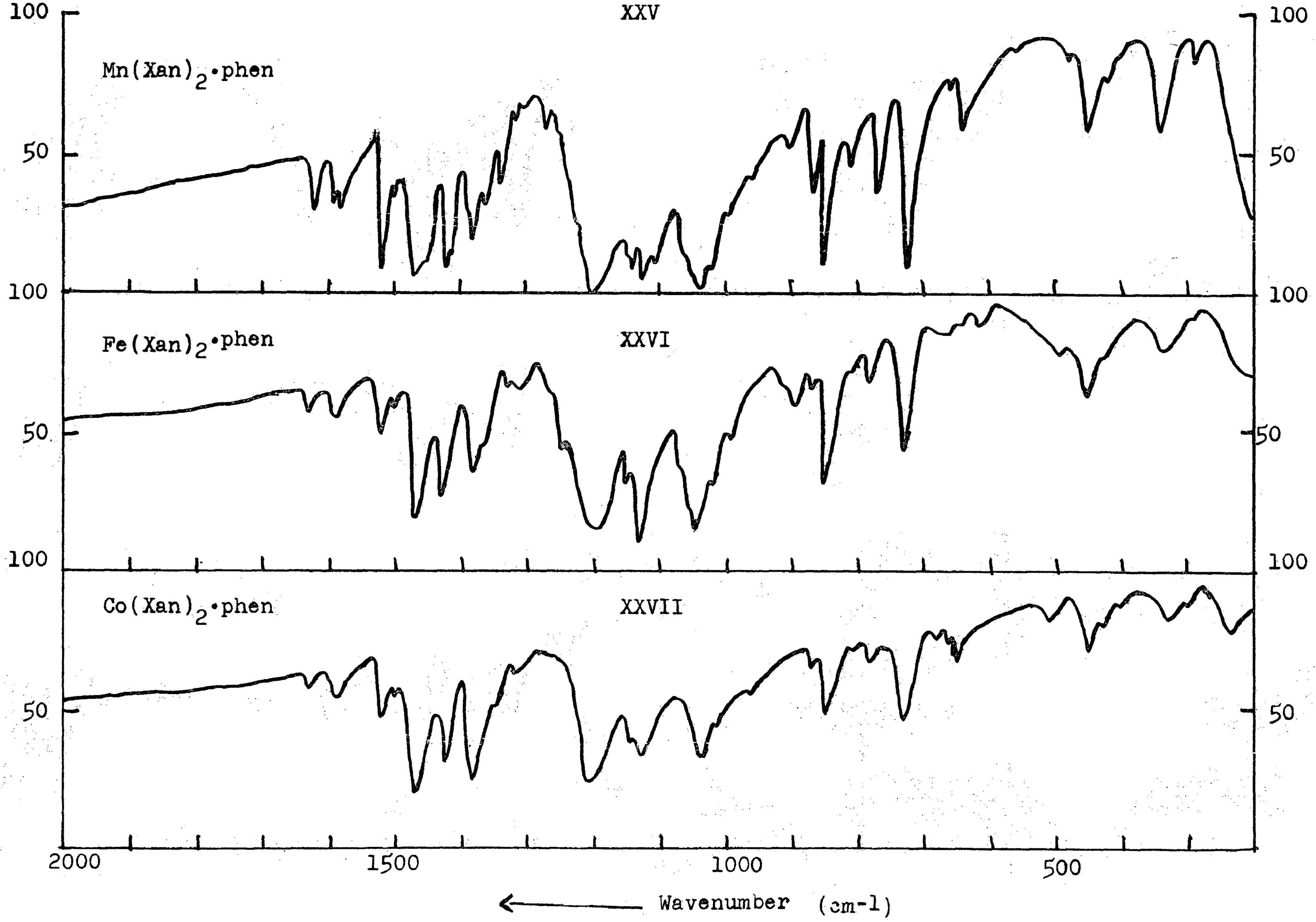


100
50
100
50
$(N(C_2H_5)_4)(Zn(Xan)_3)$
2000
1500
1000
500
Wavenumber (cm^{-1})

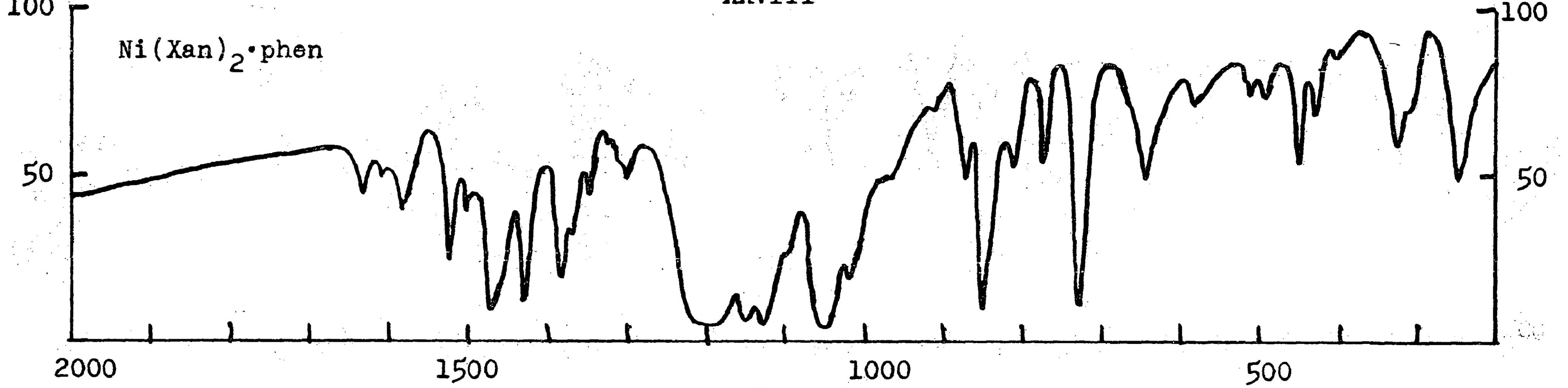

XVI
∝-Mn(Xan)$_2$•bipy
XVII
∝-Fe(Xan)$_2$•bipy
XVIII
β-Fe(Xan)$_2$•bipy
100
50
100
50
100
50
2000
1500
1000
500
← Wavenumber (cm^{-1})


XIX
α-Co(Xan)$_2$•bipy
XX
β-Co(Xan)$_2$•bipy
XXI
α-Ni(Xan)$_2$•bipy
100
50
100
50
100
50
2000
1500
1000
500
Wavenumber (cm^{-1})

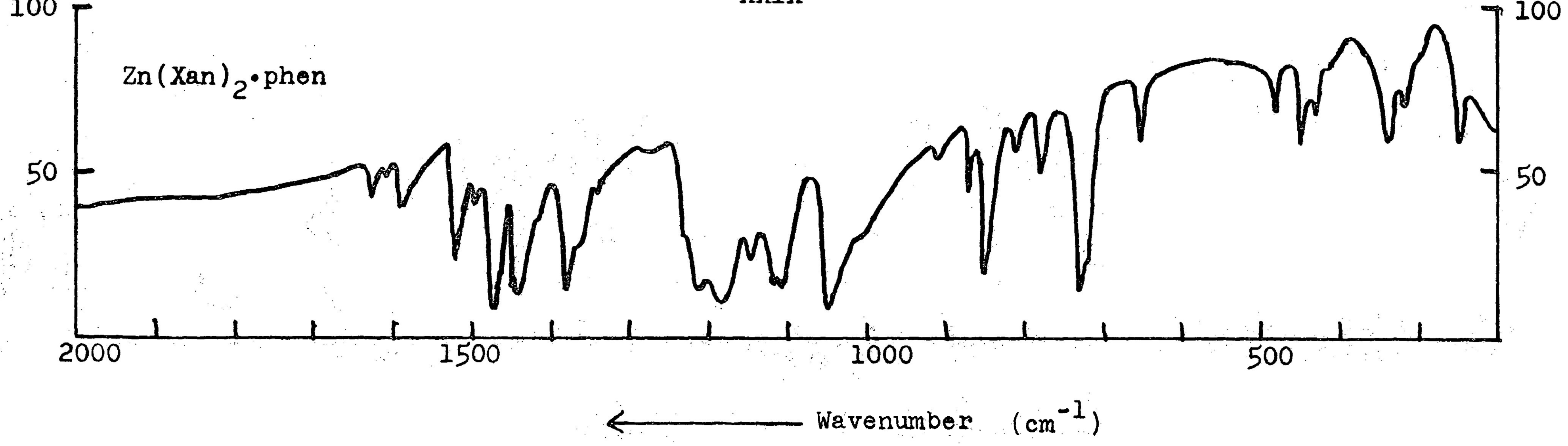

XXII
β-Ni(Xan)$_2$·bipy
XXIII
β-Zn(Xan)$_2$·bipy
XXIV
insoluble Zn residue
100
50
100
50
100
50
2000
1500
1000
500
Wavenumber (cm^{-1})

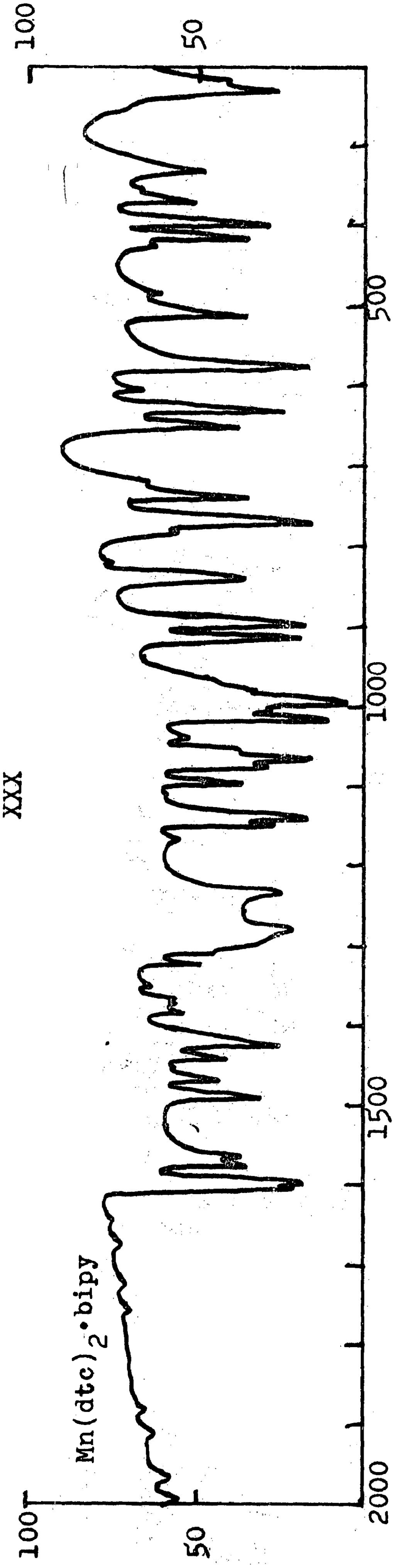

100
50
100
50
100
50
100
50
100
50
100
50
Mn(Xan)$_2$•phen
XXV
Fe(Xan)$_2$•phen
XXVI
Co(Xan)$_2$•phen
XXVII
2000
1500
1000
500
← Wavenumber (cm-1)

XXVIII


100
50
Ni(Xan)$_2$·phen
100
50
2000
1500
1000
500

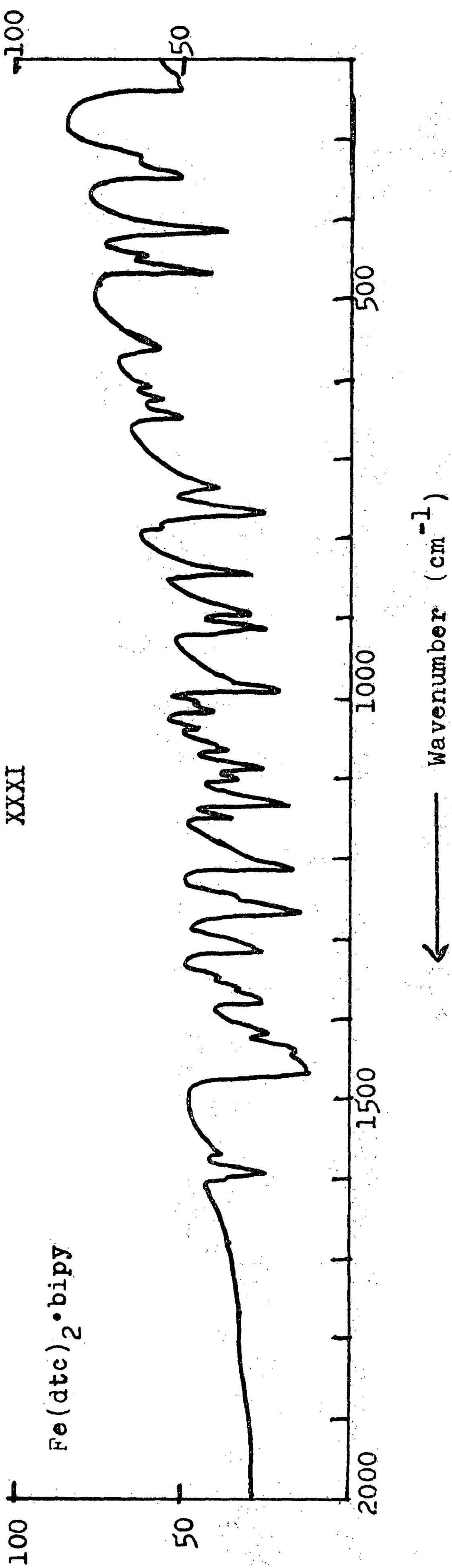
XXIX


100
50
Zn(Xan)$_2$·phen
100
50
2000
1500
1000
500
Wavenumber (cm^{-1})



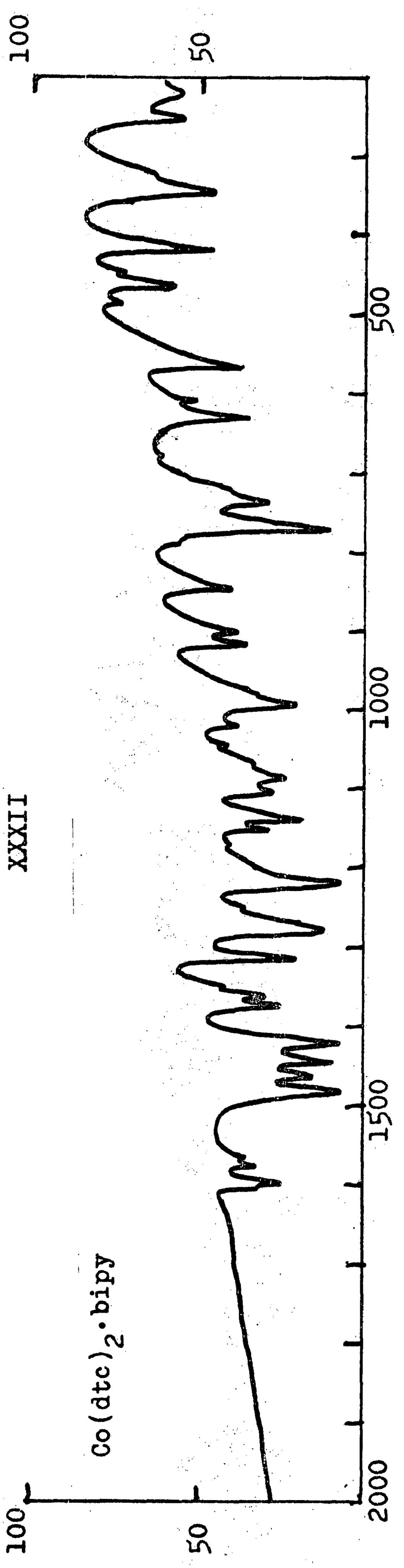
XXX

Mn(dtc)$_2$·bipy
100
50
500
1000
1500
2000



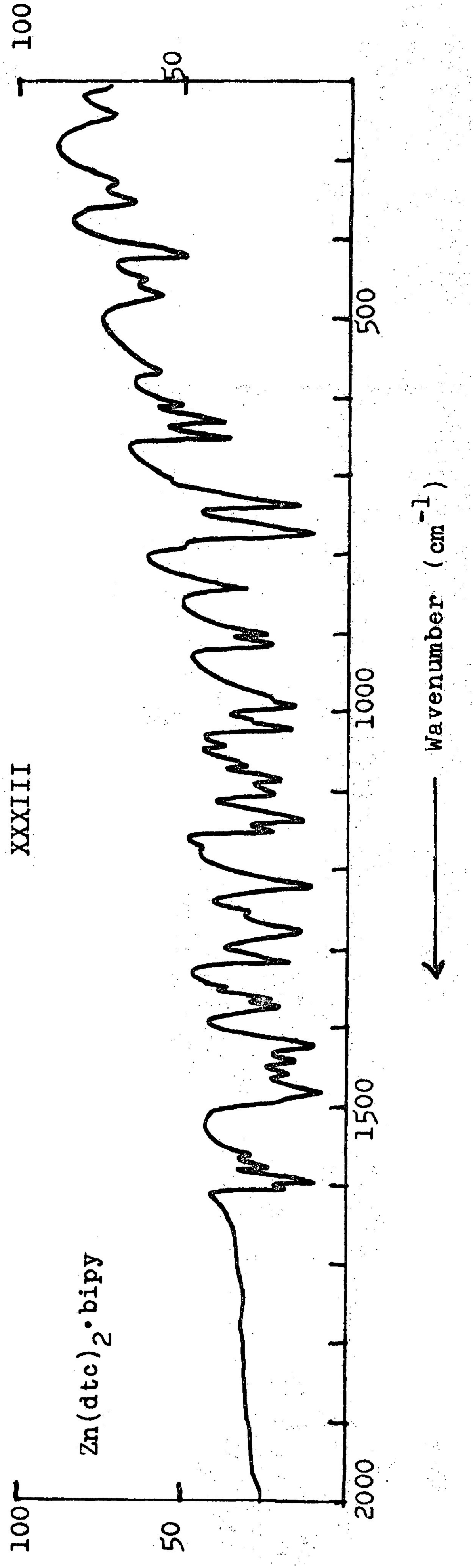
XXXI

Fe(dtc)$_2$·bipy
100
50
500
1000
1500
2000
Wavenumber (cm^{-1})



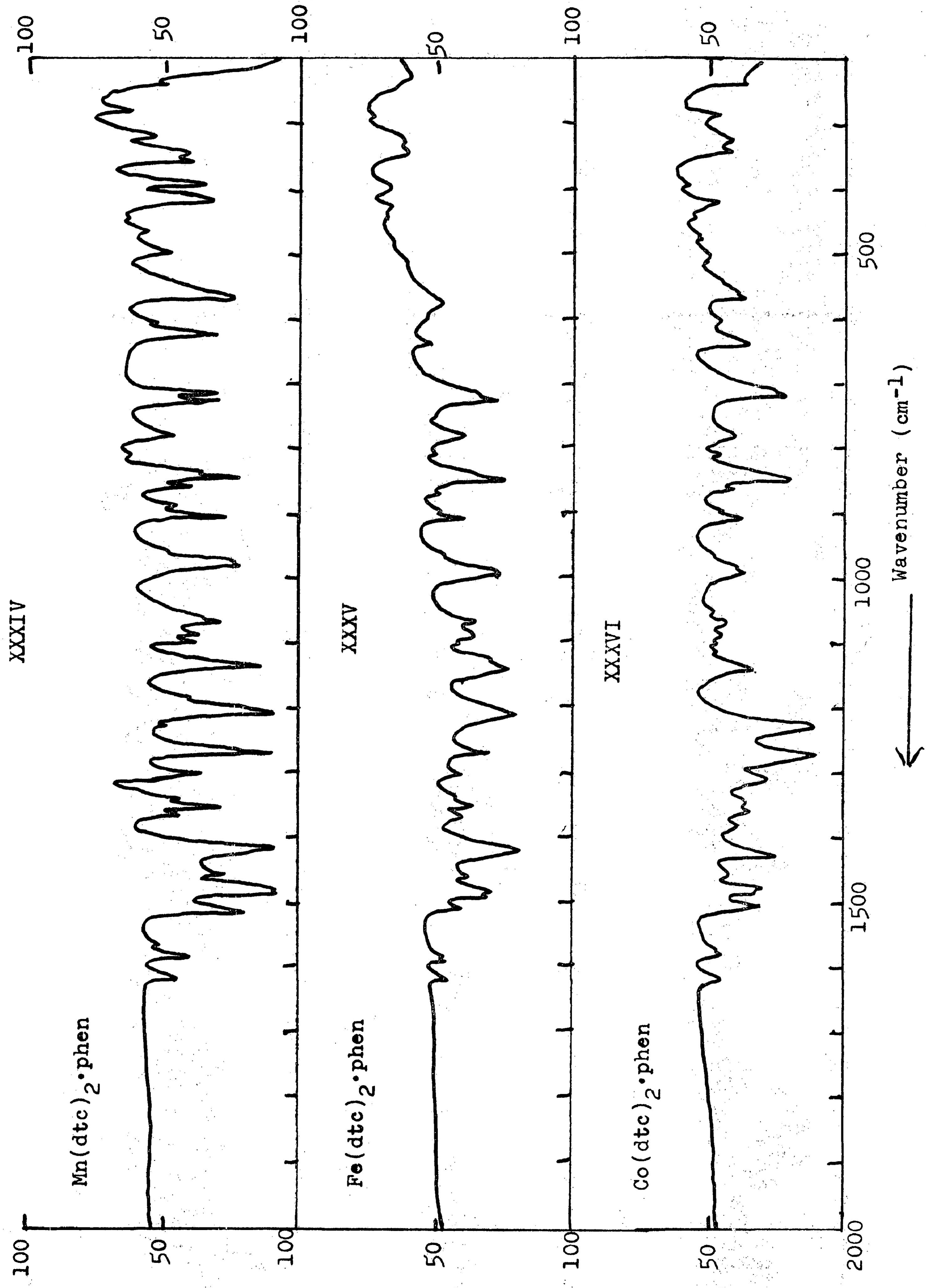
XXXII

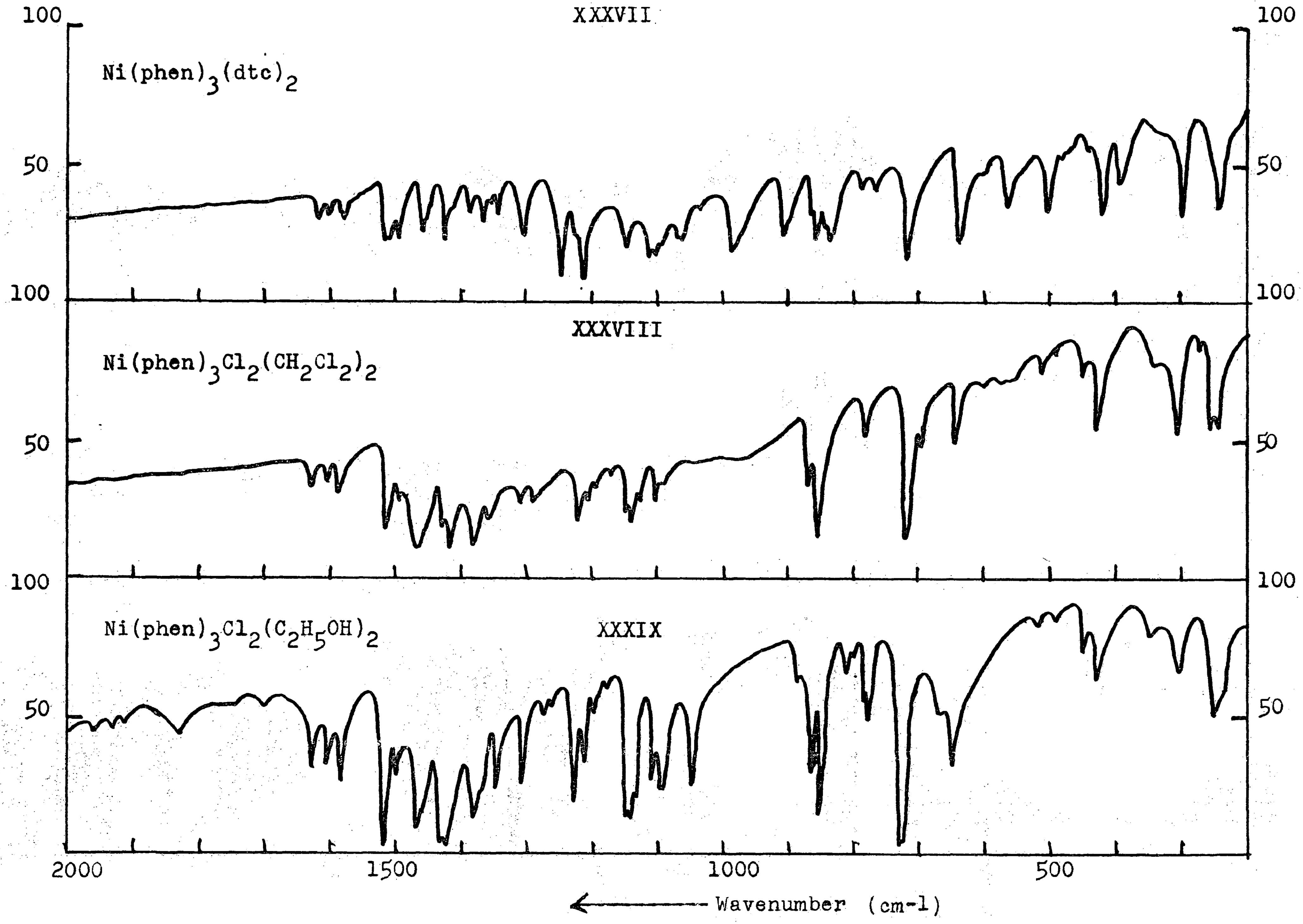
Co(dtc)$_2$·bipy



XXXIII

Zn(dtc)$_2$·bipy


XXXIV
Mn(dtc)$_2$·phen
XXXV
Fe(dtc)$_2$·phen
XXXVI
Co(dtc)$_2$·phen
100
50
100
50
100
50
2000
1500
1000
500
Wavenumber (cm^{-1})

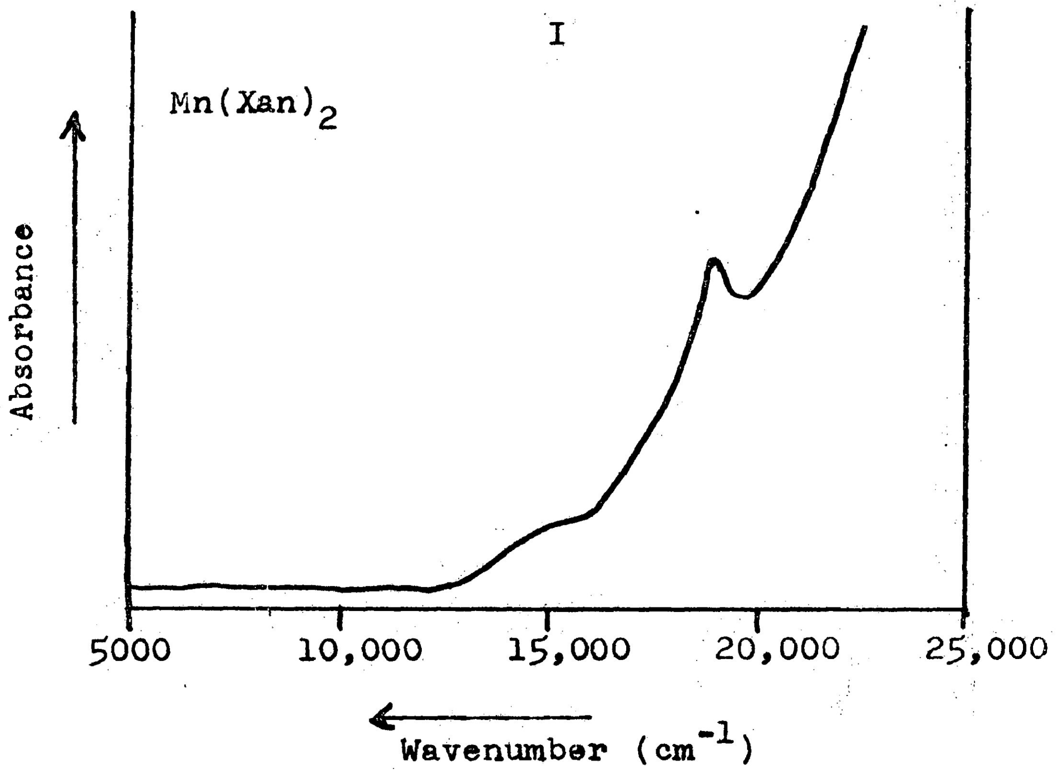

XXXVII
$Ni(phen)_3(dtc)_2$
XXXVIII
$Ni(phen)_3Cl_2(CH_2Cl_2)_2$
XXXIX
$Ni(phen)_3Cl_2(C_2H_5OH)_2$
100
50
100
50
100
50
2000
1500
1000
500
← Wavenumber (cm-1)

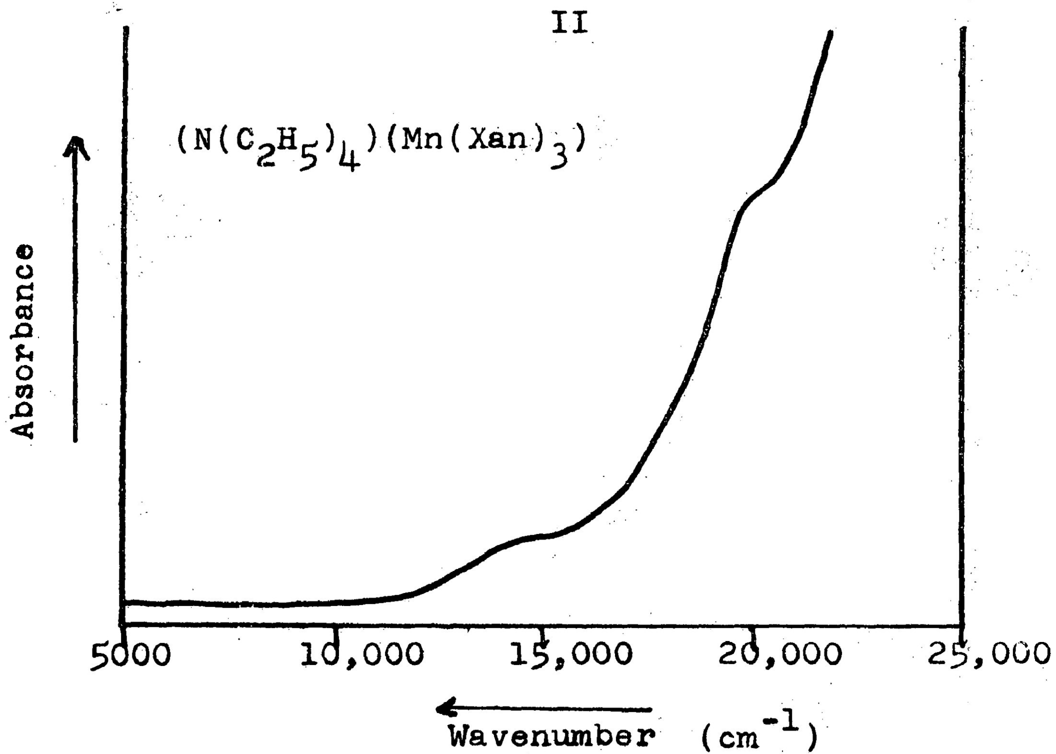
APPENDIX IV

The visible and near infra-red spectra of the complexes studied in this thesis:

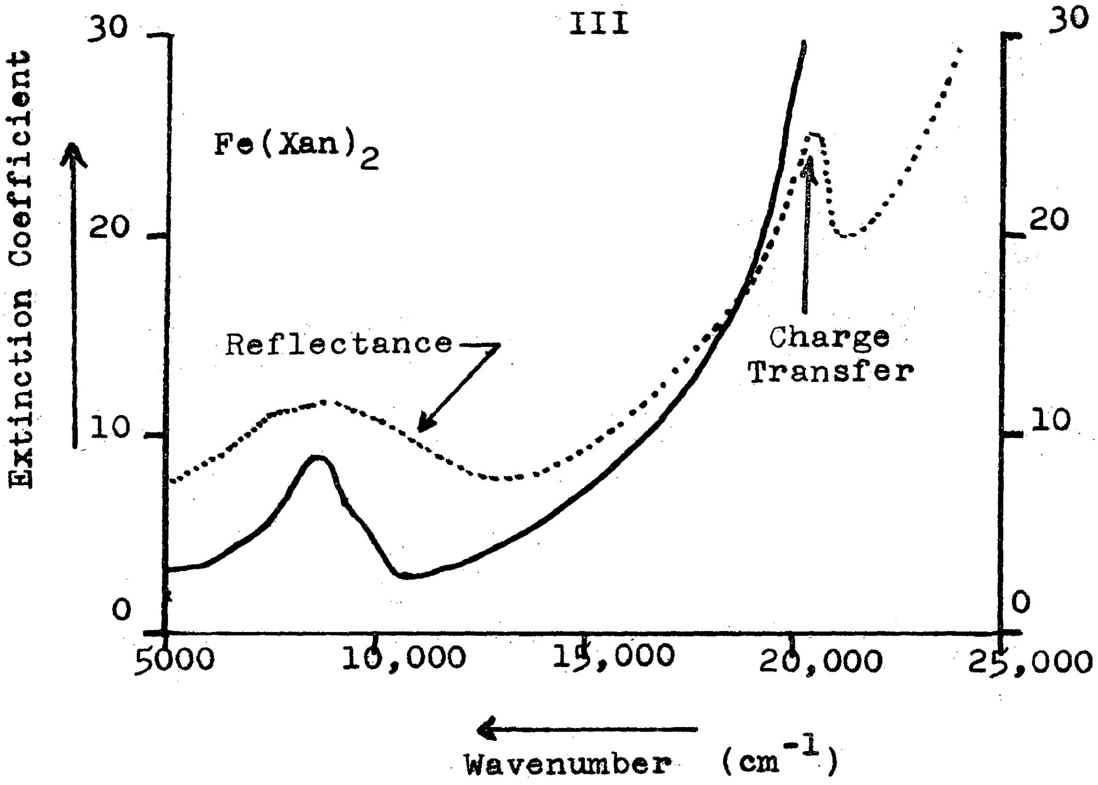
$Mn(Xan)_2$	I
$(N(C_2H_5)_4)(Mn(Xan)_3)$	II
$Fe(Xan)_2$	III
$(N(C_2H_5)_4)(Fe(Xan)_3)$	IV
$Ni(Xan)_2$	V
$(N(C_2H_5)_4)(Ni(Xan)_3)$	VI
product from the addition of KXan to a suspension of $CrCl_2$ and 2,2'-bipyridyl	VII
α-$Mn(Xan)_2\cdot$bipy	VIII
α-$Fe(Xan)_2\cdot$bipy	IX
β-$Fe(Xan)_2\cdot$bipy	X
α-$Co(Xan)_2\cdot$bipy	XI
β-$Co(Xan)_2\cdot$bipy	XII
α-$Ni(Xan)_2\cdot$bipy	XIII
β-$Ni(Xan)_2\cdot$bipy	XIV
$Mn(Xan)_2\cdot$phen	XV
$Fe(Xan)_2\cdot$phen	XVI
$Co(Xan)_2\cdot$phen	XVII
$Ni(Xan)_2\cdot$phen	XVIII
$Mn(dtc)_2\cdot$bipy	XIX
$Fe(dtc)_2\cdot$bipy	XX

$Co(dtc)_2\cdot bipy$	XXI
$Mn(dtc)_2\cdot phen$	XXII
$Fe(dtc)_2\cdot phen$	XXIII
$Co(dtc)_2\cdot phen$	XXIV
$Ni(phen)_3(dtc)_2$	XXV
$Ni(phen)_3Cl_2 2(CH_2Cl_2)$	XXVI
$Ni(phen)_3Cl_2 2(EtOH)$	XXVII

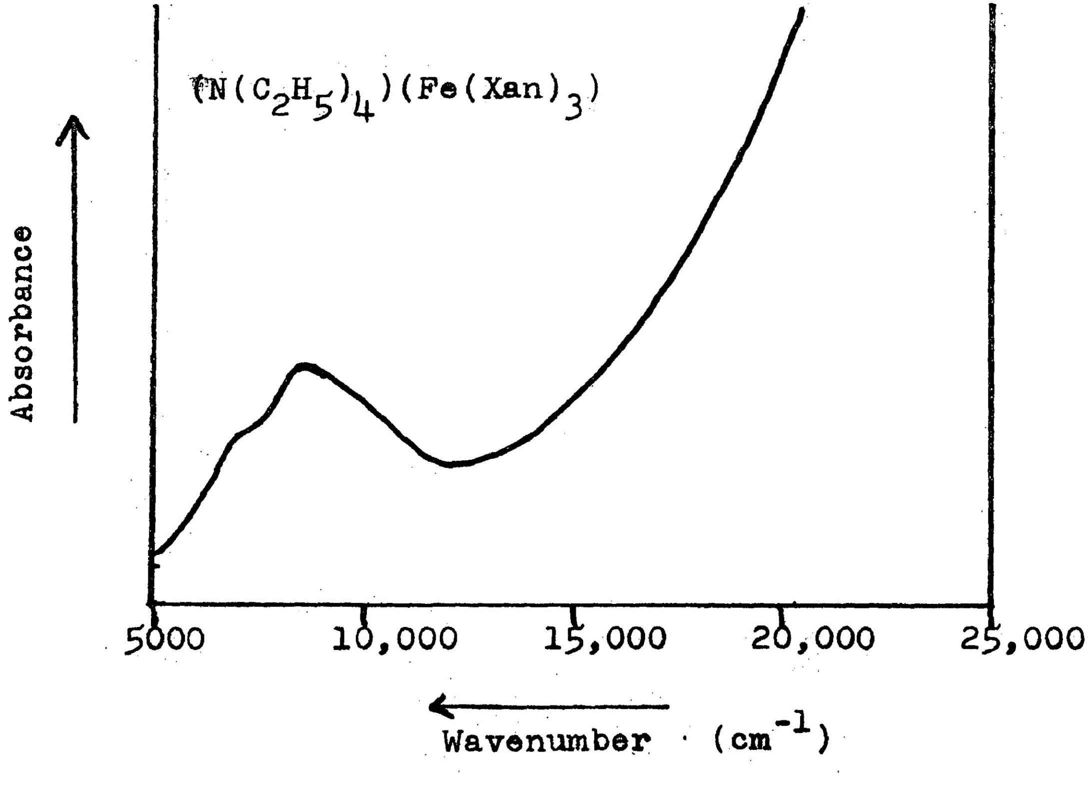

I
Mn(Xan)$_2$
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})


II
(N(C$_2$H$_5$)$_4$)(Mn(Xan)$_3$)
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

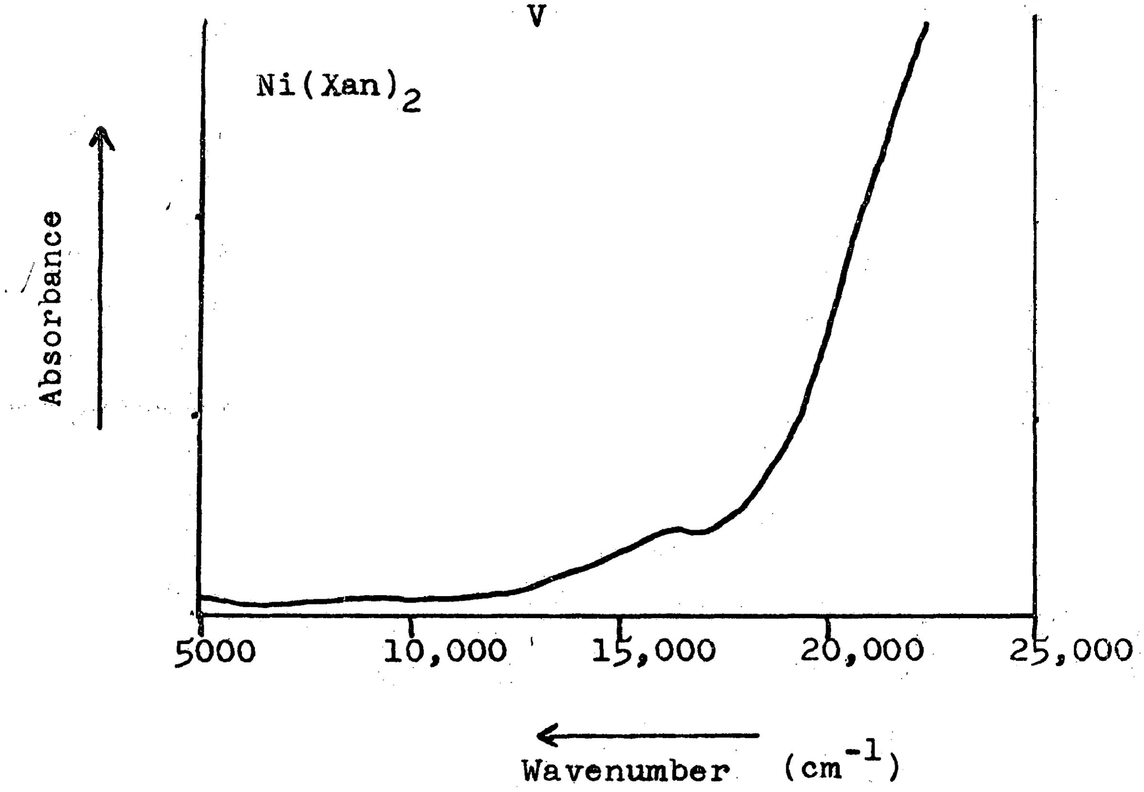
III


30
20
10
0
30
20
10
0
Extinction Coefficient
Fe(Xan)$_2$
Reflectance
Charge Transfer
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

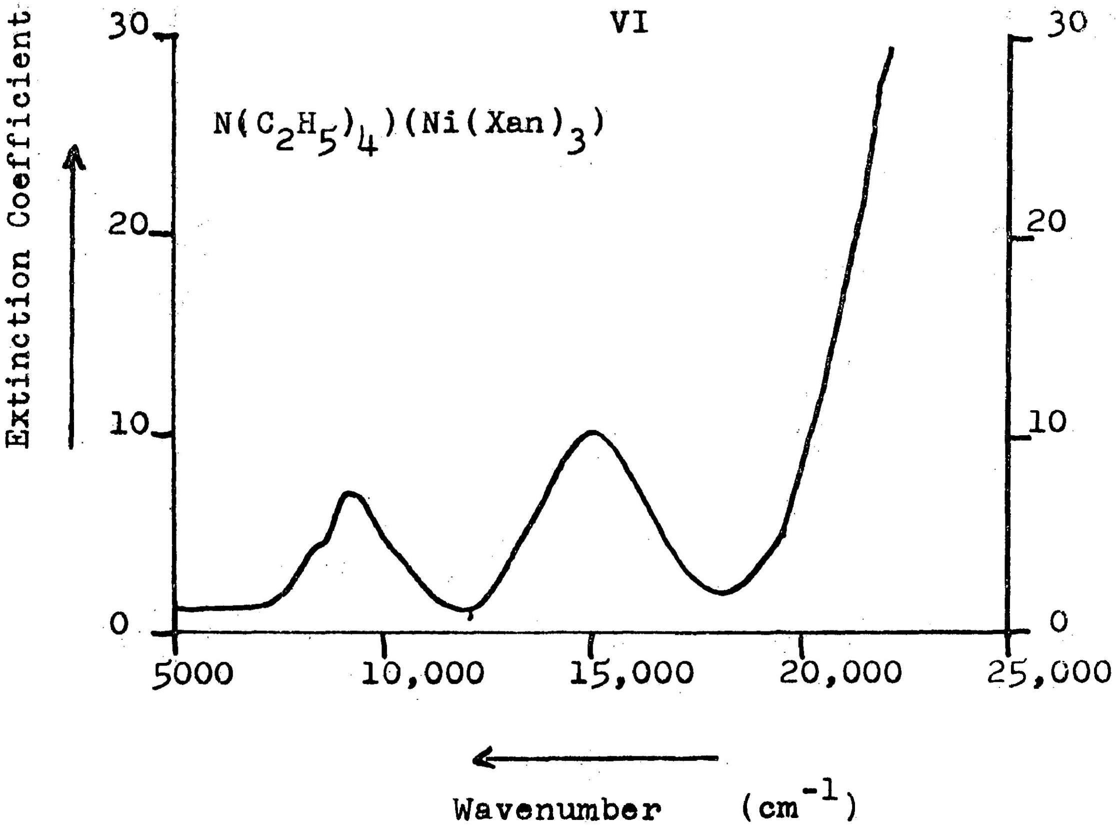
IV


(N(C$_2$H$_5$)$_4$)(Fe(Xan)$_3$)
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

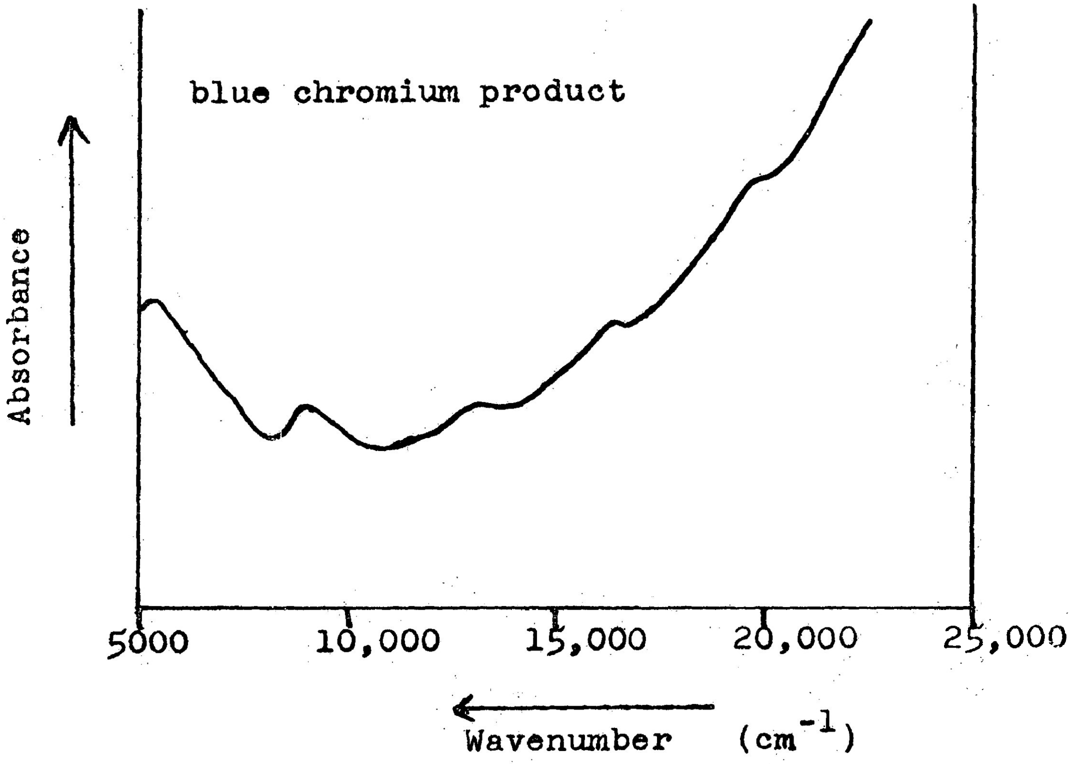
V


$Ni(Xan)_2$
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

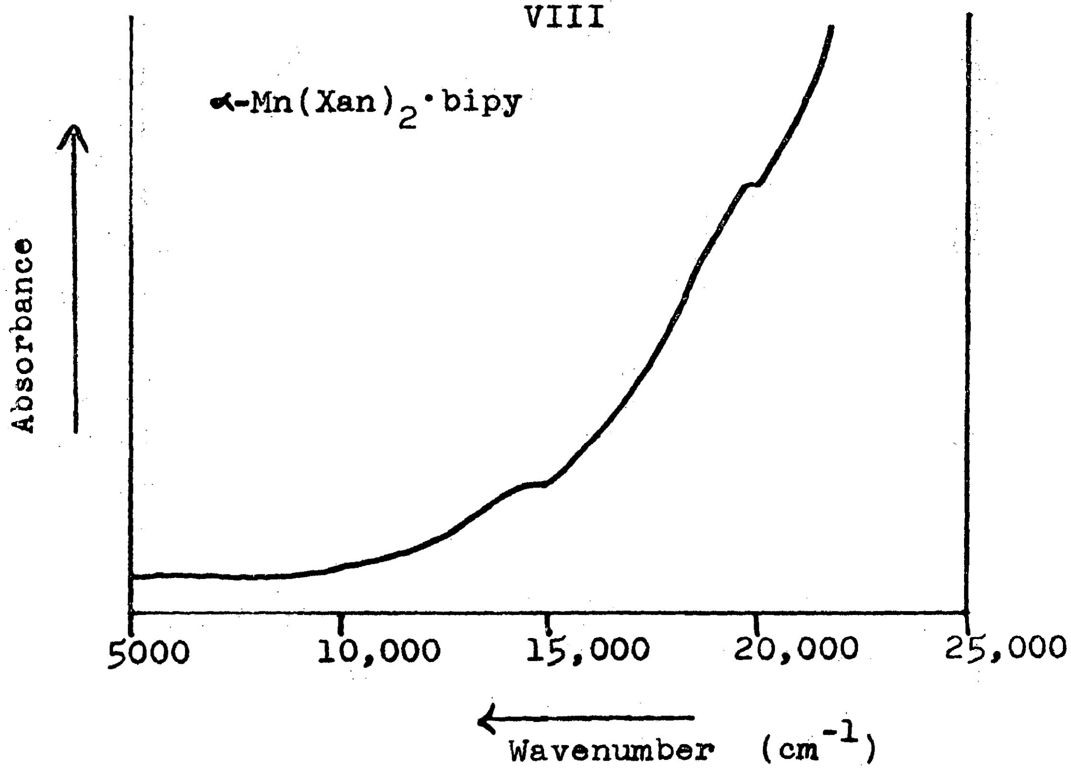
VI


$N(C_2H_5)_4(Ni(Xan)_3)$
Extinction Coefficient
30
20
10
0
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

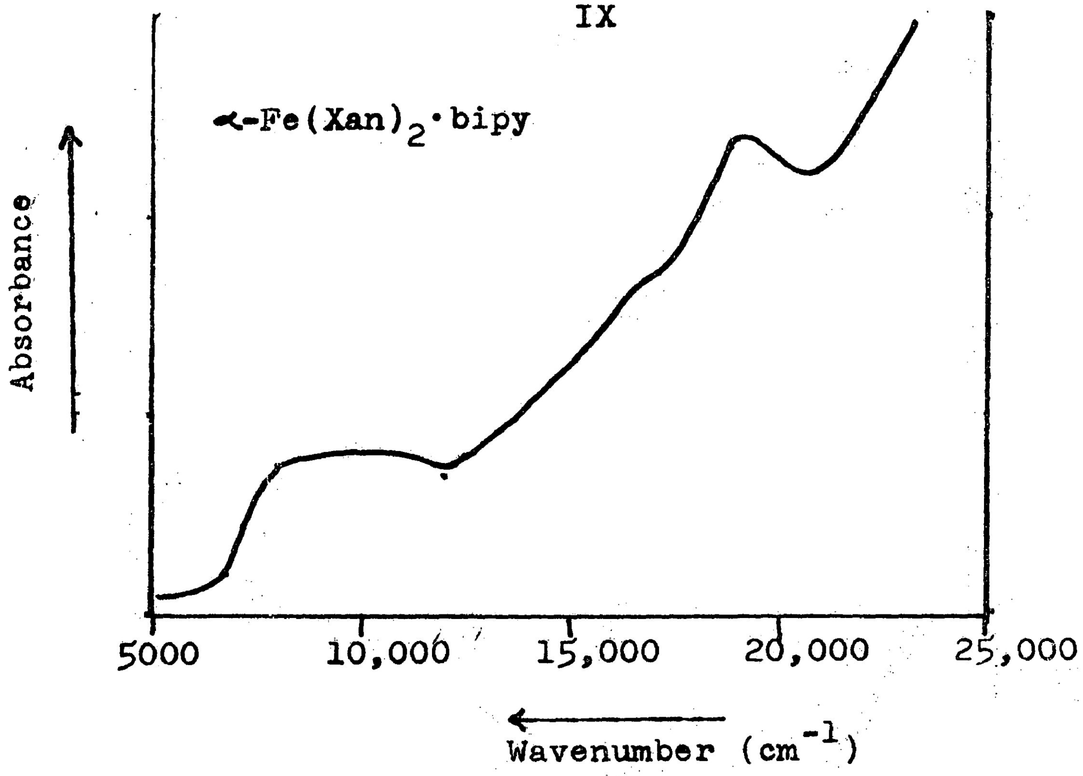
VII


blue chromium product
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

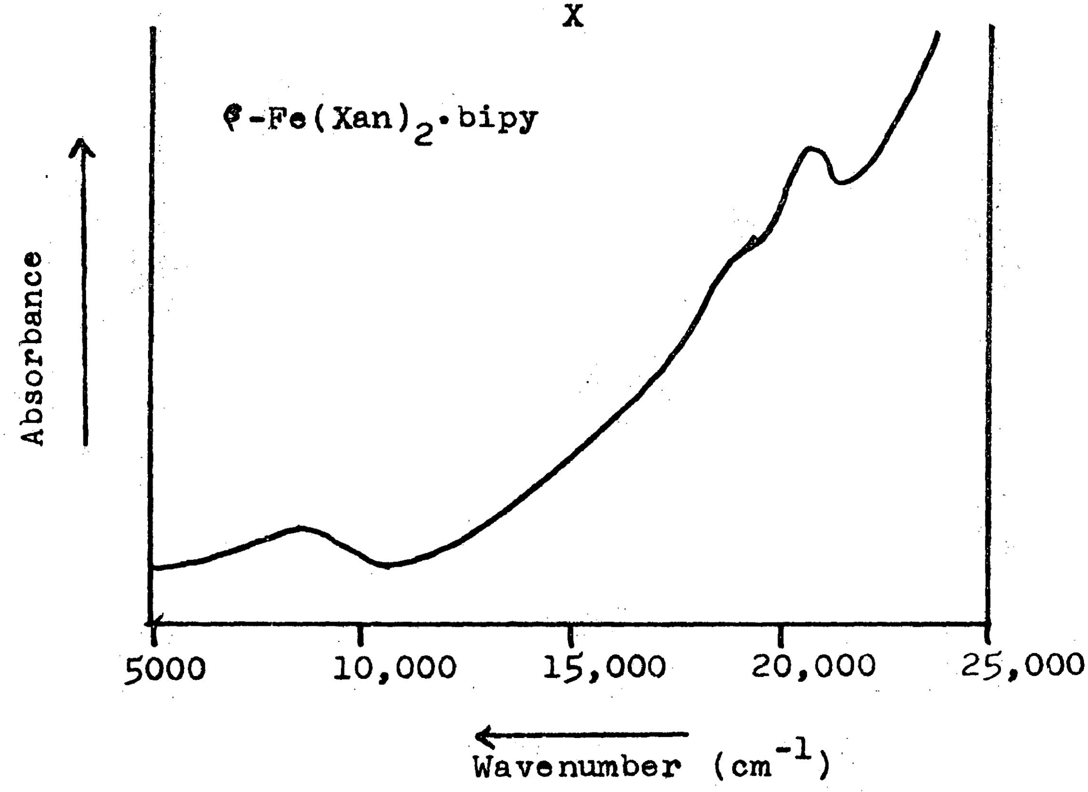
VIII

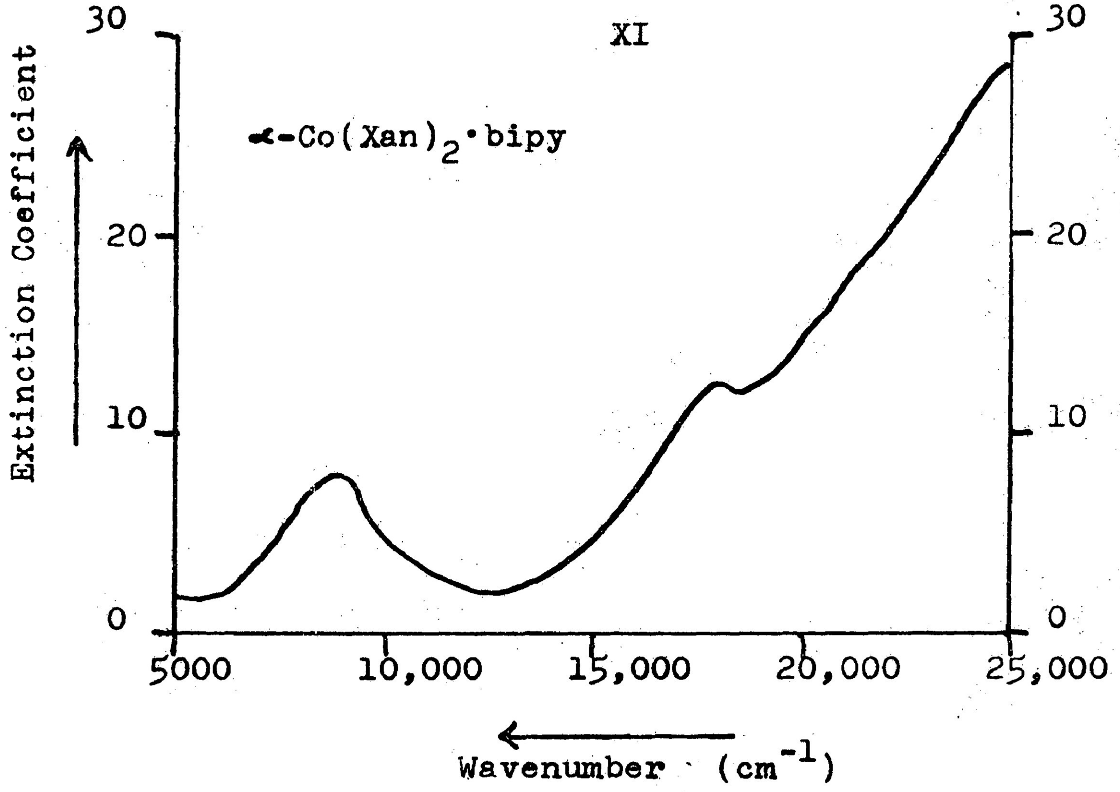

α-Mn(Xan)$_2$·bipy
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

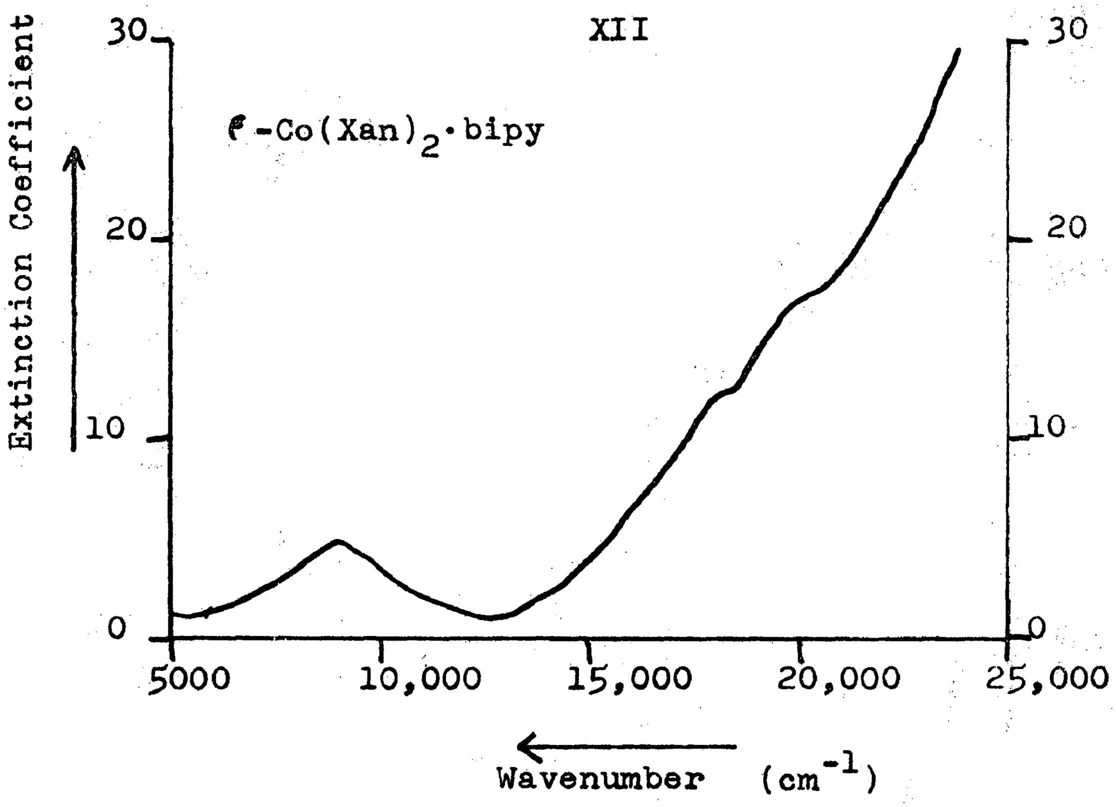
IX


α-Fe(Xan)$_2$·bipy
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

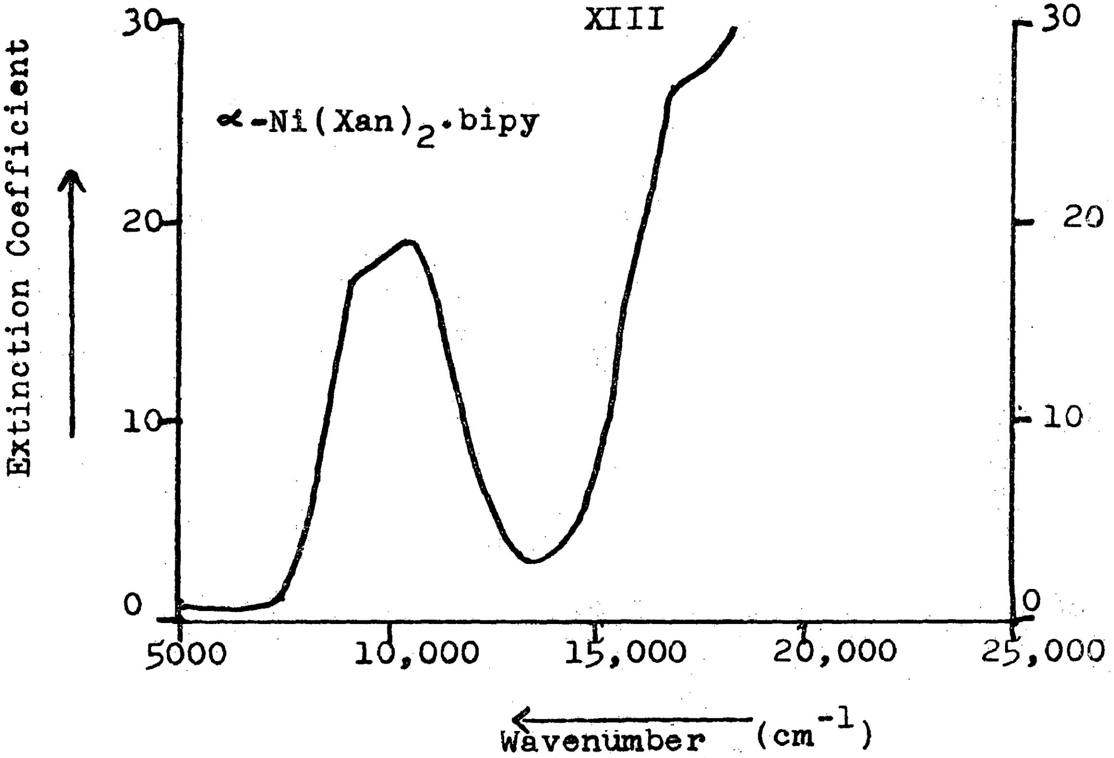
X


β-Fe(Xan)$_2$·bipy
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

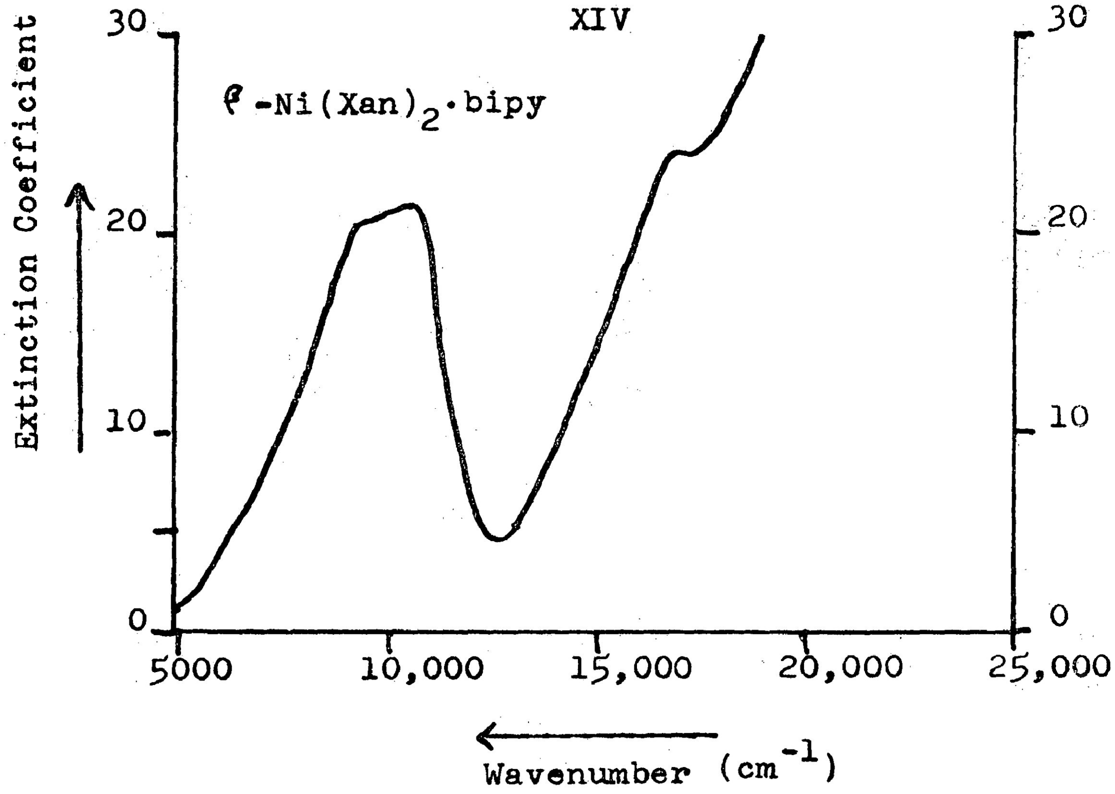

XI
α-Co(Xan)$_2$·bipy
Extinction Coefficient
30
20
10
0
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})


XII
β-Co(Xan)$_2$·bipy
Extinction Coefficient
30
20
10
0
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

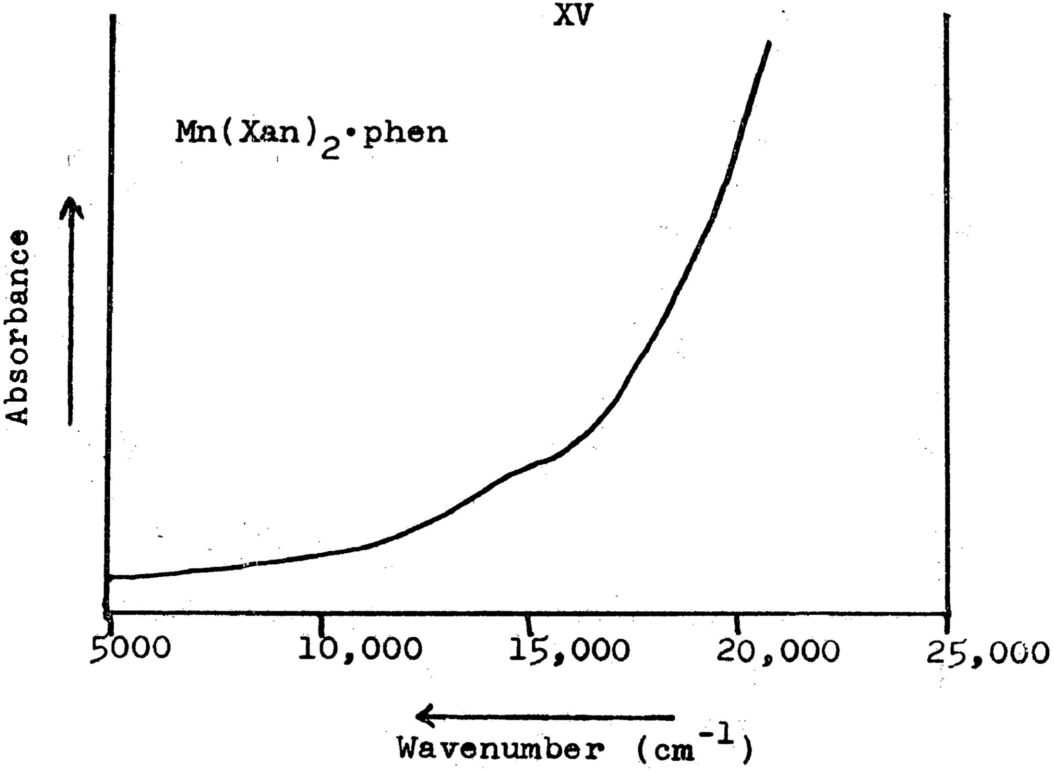
XIII


α-Ni(Xan)$_2$·bipy
Extinction Coefficient
30
20
10
0
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

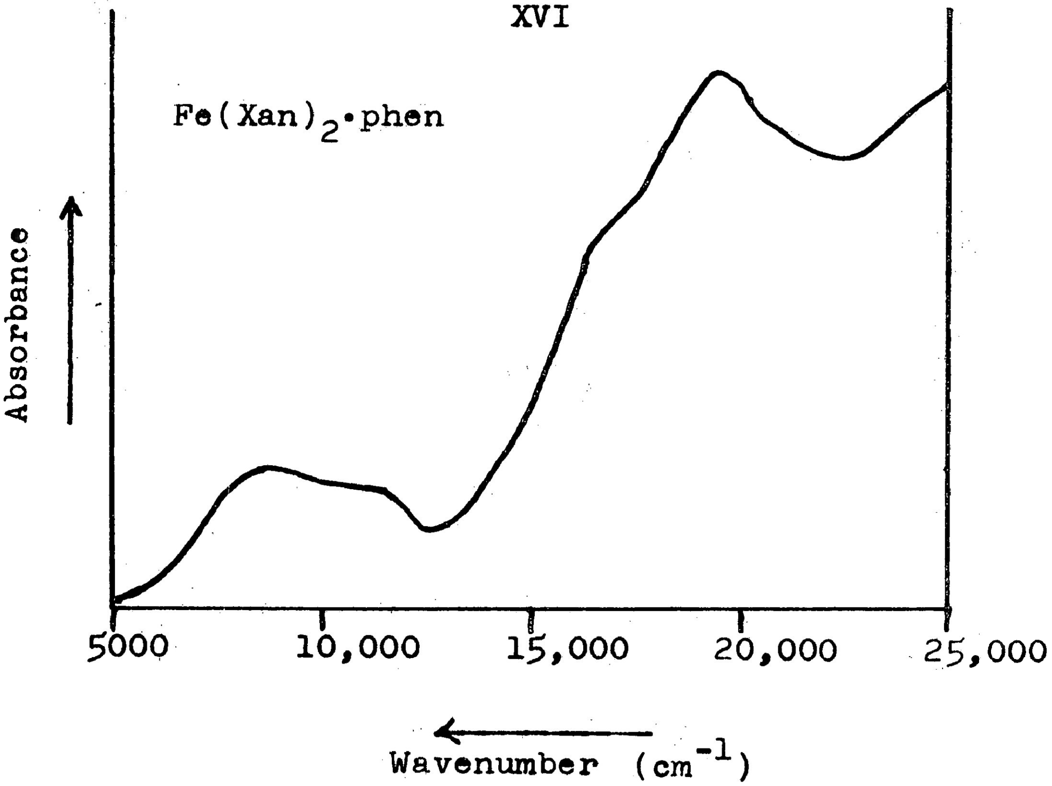
XIV

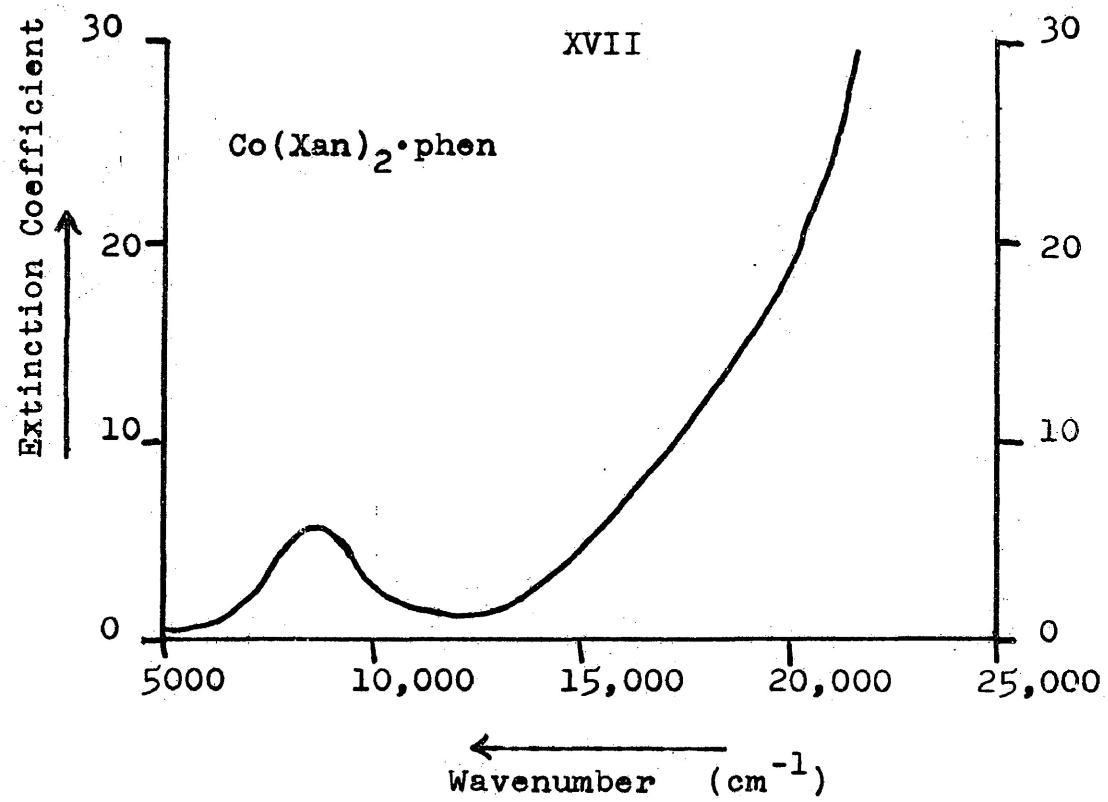

β-Ni(Xan)$_2$·bipy
Extinction Coefficient
30
20
10
0
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

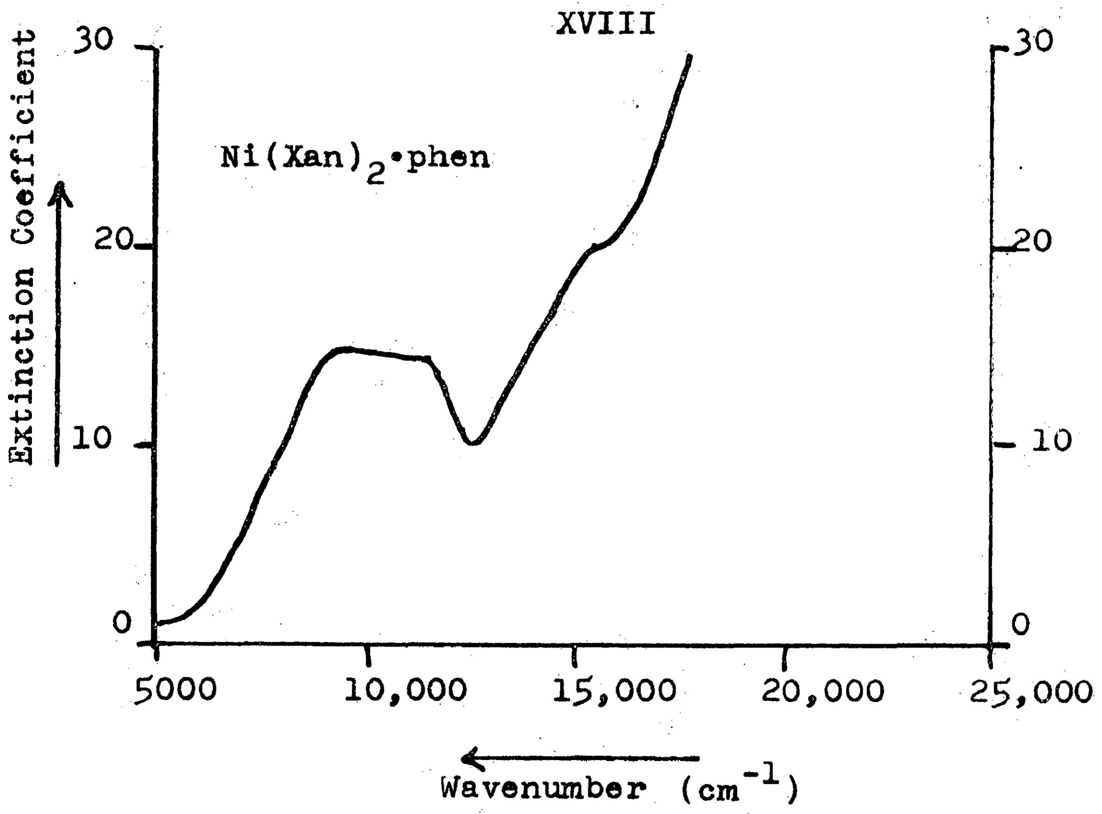
XV


Mn(Xan)$_2$•phen
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

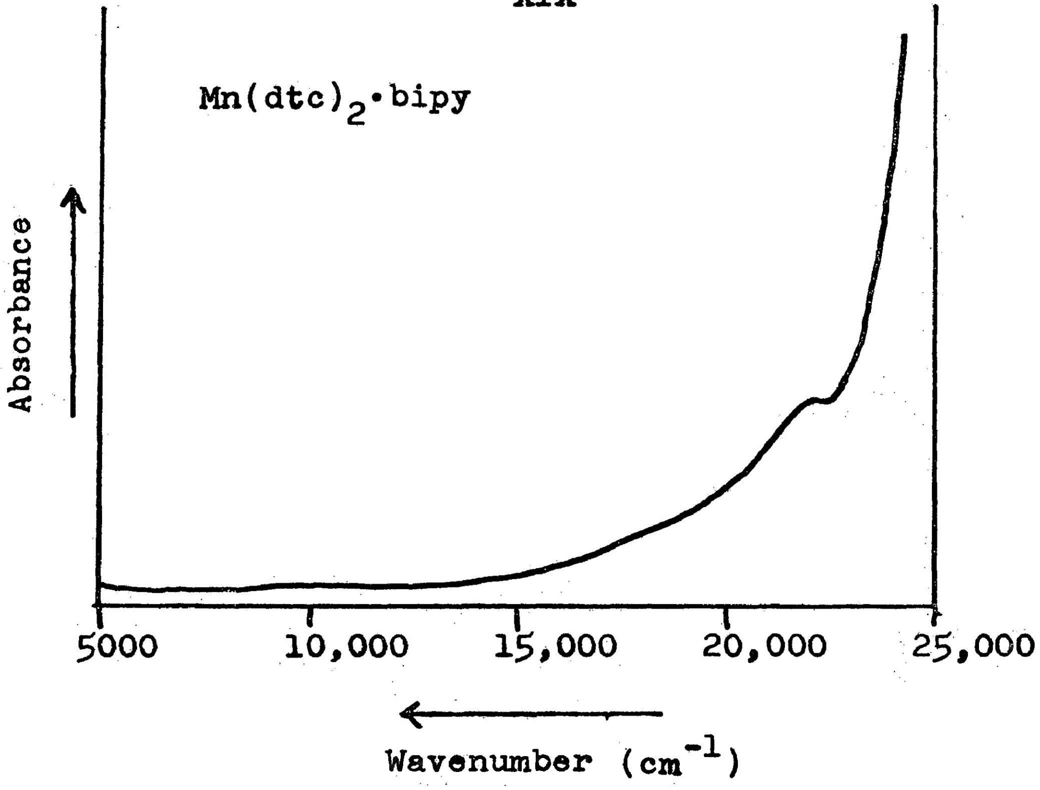
XVI


Fe(Xan)$_2$•phen
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

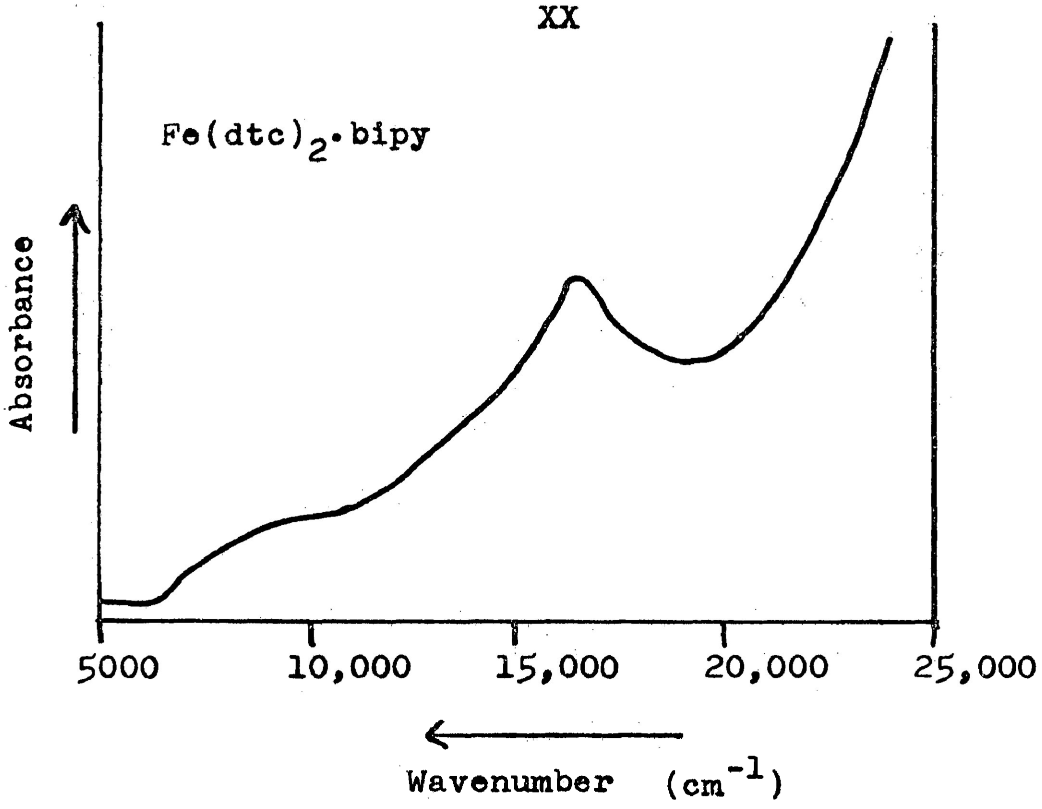

XVII
Co(Xan)$_2$•phen
Extinction Coefficient
30
20
10
0
30
20
10
0
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})


XVIII
Ni(Xan)$_2$•phen
Extinction Coefficient
30
20
10
0
30
20
10
0
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

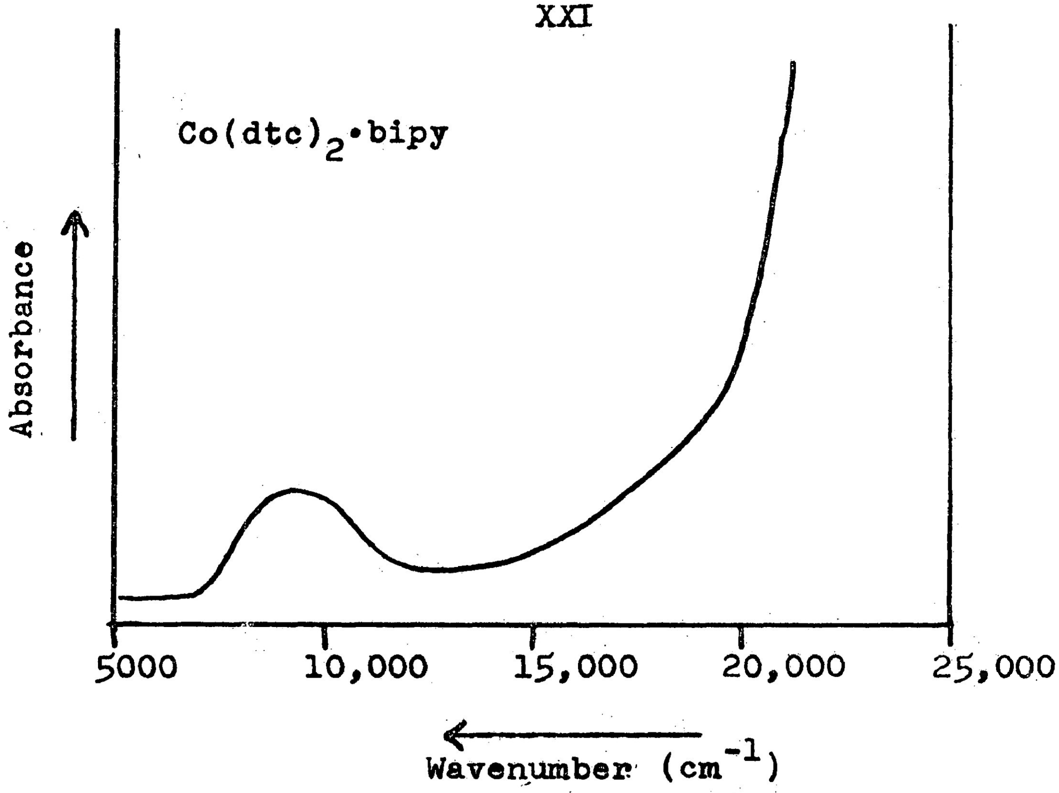
XIX


Mn(dtc)$_2$•bipy
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

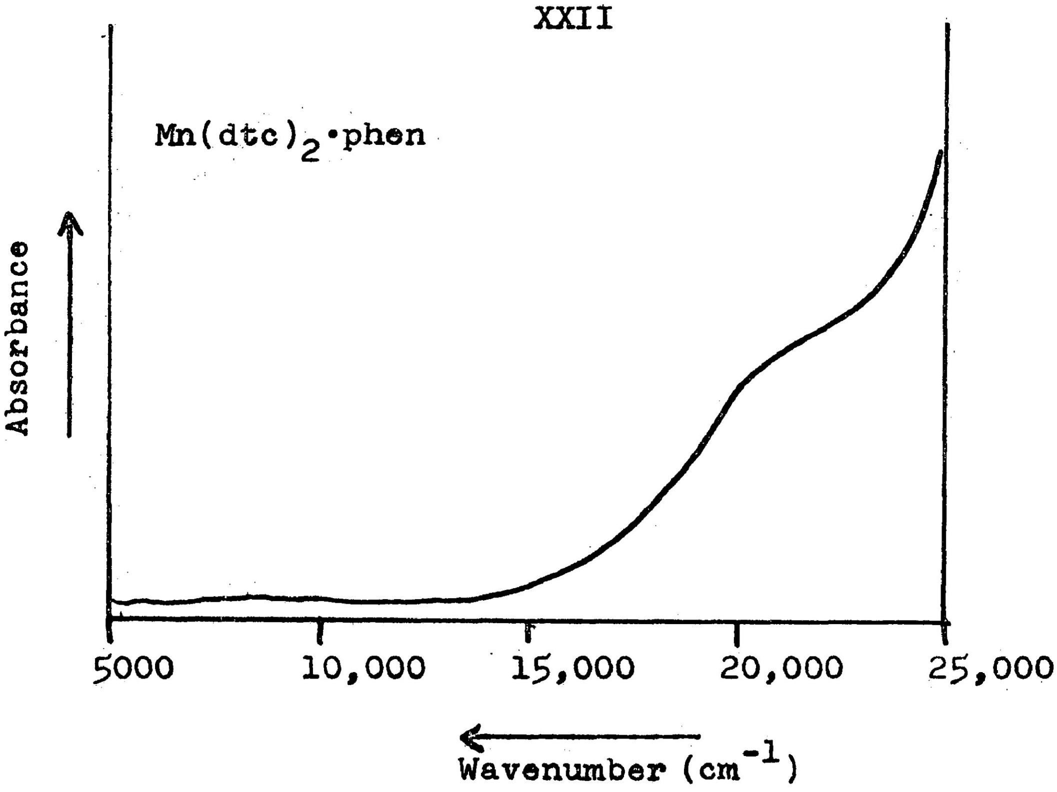
XX


Fe(dtc)$_2$•bipy
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

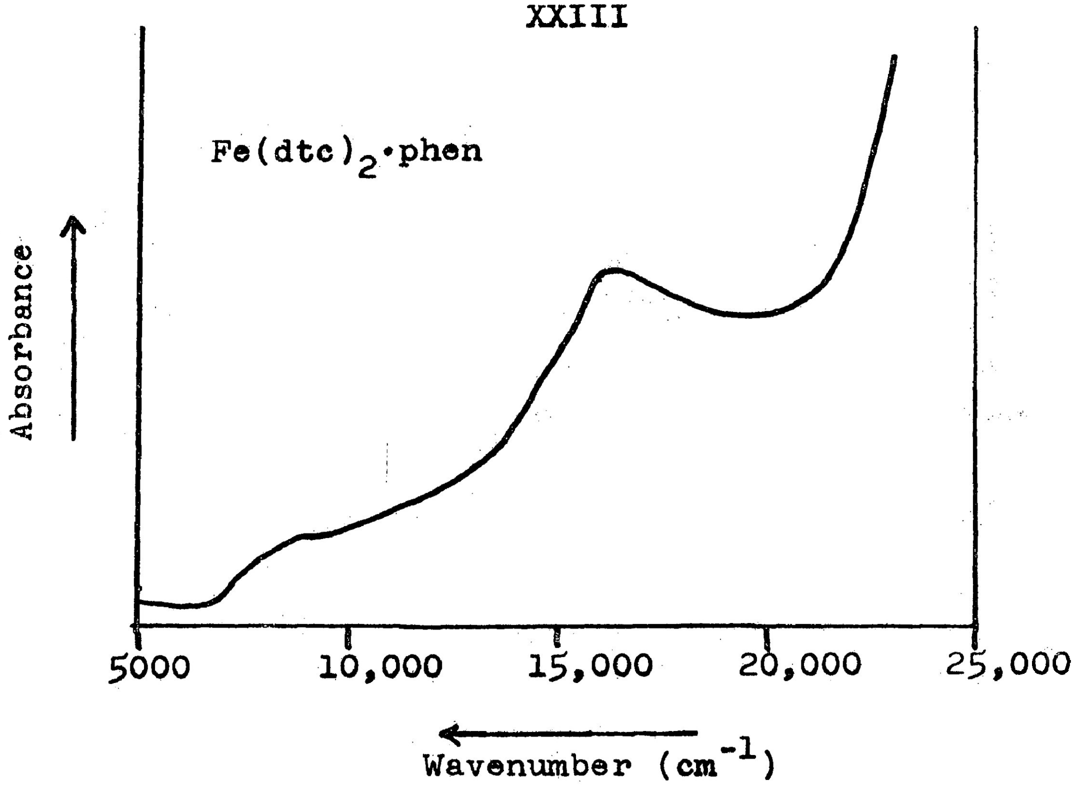
XXI


Co(dtc)$_2$•bipy
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

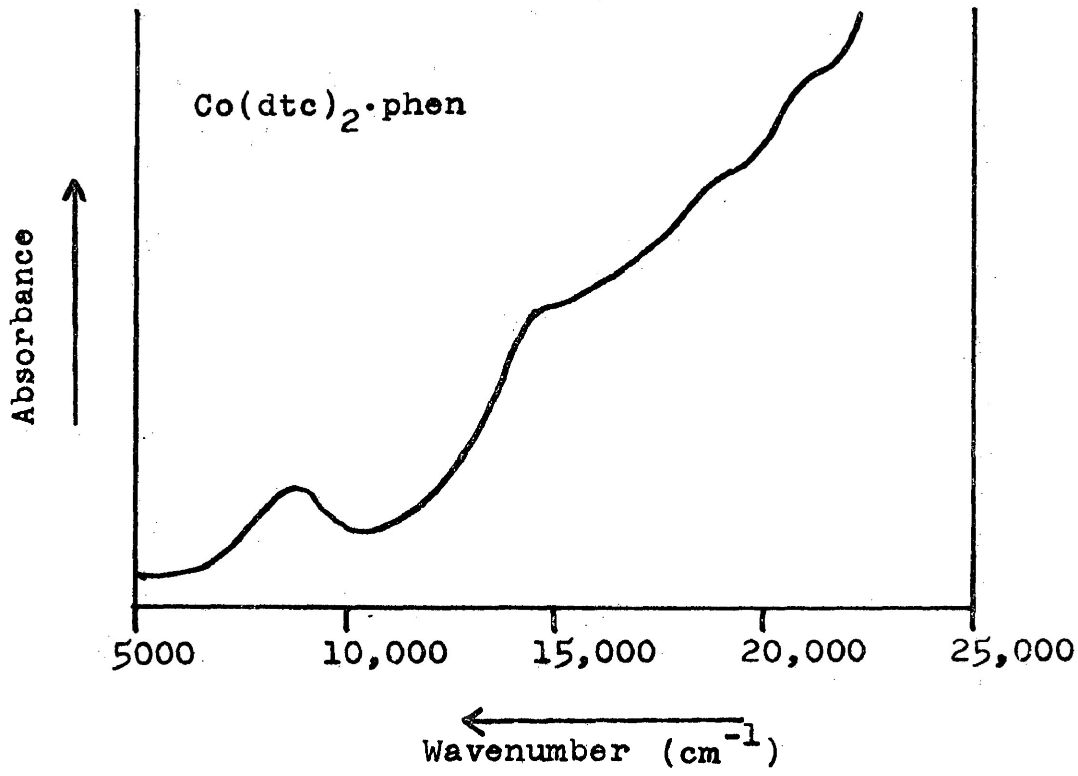
XXII


Mn(dtc)$_2$•phen
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

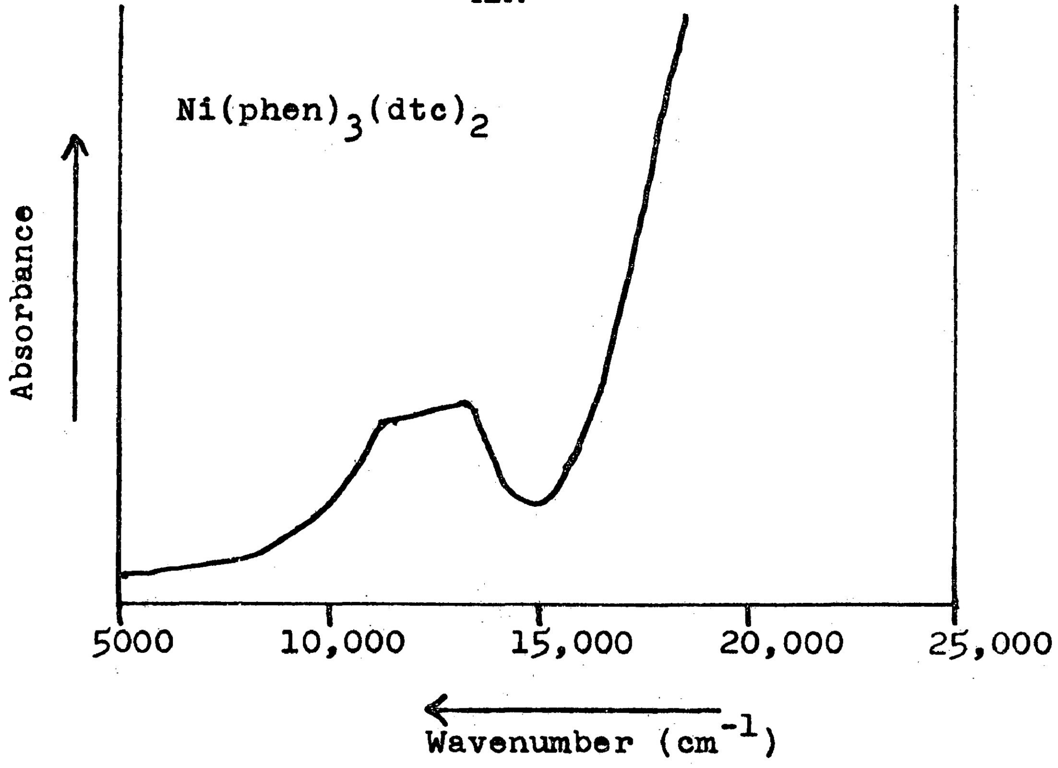
XXIII


Fe(dtc)$_2$·phen
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

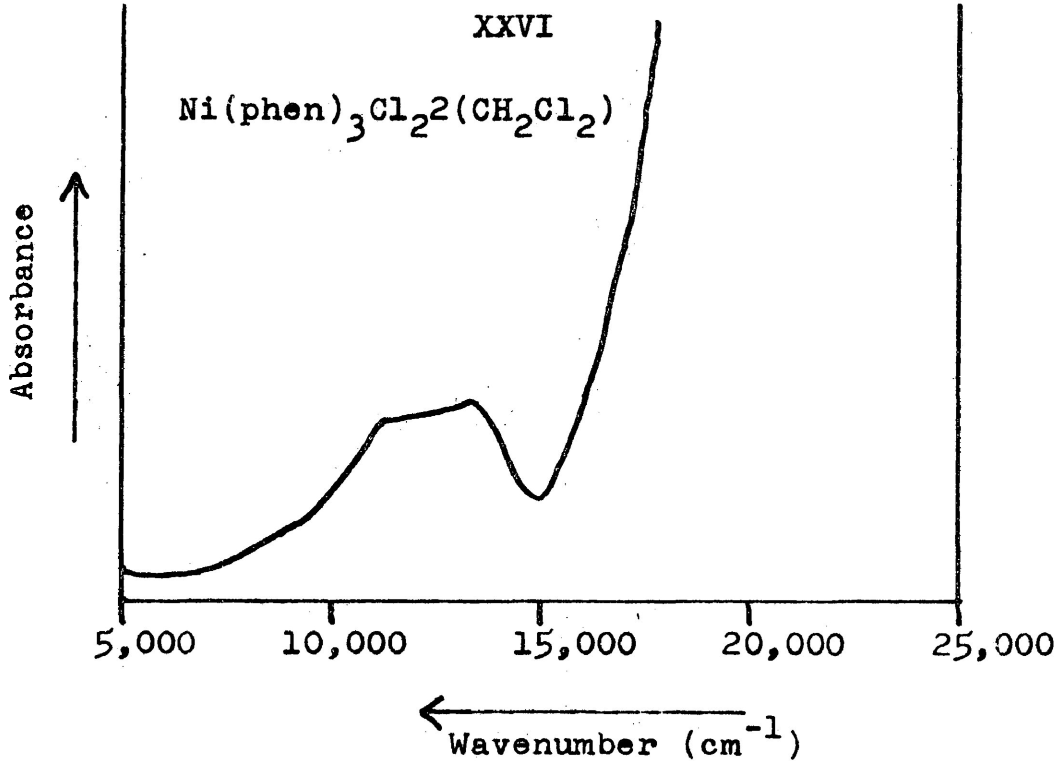
XXIV


Co(dtc)$_2$·phen
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

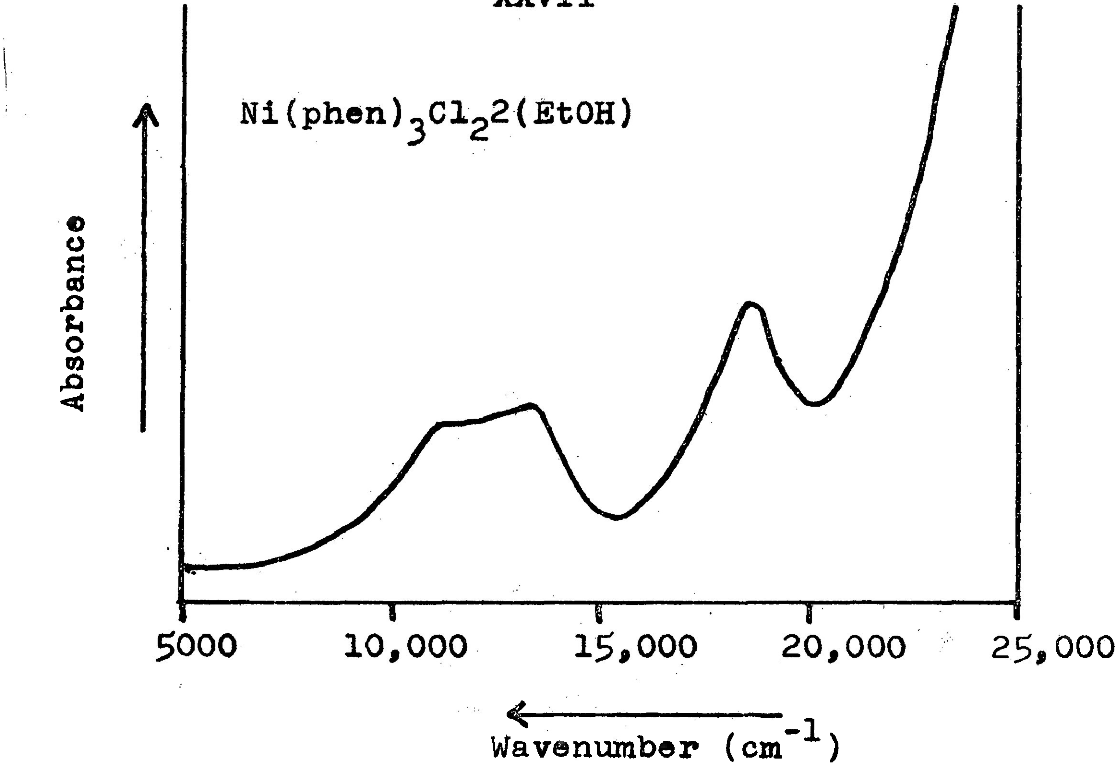
XXV


$Ni(phen)_3(dtc)_2$
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

XXVI


$Ni(phen)_3Cl_2 2(CH_2Cl_2)$
Absorbance
5,000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

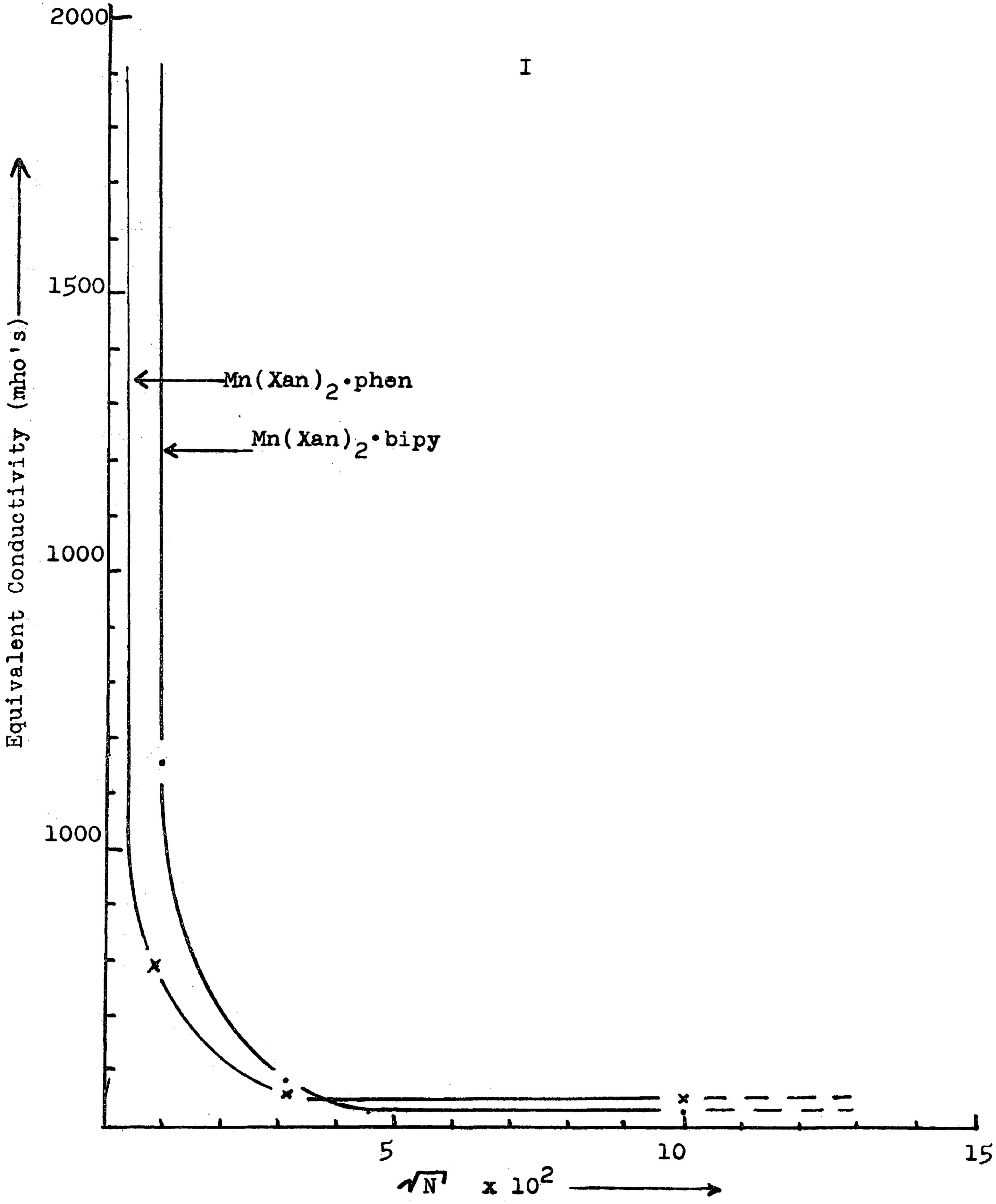
XXVII

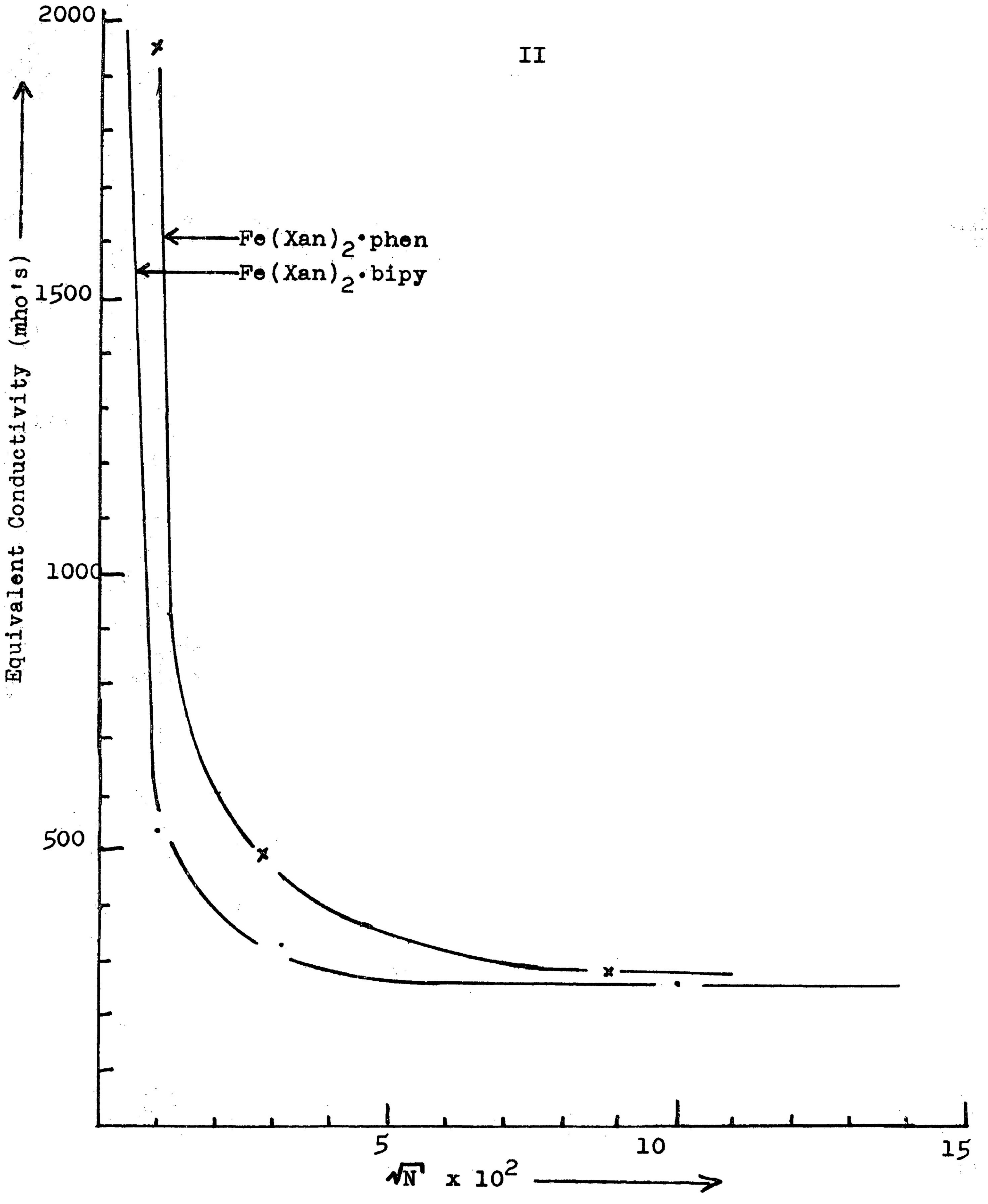

Ni(phen)$_3$Cl$_2$2(EtOH)
Absorbance
5000
10,000
15,000
20,000
25,000
Wavenumber (cm^{-1})

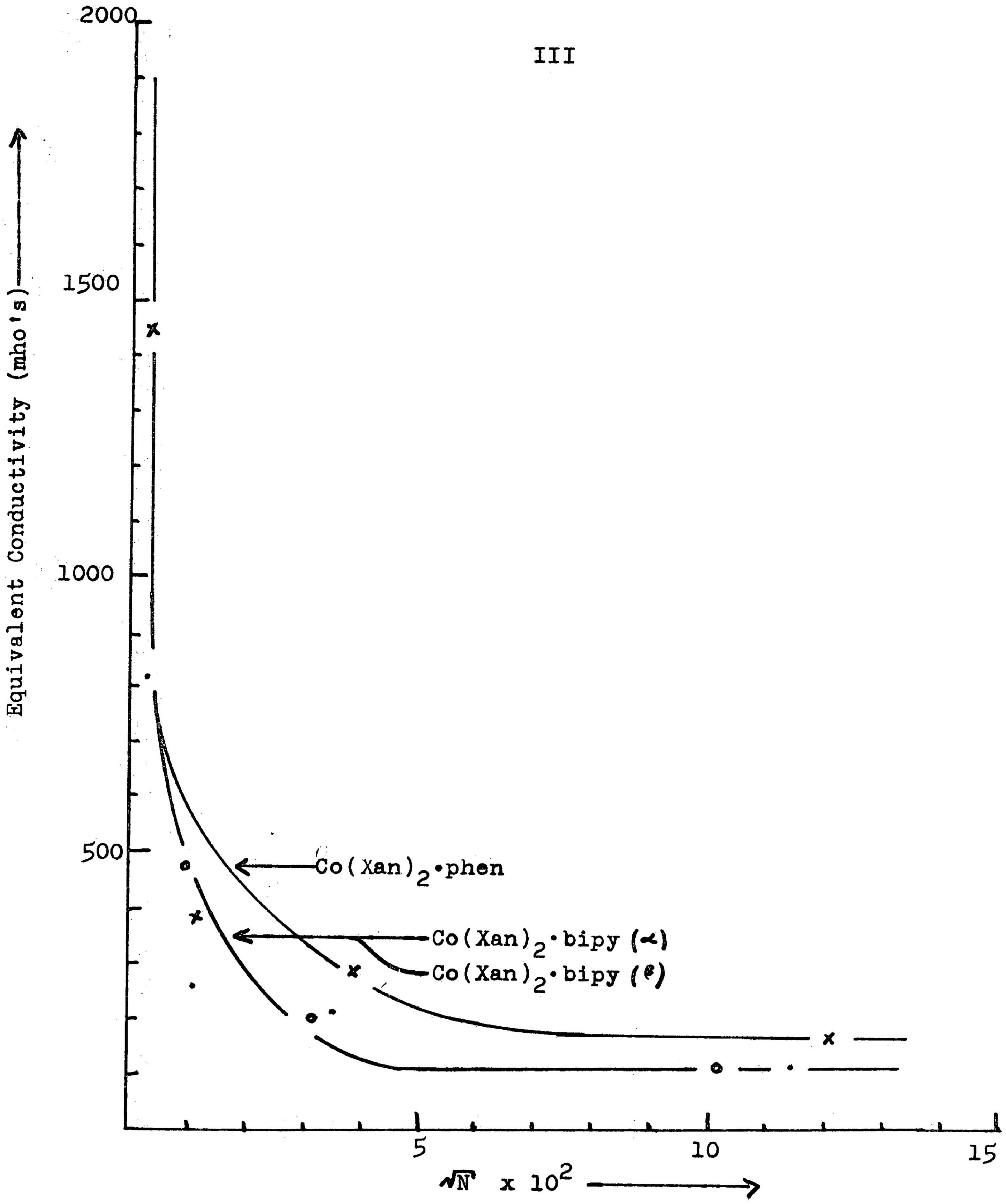
APPENDIX V

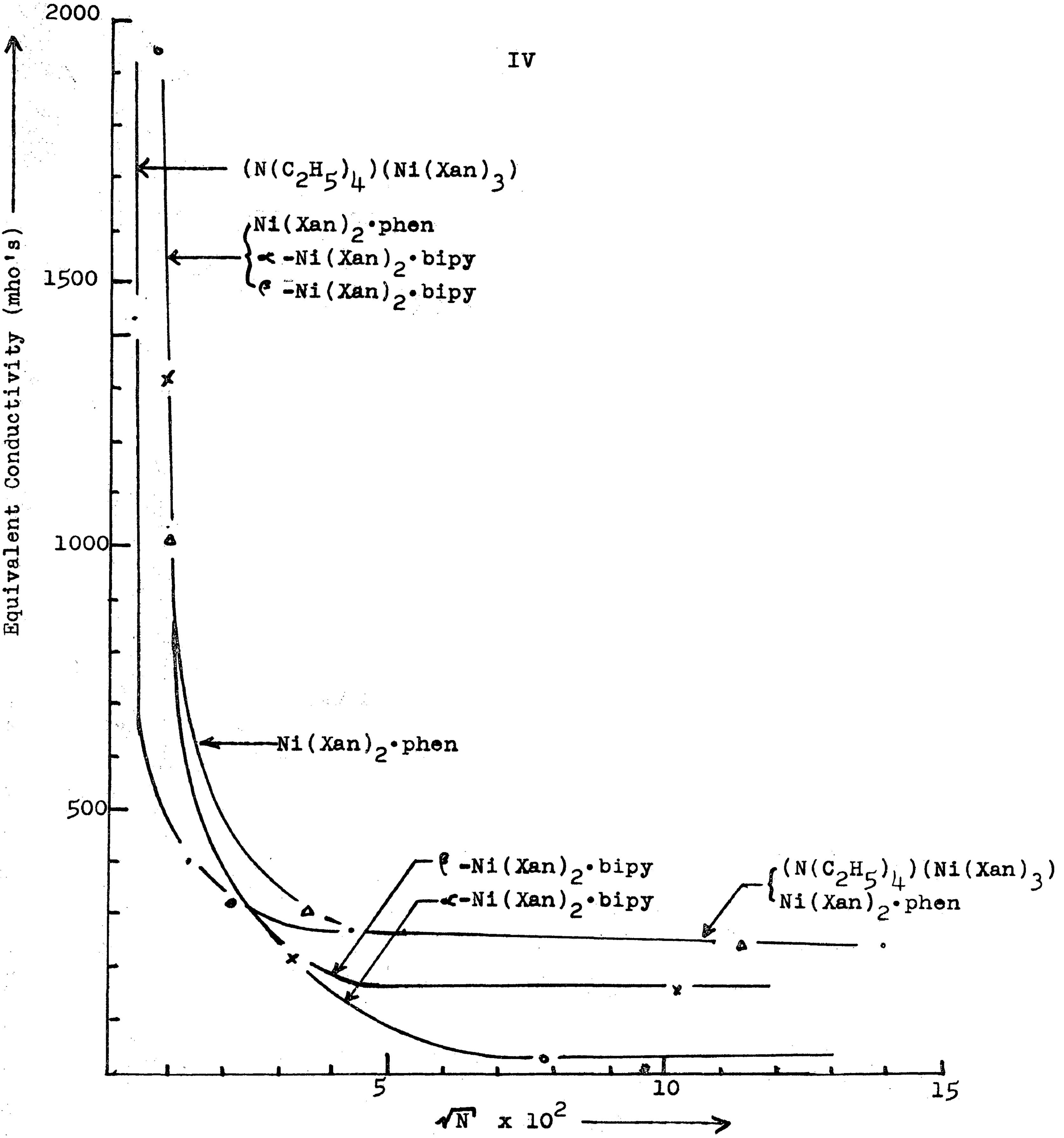
The dependence of the equivalent conductivity on the square root of the normality for the complexes studied in this thesis:

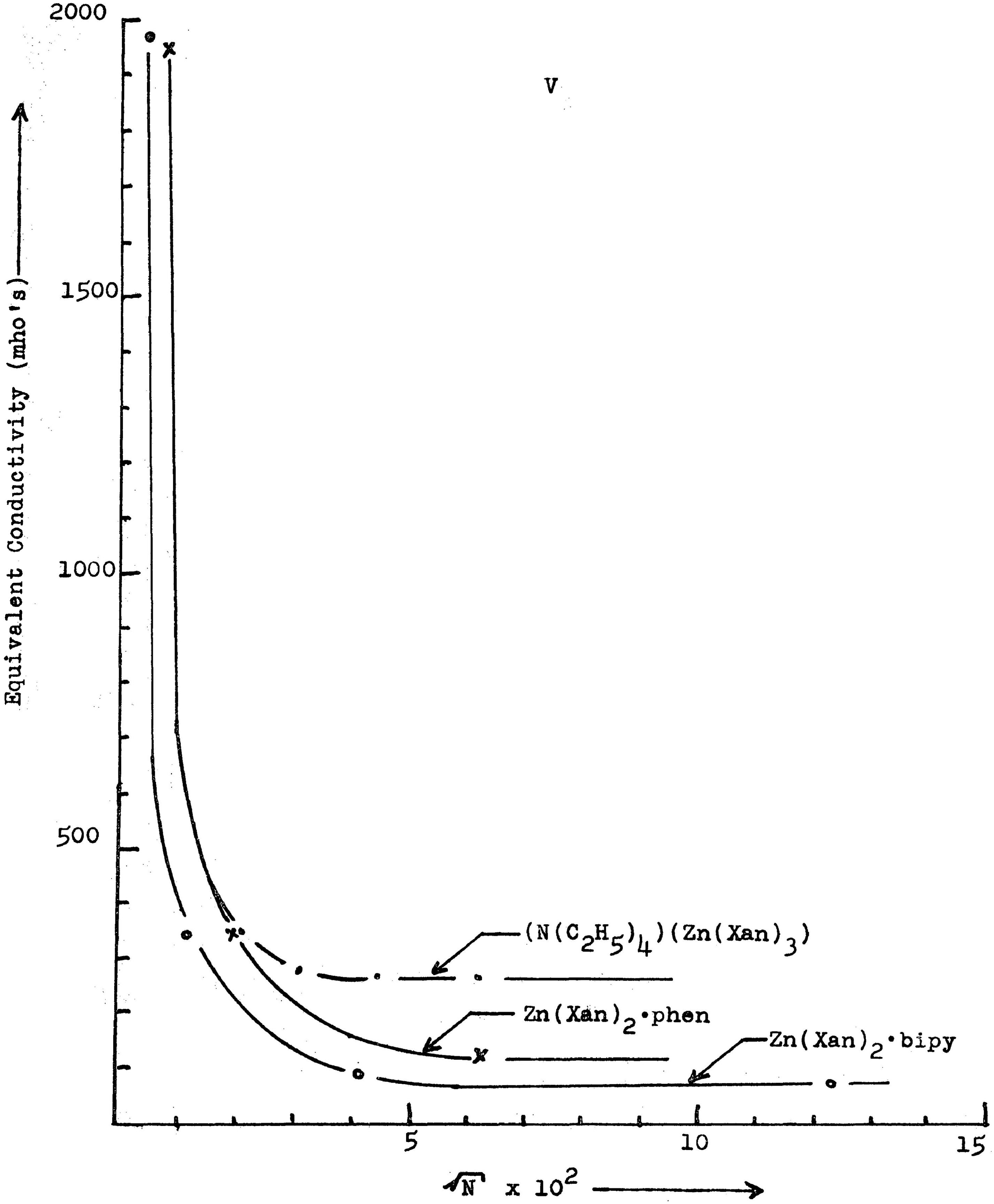
Manganese Complexes	I
Iron Complexes	II
Cobalt Complexes	III
Nickel Complexes	IV
Zinc Complexes	V


2000
1500
1000
1000
I
Equivalent Conductivity (mho's)
Mn(Xan)₂•phen
Mn(Xan)₂•bipy
5
10
15
√N x 10²


2000
1500
1000
500
II
Fe(Xan)$_2$·phen
Fe(Xan)$_2$·bipy
Equivalent Conductivity (mho's)
5
10
15
$\sqrt{N}$ x 10^2


III
2000
1500
1000
500
Equivalent Conductivity (mho's)
$Co(Xan)_2 \cdot phen$
$Co(Xan)_2 \cdot bipy$ (α)
$Co(Xan)_2 \cdot bipy$ (β)
5
10
15
$\sqrt{N} \times 10^2$


IV
Equivalent Conductivity (mho's)
2000
1500
1000
500
$(N(C_2H_5)_4)(Ni(Xan)_3)$
$Ni(Xan)_2 \cdot phen$
α-$Ni(Xan)_2 \cdot bipy$
β-$Ni(Xan)_2 \cdot bipy$
$Ni(Xan)_2 \cdot phen$
β-$Ni(Xan)_2 \cdot bipy$
α-$Ni(Xan)_2 \cdot bipy$
$(N(C_2H_5)_4)(Ni(Xan)_3)$
$Ni(Xan)_2 \cdot phen$
5
10
15
$\sqrt{N} \times 10^2$


V
2000
1500
1000
500
Equivalent Conductivity (mho's)
5
10
15
$\sqrt{N}$ x 10^2
$(N(C_2H_5)_4)(Zn(Xan)_3)$
$Zn(Xan)_2$·phen
$Zn(Xan)_2$·bipy

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