Synthetic and Spectroscopic Studies of Xanthato-Bridged Heterobimetallic Complexes Containing Diamagnetic and Paramagnetic Metal Ions

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A series of heterobimetallic complexes of the form M[M'(Etxant)$_3$] and M[M'(Etxant)$_3$]$_2$ have been prepared by the reaction of K[M'(Etxant)$_3$] [M'=Ni(II), Cd(II), or Pb(II)] and metal nitrate or sulfate [M=Co(II), Ni(II), Cd(II), Tl(I), Pb(II), or Ag(I), Etxant=ethylxanthate]. These complexes have been characterized by elemental analysis, molecular weight, molar conductance, magnetic susceptibility, (^{1}H, ^{13}C) NMR, electronic, and infrared spectral studies. Magnetic moment and electronic spectral data indicate square planar geometry around Co(II) or Ni(II), except Tl[Ni(Etxant)$_3$] in which Ni(II) is octahedrally coordinated. NMR spectra of M[M'(Etxant)$_3$]$_2$ clearly indicate the presence of two different ethylxanthate moieties, one attached to the diamagnetic Ni(II), Cd(II), or Pb(II) and the other to the paramagnetic Co(II) centre. Electrical conductance values indicate their nonelectrolytic behavior. Interaction of heterobimetallic complexes with different solvent have been studied and solvent characteristics (donor number, dielectric constant, EB (electrovalent) and CB (covalent) parameters) have been related to the structural properties of the complexes. On the basis of these studies, monomeric structure for M[M'(Etxant)$_3$]$_2$ and polymeric structure for M[M'(Etxant)$_3$] have been suggested.

The synthesis and study of heterobimetallic complexes have been the subject of active research over the past few years. The interest in heterobinuclear transition metal complexes has risen sharply in recent years for several reasons.[1-8] The combination of an electron-deficient and an electron-rich metal in a single complex presents the possibility of Lewis acid activation of a substrate molecule bound to the electron rich metal center. This type of cooperative heterobimetallic activation holds potential for applications in catalysis. Heterobinuclear complexes have been used as models for the active sites of many enzyme systems.[9] In addition to enzyme modeling, heteronuclear complexes are of interest in evaluating the factors that contribute to magnetic exchange.[10] Formation of heterobinuclear complexes with bridging ligands as precursor complex is of extreme importance in electron-transfer reaction[11,12] via inner sphere mechanism. Binary and ternary complexes[13,14] of xanthate ion have been extensively studied. Ample work has been done on heterobimetallic complexes of ambidentate ligands, such as SCN^-, $SeCN^-$ etc., involving different donor atoms of these ligands in bridging the two different metal ions. Despite this intensive interest, scarce of work[15,16] has been done on heterobimetallic complexes of dithioligands where two identical sulfur donor atoms are involved in bridging the two different metal ions. We wish to report our investigation on heterobimetallic xanthates of the form M[M'(Etxant)$_3$] and M[M'(Etxant)$_3$]$_2$ containing both univalent and bivalent as well as diamagnetic and paramagnetic metal ions.

Experimental

Material and Methods: All the chemicals used in the preparative work were BDH (AR) or equivalent grades. The solvents were freshly distilled and where necessary dried before use. Potassium ethylxanthate used in the preparative work was prepared by standard literature procedure.[17]

Preparation of the Complexes M[M'(Etxant)$_3$] and M[M'(Etxant)$_3$]$_2$. K[M'(Etxant)$_3$] required for the synthesis of M[M'(Etxant)$_3$] or M[M'(Exant)$_3$]$_2$ [M'=Ni(II), Pb(II), or Cd(II)] was prepared in situ by mixing 25 cm^3 aqueous solution of (2 mmol) potassium ethylxanthate (0.32 g) and (2 mmol) solution/suspension of Ni(Etxant)$_2$ (0.602 g), Cd(Etxant)$_2$ (0.70 g) or Pb(Etxant)$_2$ (0.90 g), in 50 cm^3 acetone/ethanol, following the reported methods.[18,19] M'(Etxant)$_2$ used in the synthesis were prepared by known methods.[13] To the above K[M'(Etxant)$_3$] solution 25 cm^3 (2 mmol/1 mmol) $AgNO_3$ (0.34 g) , Tl_2SO_4 (0.50 g), $Pb(NO_3)_2$ (0.33 g), $Co(NO_3)_2 \cdot 6H_2O$ (0.29 g), or $Ni(NO_3)_2 \cdot 6H_2O$ (0.29 g) dissolved in 80:20 water-acetone/water-ethanol (v/v) was gradually added with constant stirring. All the heterobimetallic complexes which precipitated as fine crystalline material were filtered, washed with acetone-water/ethanol-water 50:50 (v/v) mixture and finally with ether, and dried in vacuum. Our attempts to synthesize similar compounds with Cu(II), Fe(II), and Mn(II) were not successful.

Analysis and Physical Measurements: All the complexes were analyzed for their metal contents following standard literature procedures.[20] Sulfur was estimated as barium sulfate. Carbon and hydrogen were determined microanalytically on a Perkin-Elmer 240C model microanalyzer.

The molecular weight of soluble complexes was determined cryoscopically in benzene. The experimental details pertaining to the measurements of electrical conductance, room temperature magnetic susceptibility, recording of electronic and infrared spectra as Nujol mull were the same as described earlier.[16] The absorption spectra of soluble complexes were obtained in $CHCl_3$, THF, DMSO, and pyridine. The infrared spectra were recorded on Perkin-Elmer 783 spectrophotometer. ^{1}H and ^{13}C NMR spectra of the complexes were recorded in $CDCl_3$ while that of potassium ethylxanthate in DMSO-d_6 using TMS as internal reference. The relevant analytical and physicochemical data are give in Tables 1, 2, and 3.

Results and Discussion

The analytical data show the formation of the heterobimetallic xanthates of general formulae M[M′(Etxant)$_3$] or M[M′(Etxant)$_3$]$_2$. The compounds are formed according to the following equations.

[1] M′(Etxant)$_2$+KEtxant ⟶ K[M′(Etxant)$_3$]

[2] K[M′(Etxant)$_2$]+MNO_3/M_2SO_4 ⟶ M[M′(Etxant)$_3$]$_2$+KNO_3/K_2SO_4

Table 1. Analytical Data, Magnetic Moment, Molecular Weight and Molar Conductance of Heterobimetallic Xanthates

Complex	Color	Decomp temp/°C	Found (Calcd)/%					μ_{eff}/ B.M.	Molecular weight	S cm^2 mol^{-1} in nitrobenzene
			M′	M	C	H	S			
Ag[Ni(Etxant)$_3$]	Yellowish green	144	10.89 (11.09)	20.65 (20.37)	20.50 (20.38)	2.90 (2.83)	36.02 (36.24)	dia.	—	—
Tl[Ni(Etxant)$_3$]	Sky blue	>250	8.96 (9.37)	32.03 (32.63)	17.40 (17.25)	2.45 (2.39)	29.75 (30.66)	2.90	—	—
Pb[Ni(Etxant)$_3$]$_2$	Dark brown	114	11.61 (11.18)	19.98 (19.73)	20.62 (20.57)	2.95 (2.85)	36.06 (36.57)	dia.	1010.00 (1050.62)	4.95
Co[Ni(Etxant)$_3$]$_2$	Dark brown	110	12.86 (13.01)	6.62 (6.52)	23.98 (23.94)	3.25 (3.32)	41.82 (42.56)	2.94	870.50 (902.35)	1.40
Ni[Pb(Etxant)$_3$]$_2$	Brown	116	34.27 (34.56)	4.34 (4.89)	18.35 (18.02)	2.58 (2.50)	31.58 (32.04)	dia.	1122.40 (1199.11)	3.19
Co[Pb(Etxant)$_3$]$_2$	Green	113	34.22 (34.46)	4.53 (4.91)	18.40 (18.02)	2.65 (2.50)	31.86 (32.02)	2.95	1125.40 (1199.33)	1.10
Ag[Pb(Etxant)$_3$]	Yellow	116	29.36 (30.56)	15.55 (15.92)	15.75 (15.93)	2.40 (2.21)	28.01 (28.32)	—	—	—
Tl[Pb(Etxant)$_3$]	White	>250	26.48 (26.76)	25.93 (26.38)	13.80 (13.94)	2.02 (1.93)	23.95 (24.79)	—	—	—
Ag[Cd(Etxant)$_3$]	Yellow	129	18.85 (19.27)	18.03 (18.51)	18.65 (18.51)	2.68 (2.57)	32.06 (32.92)	—	—	—
Co[Cd(Etxant)$_3$]$_2$	Green	158	21.96 (22.25)	5.62 (5.84)	21.55 (21.44)	3.02 (2.97)	37.98 (38.07)	2.88	970.00 (1009.73)	1.76
Pb[Cd(Etxant)$_3$]$_2$	Light yellow	125	19.02 (19.41)	17.88 (17.89)	18.70 (18.66)	2.65 (2.59)	32.89 (33.16)	—	1095.50 (1158.00)	2.42

Table 2. Electronic Spectral Bands and Their Assignments in Heterobimetallic Complexes

Complex	Medium	B and Maxima[a]/cm^{-1}		Assignment
Ti[Ni(Etxant)$_3$]	Nujol	8700,	14080—15400, 26300	$^3A_{2g}\rightarrow{}^3T_{2g}(F),\rightarrow{}^3T_{1g}(F),\rightarrow{}^3T_{1g}(P)$
Ag[Ni(Etxant)$_3$]	Nujol		14800, 21000, 25000	$^1A_{1g}\rightarrow{}^1B_{1g},\rightarrow{}^1A_{2g}$
Pb[Ni(Etxant)$_3$]$_2$	Nujol		16000, 20600, 23800	$^1A_{1g}\rightarrow{}^1B_{1g},\rightarrow{}^2A_{2g}$
	$CHCl_3$		15380(400), 20600(475)	
	THF		15800(350), 20800(400)	
	DMSO	9350(85),	14810(140)	$^3A_{2g}\rightarrow{}^3T_{2g}(F),\rightarrow{}^3T_{1g}(F)$
	Pyridine	10310(85),	15870(130)	$^3A_{2g}\rightarrow{}^3T_{2g}(F),\rightarrow{}^3T_{1g}(F)$
Ni[Pb(Etxant)$_3$]$_2$	Nujol		16000, 20600, 23800	$^1A_{1g}\rightarrow{}^1B_{1g},\rightarrow{}^1A_{2g}$
	$CHCl_3$		15380(330), 20800(224)	
	THF		15870(360), 20830(232)	
	DMSO	9400(80),	15000(120)	$^3A_{2g}\rightarrow{}^3T_{2g}(F),\rightarrow{}^3T_{1g}(F)$
	Pyridine	10600(100),	16100(150)	$^3A_{2g}\rightarrow{}^3T_{2g}(F),\rightarrow{}^3T_{1g}(F)$
Co[Pb(Etxant)$_3$]$_2$	Nujol	6500,	11000, 15800, 20600	$^2A_{1g}\rightarrow{}^2E'_g,\rightarrow{}^2E_{2g}$
	$CHCl_3$		11760(55), 15870(390), 20830(500)	
	THF		11760(45), 15870(390), 20830(500)	
	DMSO		11760(60), 16000(385), 20830(540)	
	Pyridine		11750(60), 16000(550), 20580(640)	
Co[Cd(Etxant)$_3$]$_2$	Nujol	6300,	10800, 1600, 20400	$^2A_{1g}\rightarrow{}^2E'_g,\rightarrow{}^2E_g$
	$CHCl_3$		11700(50), 15800(360), 20800(450)	
	THF		11700(45), 15800(350), 20800(430)	
	DMSO		11750(50), 16100(320), 20750(500)	
	Pyridine		11760(55), 15870(310), 20830(420)	
Co[Ni(Etxant)$_3$]$_2$	Nujol	6000,	11700, 15000—16100, 20600, 24000	$^2A_{1g}\rightarrow{}^2E'_g,\rightarrow{}^2E_g$
	$CHCl_3$		12050(75), 15750(350), 20830(400)	
	THF		12120(50), 15750(315), 20830(435)	
	DMSO	9300(120)	15150(220), 21050(300)	
	Pyridine	10200(100)	15870(190), 20830(185)	

a) Molar absorption coefficients are given in parentheses.

Table 3. Selected Infrared Spectral Bands and (^{1}H, ^{13}C) NMR Chemical Shifts of the Complexes

Complex	IR bands/cm^{-1}			^{1}H NMR (δ/ppm)		^{13}C NMR (δ/ppm)	
	ν(C-O)	ν(C⋯S)	ν(M-S)	$-\underline{C}H_3$	$-O\underline{C}H_2$	$-\underline{C}H_3$	$-O\underline{C}H_2$
Co[Cd(Etxant)$_3$]$_2$	1255(m,b)	1030(m)	395(m)	1.57t	4.57(5)	13.81	67.07
			290(w)				68.50
Co[Ni(Etxant)$_3$]$_2$	1260(m)	1030(m)	390(m)	1.48q	4.57(6)	13.81	67.07
			380(w)				68.48
Co[Pb(Etxant)$_3$]$_2$	1260(m)	1030(m)	390(w)	1.48t	4.62(5)	13.81	67.07
			270(m,b)				69.18
Pb[Ni(Etxant)$_3$]$_2$	1260(m)	1020(s)	380(m)	1.48t	4.57q	13.81	68.80
			280(w)				
Ni[Pb(Etxant)$_3$]$_2$	1250(m)	1025(s)	380(m)	1.48t	4.57q	13.81	68.80
			290(w)				
Pb[Cd(Etxant)$_3$]$_2$	1210(m,b)	1020(m)	290(w)	1.57t	4.57q	13.81	67.07
			275(w)				
Tl[Ni(Etxant)$_3$]	1170(m)	1020(w)	395(s)	—	—	—	—
			260(m)				
Ag[Ni(Etxant)$_3$]	1260(m,b)	1020(s)	380(m)	—	—	—	—
			270(w)				
Ag[Pb(Etxant)$_3$]	1220(s)	1020(s)	270(w)	—	—	—	—
			260(w)				
Tl[Pb(Etxant)$_3$]	1200(m,s)	1030(s)	270(w)	—	—	—	—
			265(w)				
Ag[Cd(Etxant)$_3$]	1220(s)	1020(s)	270(w)	—	—	—	—
			265(w)				

[3] $2K[M'(Etxant)_3]+M(NO_3)_2 \longrightarrow M[M'(Etxant)_3]_2+2KNO_3$

M′=Ni(II), Pb(II), Cd(II)

M=Ag(I), Tl(I), Ni(II), Co(II), Pb(II).

All the complexes are insoluble in water and common organic solvents, such as ethanol, methanol, acetone, but M[M′(Etxant)$_3$]$_2$ are considerably soluble in chloroform and benzene. M[M′(Etxant)$_3$] are only moderately soluble in nitrobenzene. Poor solubility of M[M′(Etxant)$_3$] indicates their polymeric nature. Electrical conductance value 1.10—4.95 S cm^2 mol^{-1} in 10^{-3} nitrobenzene solution indicate their nonionic nature.[21] The observed molecular weight for M[M′(Etxant)$_3$]$_2$ is well in the range of their monomeric formulation.

Magnetic and Spectroscopic (Electronic, Infrared, ^{1}H and ^{13}C NMR) Studies: The diamagnetism of Ag[Ni(Etxant)$_3$], Pb[Ni(Etxant)$_3$]$_2$, and Ni[Pb(Etxant)$_3$]$_2$ indicate square planar geometry around Ni(II).

Three bands are observed in the visible spectral region of these compounds in 14800—16000 (ν_1), 20600—21000(ν_2), and 23800—25000 cm^{-1} (ν_3) regions which are well in the range reported for square-planar Ni(II) xanthate.[22] The first two bands in each case may be assigned to $^1A_{1g}\rightarrow{}^1B_{1g}$ and $^1A_{1g}\rightarrow{}^1A_{2g}$ transitions[23] respectively in D_{4h} symmetry around Ni(II). The single electron parameter Δ_1 for these complexes have been calculated following the method of Gray and Ballhausen[24] as modified by Shupack,[25] assuming $F_2=10F_4=800$ cm^{-1} in the equation $\Delta_1=35F_4+\nu_1$. The Δ_1 values thus obtained for the above Ni(II) complexes are almost of the same magnitude as for a number of square-planar Ni(II) complexes of dithioligands[26,27] such as dithiocarbamate, isomaleonitrile dithiolate, and trithiocarbonate.

The magnetic moment of 2.90 BM and the presence of electronic spectral bands at 8700; 14080, 15400 (doublet), and 26300 cm^{-1} suggest octahedral coordination around Ni(II) in Tl[Ni(Etxant)$_3$]. These bands may be assigned to $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}$, and $^3A_{2g}\rightarrow{}^3T_{1g}$(P) transitions[28] respectively. Splitting in ν_2 band is observed because the D_q/B value is nearly unity which is mainly due to mechanism of spin-orbit coupling where spin-forbidden transition has stolen intensity from spin-allowed transition. The μ_{eff} values (2.88—2.95 BM) for Co[Pb(Etxant)$_3$]$_2$, Co[Cd(Etxant)$_3$]$_2$, and Co[Ni(Etxant)$_3$]$_2$ and electronic spectral bands observed in the region 6000—6500, 10800—11000, 15900—16000, and 20400—20600 cm^{-1} suggest square-planar geometry around Co(II). The magnetic moments are almost temperature independent down to 90 K ruling out any possibility of antiferromagnetic interaction in these complexes. The first and third bands are assigned to $^2A_{1g}\rightarrow{}^2E'_g$ and $^2A_{1g}\rightarrow{}^2E_{2g}$ transitions respectively.[29,30] As suggested by Nishida and Kida,[30] the most characteristic band at ca. 11000 cm^{-1} for square-planar Co(II) complexes may be taken as equal to 15B which gives the value of B=720 cm^{-1}. Appearance of a broad band between 14880—16100 cm^{-1} and an additional band at 24000 cm^{-1} in Co[Ni(Etxant)$_3$]$_2$ similar to other heterobimetallic complexes of Ni(II) in the present series suggests square-planar geometry around Ni(II).

The bands occurring in the infrared spectra of M[M′(Etxant)$_3$] and M[M′(Etxant)$_3$]$_2$ in 1200—1260

cm^{-1} and 1020—1030 cm^{-1} regions are consistently assigned to ν(C-O) and ν(C=S) modes respectively,[13,16,19] which are characteristic of the C_2H_5-O-CS_2^- group. ν(C-O) is observed at a lower frequency (ca. 1170 cm^{-1}) in Tl[Ni(Etxant)$_3$]. This marked negative shift in ν(C-O) is probably due to octahedral geometry around nickel(II) as observed[18] with other octahedral complexes. The occurrence of a single band for ν(C⋯S) and its position indicate uninegative bidentate behavior of xanthate ion[31] in the above complexes.

In all the complexes, the bands occurring below 400 cm^{-1} have been tentatively assigned[18,32] to ν(M-S) modes, the lower one may be due to Ag-S, Tl-S, Pb-S and the higher one due to Co-S or Ni-S stretching modes respectively.

The purity and composition of the complexes have been confirmed by ^{1}H and ^{13}C NMR spectral studies. Proton NMR spectrum of potassium ethylxanthate yields a triplet at δ 1.32 and a quartet at δ 4.33 due to -CH_3 and -OCH_2 protons respectively. The spectra of M[M′(Etxant)$_3$]$_2$ [M=Ni(II), Pb(II); M′=Ni(II), Pb(II), Cd(II)], where both metal centers are diamagnetic show a triplet at δ 1.48—1.57 and a quartet at δ 4.57—4.62 (Fig. 1), in the intensity ratio of 3 : 2 for -CH_3 and -OCH_2 protons respectively. The downfield shifts observed for these protons as compared to the ionic potassium ethylxanthate clearly indicate the deshielding of ethoxyl protons in these complexes. For paramagnetic compounds, Co[Ni(Etxant)$_3$]$_2$, Co[Pb(Etxant)$_3$]$_2$, and Co[Cd(Etxant)$_3$]$_2$, the number of peaks (Fig. 1) for -OCH_2 protons are 5 or 6. The increased number of peaks may be due to the mixing of -OCH_2 protons attached to the paramagnetic Co(II) and the diamagnetic Ni(II), Cd(II), or Pb(II) in the heterobimetallic compounds.

^{13}C NMR spectra of the diamagnetic complexes give two signals at δ 13.8 and 67.1—68.6 for -CH_3 and -CH_2 carbons which are comparable to those reported for $Me_2AuS_2COC_2H_5$[33] in which ethylxanthate group is bidentate. However, the spectra of paramagnetic compounds (Fig. 2) show splitting in the peak appearing at δ ca. 67 due to -OCH_2 carbon indicating the presence of two different types of ethoxylcarbon arising from the influence of the unpaired electron of Co(II). But such splitting is absent in case of diamagnetic compounds.

These observations clearly indicate the presence of two different ethylxanthate moieties, one of which attached to the diamagnetic Ni(II), Pb(II), or Cd(II) and the other to the paramagnetic Co(II) center.

Effect of Solvents on the Complexes: While describing their bonding and structure on the basis of various physicochemical studies, it was considered worthwhile to see the effect of solvents on the complexes. Accordingly, they have been treated with a number of solvent and their electronic spectra studied. The effect of solvents on Co(II) and Ni(II) heterobimetallic complexes have been related to their donor numbers, dielectric constant and CB (covalent) and EB (electrovalent) parameters. The results of absorption maxima given in Table 2 show the following:

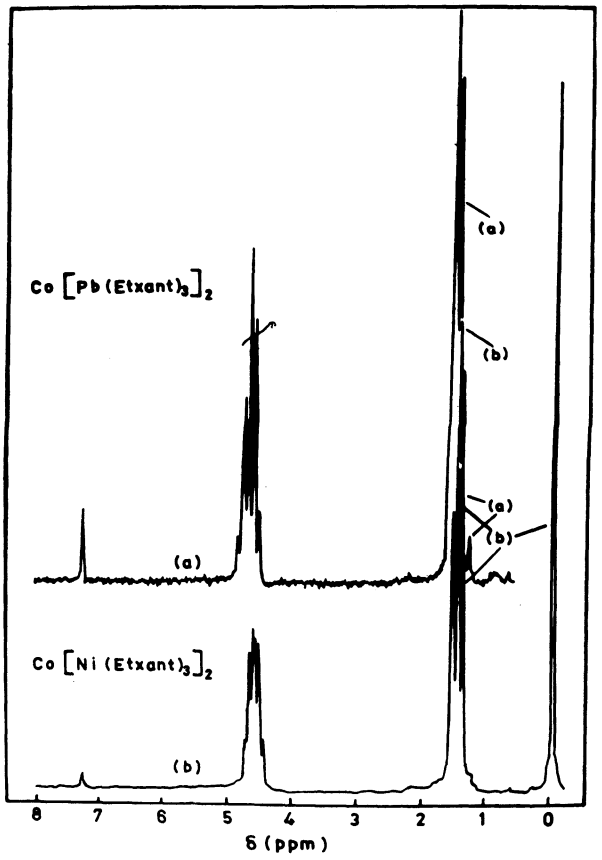


Fig. 1. ^{1}H NMR spectrum in $CDCl_3$.

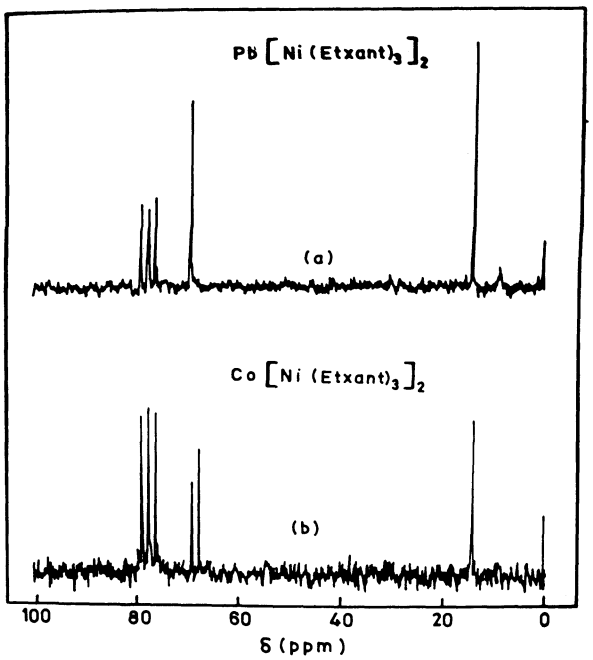


Fig. 2. ^{13}C NMR spectrum in $CDCl_3$.

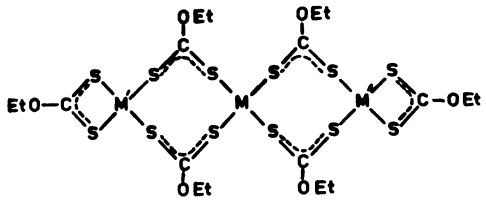
(1) The complexes Pb[Ni(Etxant)$_3$]$_2$, Ni[Pb(Etxant)$_3$]$_2$, and Co[Ni(Etxant)$_3$]$_2$ are fairly soluble in solvents, such as DMSO and pyridine, having donor number (29.8—33.1) and dielectric constant (12.3—45.0) with a change in color due to coordination of the solvent molecules. The positions of their band maxima and molar absorption coefficient at maximum (Table 2) in DMSO and pyridine clearly indicate that these solvents are coordinated to NiS_4 chromophore bringing octahedral stereochemistry around Ni(II). Co[Pb(Etxant)$_3$]$_2$ and Co[Cd(Etxant)$_3$]$_2$ are also highly soluble in the above solvents. The wavenumbers of their absorption maximum are indicative of square planar geometry around Co(II) ruling out any possibility of solvent coordination to Co(II).

(2) All the above complexes are also soluble in THF with donor number (20.0) and dielectric constant (7.3) but, as indicated by their band maxima, it does not coordinate to either Co(II) or Ni(II).

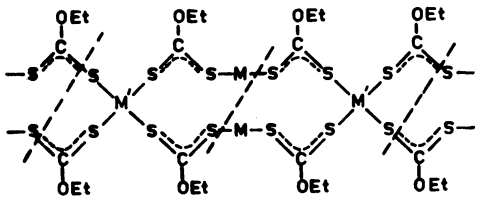
(3) The absorption maxima of the above complexes recorded in nonpolar solvents like chloroform and benzene with donor number (0.1) and dielectric constant (2.3—4.8) indicate their noncoordinating behavior.

(4) Solvents like ethanol, methanol, acetone, acetonitrile, and water having donor number (14.0—20.0) and dielectric constant (20.7—81.7) neither dissolve nor coordinate but on boiling they decompose M[M′(Etxant)$_3$] because of the disruption of -S-C-S- bridge in their polymeric structure.

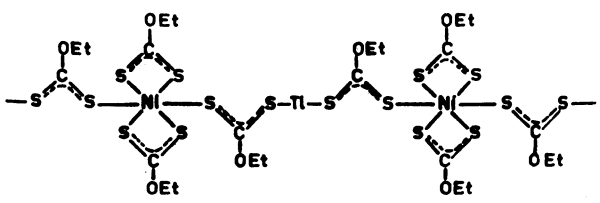
Based on chemical composition and physicochemical studies, dimeric structure (**1**) and polymeric structures (**2** and **3**) are proposed for the complexes subject to final confirmation by single crystal X-ray analysis. The arrangement of xanthate group around Ag(I) is nonlinear possibly due to d-electron contribution to the expected linear sp-hybridization scheme as observed when sulfur is the donor atom.[34,35] Zn(II), Cd(II), and Pb(II) presumably possess their preferential tetrahedral geometry as in the case of simple xanthate complexes.[36]



1. M [M′(Etxant)$_3$]$_2$



2. M[M′(Etxant)$_3$]



3. Tl [Ni(Etxant)$_3$]

Conclusion

On the basis of the foregoing studies, following conclusions are drawn regarding the present series of complexes:

(1) On the basis of the solubility and molecular weight determination, the complexes are categorised in two classes, viz., monomeric M[M′(Etxant)$_3$]$_2$ and polymeric M[M′(Etxant)$_3$].

(2) Borderline metal ions Ni(II), Co(II), Pb(II), when present together in a complex, form monomeric xanthato-bridged complex, M[M′(Etxant)$_3$]$_2$ with soft sulfur donor atoms of the xanthate moiety. However, if one of the metal ions is soft and the other is soft or borderline, e.g. Ni(II), Ag(I); Ni(II), Tl(I); Ag(I), Pb(II); Tl(I), Pb(II), polymeric bridged complexes are formed.

(3) The low-spin planar geometry of Co(II) and Ni(II) are stabilized in their heterobimetallic complexes except in Tl[Ni(Etxant)$_3$].

(4) As observed by absorption maxima and molar absorption coefficient data, solvents like pyridine and DMSO having higher donor number[37] and CB parameter (2.85—6.40)[38] show coordinating ability towards M[Ni(Etxant)$_3$]$_2$ and Ni[Pb(Etxant)$_3$]$_2$.

(5) Infrared spectral studies invariably indicate uninegative bidentate behavior of xanthate group.

(6) NMR data clearly indicate two types of ethylxanthate in the paramagnetic complexes.

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