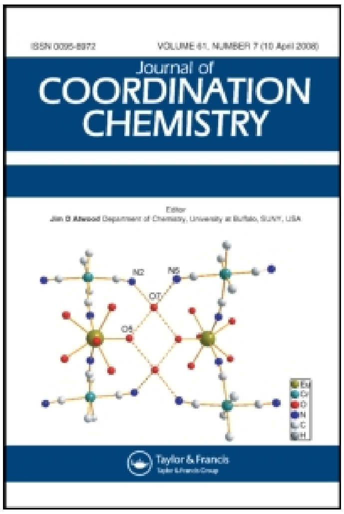

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SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF FORMYLHYDRAZIDE

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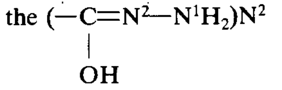
Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II) complexes have been prepared with formylhydrazide employing the chloride, bromide, iodide, sulphate, perchlorate, thiocyanate and nitrate salts. Complexes having 1 : 3, 1 : 2 and 1 : 1 metal ion to ligand ratios have been isolated. Characterization has been accomplished by elemental analyses, magnetic moment, conductance and spectra (visible, i.r. and far-i.r.). The ligand is bidentate and coordination occurs through carbonyl oxygen and terminal nitrogen.

INTRODUCTION

It was previously shown by us that the hydrazide unit of metal complexes of malondihydrazide,[1] succindihydrazide,[2] acetylhydrazide,[2] benzoylhydrazide,[2] phenylacetylhydrazide,[3] α-methylmalondihydrazide[4] and α-allylmalondihydrazide[5] is unidentate in character, coordinating through the  $(\text{—}\underset{\displaystyle\text{OH}}{\underset{|}{\text{C}}}\text{=N}^2\text{—N}^1\text{H}_2)\text{N}^2$ nitrogen atom. Similar observations were also noted by other groups in this laboratory while studying the rare earth complexes of malondihydrazide[6] and succindihydrazide.[7] Kharitanov *et al.*[8] and Agarwal *et al.*[9–11] studied the metal complexes of some acid-hydrazides and reported the hydrazide unit coordinating through carbonyl oxygen and terminal nitrogen. Saha *et al.*[12] reported both unidentate and bidentate character of the hydrazide unit. It is expected that the ligation behaviour of the hydrazide unit may depend on the groups attached to N^1, N^2 or carbonyl carbon atom. With this idea we chose most simple hydrazide, i.e. formylhydrazide, ever studied. This hydrazide possibly can show the real ligation behaviour of the hydrazide unit as this hydrazide unit is practically free from the influence of other groups. The present work reports the preparation and characterization of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II) complexes with formylhydrazide employing the chloride, bromide, iodide, sulphate, perchlorate, thiocyanate and nitrate salts.

EXPERIMENTAL

The materials used were all of chemically pure grade.

Preparation of ligand

The ligand (formylhydrazide, L) was prepared by mixing ethylformate and hydrazine hydrate (80%) in equimolecular proportion following the method of Pellizari.[13] It was recrystallised from ethanol. The crystals are very hygroscopic (m.p. 54°C).

Preparation of metal sulphate complexes

The metal sulphate (1 mmol) dissolved in water (10 ml) was added dropwise with stirring to the aqueous solution (2 ml) of ligand (4 mmol). The resulting mixture was filtered and the filtrate was kept over night at ~25°C‡. The shining solid crystals were separated. The separated crystals are moderately soluble in water and insoluble in ethanol. These§ were recrystallised from water. The crystals were collected,

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‡While preparing copper complexes the temperature was maintained below 10°C to avoid reduction.

§Chromic sulphate complex is insoluble in water. This was purified by thorough washing with water.

washed initially with ice-cold water and then with ethanol and dried in vacuum desiccator. The purity of the complexes was checked by TLC.

Preparation of metal halide, perchlorate, nitrate and thiocyanate complexes

The metal salt† (1 mmol) dissolved in 25 ml ethanol was added dropwise with stirring to the ethanolic solution (5 ml) of ligand (4 mmol). The shining solid crystals separated slowly from the mixture at ~25°C. The separated crystals are highly soluble in water and insoluble in ethanol but moderately soluble in water-ethanol (1 : 1) mixture. These‡ were recrystallised from a water-ethanol (1 : 1) mixture. The crystals were collected, washed with ethanol and dried in a vacuum desiccator. The purity of the complexes was checked by TLC.

Physical measurements

Infrared spectra in the range 4000–400 cm^{-1} and 500–20 cm^{-1} were recorded on Beckman Model-20A and 720M spectrophotometers respectively. Spectra in the range 4000–400 cm^{-1} were obtained as Nujol mulls and KBr pellets and in 500–20 cm^{-1} as polythene pellets. Electronic spectra in the visible and near infrared ranges were recorded on Hilger 402 and Cary 17D spectrophotometers respectively. The magnetic susceptibility measurements were made at room temperature by Gouy's method using cobalt mercury tetrathiocyanate as reference.[14] Diamagnetic corrections were also made using Pascal's constants.[15] Molar conductance of the complexes was measured using Philips model PR 9500 conductivity meter. Thermal analysis was carried out using MOM Derivatograph.

RESULTS AND DISCUSSION

The complexes which were isolated and characterized by elemental analyses, magnetic moment and conductance data are shown in Table I. The complexes have the following composition: ML_3X_3, $ML_3X_2{\cdot}H_2O$, ML_3X_2, ML_2X_2 and MLX_2, where L = formylhydrazide. M = Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II), X = Cl^-, Br^-, I^-, $\frac{1}{2}SO_4^=$, ClO_4^-, SCN^- and NO_3^-. All the nickel(II) halides, sulphate, nitrate and perchlorate complexes are tris, whereas the nickel(II) thiocyanate complex is bis. On the other hand, cobalt(II) nitrate and perchlorate complexes are tris and cobalt(II) halides, sulphate and thiocyanate complexes are bis together with copper(II), manganese(II), iron(II), zinc(II) and cadmium(II) complexes. Chromium(III) salts give tris complexes and palladium(II) gives a monoligand complex. Complexes of chromium(III), manganese(II), iron(II), cobalt(II) and nickel(II) halides with formylhydrazide are similar in composition to the corresponding metal chloride complexes of acetylhydrazide reported earlier by this laboratory.[2] We could not prepare tris complexes of copper(II) chloride and zinc(II) sulphate as isolated with acetylhydrazide.[2] We have also failed to isolate PdL_4Cl_2 as expected from the study of acetylhydrazide.[2]

Electronic spectral data of the complexes in water, in water with excess ligand and in mulls are given in Table II. The spectra of nickel(II) complexes are consistent with their octahedral stereochemistry showing three $d \rightarrow d$ transition bands in the range 9,708–10,638 cm^{-1}, 15,870–17,860 cm^{-1} and 26,316–27,397 cm^{-1} which may be assigned to the transitions. ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ respectively. However, these assignments are tentative because we are dealing with tris-chelated complexes. In such complexes or in complexes of any other symmetry than O_h, the degeneracy of the levels, implied in the letters T of the spectroscopic states, is doubtful and all of such transitions will become multiple. The ν_2/ν_1 ratio lying in the range 1.63 ~ 1.67 also supports the octahedral geometry for nickel(II) complexes.[16] The cobalt(II) complexes are also consistent with their octahedral stereochemistry showing $d \rightarrow d$ transition bands in the range 9,090–9,260 and 19,600–19,800. The bands are tentatively assigned to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ respectively. The chromium(III) complex shows a band at 18,868 cm^{-1} which may be assigned to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ for octahedral symmetry.[17] The spectra of copper(II) complexes show symmetrical bands at 13,158 cm^{-1} with shoulders and tails on the low energy side indicating a tetra-coordinated planar configuration.[18] The palladium complex shows a shoulder at 25,000 cm^{-1} which may be due to the square planar geometry. The spectral band positions of the complexes in aqueous solutions with excess ligand and also in mulls shift slightly to higher energy with respect to the values of aqueous solutions (Figure 1). This variation of energy in the spectral bands of the complexes owing

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†Sodium chloropalladite and ferric chloride were used as starting material for the preparation of palladium chloride and ferrous chloride[2] complexes respectively.

‡Palladium chloride and nickel thiocyanate complexes are insoluble in any common solvent. These two complexes were purified by washing several times with water.

TABLE I
Physical and analytical data for the metal complexes of formylhydrazide

Complex	Color	Found (Calcd.) % Metal	S	N	X	μ eff (B.M.)	Λ^c (mho cm^2 mol^{-1})
CrL_3Cl_3	Chocolate	15.36(15.21)	–	24.81(24.82)	31.46(31.57)	4.06	480
$CrL_3(SO_4)_{3/2}$	Chocolate	13.82(13.77)	12.76(12.81)	22.34(22.01)	–	3.85	[b]
MnL_2Cl_2	White	22.35(22.01)	–	22.76(22.63)	28.86(28.24)	6.00	240
MnL_2SO_4	White	20.29(19.01)	11.80(11.50)	20.66(20.33)	–	5.92	245
FeL_2Cl_2	White	19.74(19.72)	–	19.79(19.36)	25.10(24.91)	5.72	220
CoL_2Cl_2	Pink	23.58(23.99)	–	22.40(22.20)	28.40(28.10)	4.74	259, 263[d]
CoL_2Br_2	Pink	17.40(17.27)	–	16.53(16.72)	47.17(47.04)	4.70	281, 275[d]
CoL_2I_2	Pink	13.62(13.16)	–	12.94(13.40)	58.66(58.23)	4.78	240
CoL_2SO_4	Pink	21.43(21.01)	11.63(11.63)	20.36(19.09)	–	4.68	232
$CoL_3(ClO_4)_2$	Pink	13.45(13.96)	–	[e]	16.10(16.21)	4.91	242
$CoL_2(SCN)_2$	Pink	19.98(20.55)	21.70(21.62)	28.48(28.65)	–	4.00	225, 230[d]
$CoL_3(NO_3)_2$	Pink	16.25(16.74)	–	30.85(30.82)	–	[a]	228
NiL_3Cl_2	Sky blue	18.96(18.52)	–	27.12(27.01)	22.92(22.61)	3.03	244
$NiL_3Br_2 \cdot H_2O$	Sky blue	14.09(14.06)	–	20.16(20.09)	38.40(38.26)	3.17	276
$NiL_3I_2 \cdot H_2O$	Sky blue	11.49(11.38)	–	16.44(16.01)	49.73(49.62)	3.00	240
NiL_3SO_4	Sky blue	17.54(17.32)	9.56(9.27)	25.10(24.43)	–	3.32	236
$NiL_3(ClO_4)_2$	Sky blue	13.44(13.55)	–	[e]	15.95(16.22)	3.23	272
$NiL_2(SCN)_2$	Sky blue	20.17(20.00)	21.98(21.72)	28.84(28.60)	–	3.10	[b]
$NiL_3(NO_3)_2$	Sky blue	16.18(15.53)	–	30.87(30.63)	–	[a]	238
CuL_2Cl_2	Green	24.95(24.71)	–	22.00(21.98)	27.89(27.43)	2.02	262
CuL_2Br_2	Green	18.43(18.50)	–	16.11(16.29)	46.43(46.56)	2.02	269
CuL_2SO_4	Green	22.19(22.73)	11.01(11.44)	19.85(20.03)	–	2.03	239
$CuL_2(ClO_4)_2$	Green	16.56(16.61)	–	[e]	18.23(18.55)	2.29	242
ZnL_2SO_4	White	23.23(22.91)	11.21(11.38)	19.90(20.01)	–	–	239
CdL_2SO_4	White	34.22(33.71)	9.74(10.62)	17.05(17.00)	–	–	242
$PdLCl_2$	Yellow	44.82(44.40)	–	11.79(11.68)	29.90(29.81)	–	[b]

[a] Magnetic susceptibility measurement could not be taken due to extreme hygroscopic character of the complex.

[b] Conductance data could not be taken due to insoluble character of the complex.

[c] Molar conductance of ~10^{-3} M aqueous solution of complexes.

[d] Molar conductance with excess ligand.

[e] Nitrogen analysis could not be done due to explosive character of the complex.

TABLE II
Electronic spectral data of the metal complexes

Compound	Medium	Band maxima, (ε max) (nm) (mol^{-1} 1 cm^{-1})	10 Dq (cm^{-1})
CrL_3Cl_3[a]	water	530(23)	18,868
	water + L	400 sh. 525(24)	19,084
CoL_2Cl_2	water	505(12), 1090(3)	10,336
	water + L	500(16), 1060(4)	10,610
	mull	490, 1075	10,497
CoL_2Br_2	water	508(24), 1085(6)	10,373
	water + L	500(27), 1065(7)	10,566
	mull	500, 1060	10,610
CoL_2I_2	water	505(9), 1090(2)	10,336
	water + L	495(14), 1060(4)	10,619
	mull	495, 1060	10,619
CoL_2SO_4	water	505(12), 1100(3)	10,250
	water + L	500(15), 1070(4)	10,522
	mull	480, 1060	10,652
$CoL_3(ClO_4)_2$[a]	water	510(12), 1080(6)	10,409
$CoL_2(SCN)_2$	water	510(22), 1080(3)	10,409
	water + L	500(25), 1060(5)	10,610
	mull	480, 1075	11,316
$CoL_3(NO_3)_2$[a]	water	505(23), 1075(6)	10,472
NiL_3Cl_2	water	380(9), 620(5), 1000(7)	10,000
	water + L	365(11), 610(8), 950(8)	10,526
	mull	560, 940	10,638
$NiL_3Br_2 \cdot H_2O$	water	380(7), 640(4), 1030(5)	9,708
	water + L	370(8), 620(6), 990(8)	10,101
	mull	590, 970	10,309
$NiL_3I_2 \cdot H_2O$	water	380(8), 640(4), 1030(6)	9,708
	water + L	370(9), 625(6), 1000(8)	10,000
	mull	600, 940	10,638
NiL_3SO_4	water	375(10), 630(5), 1030(6)	9,708
	water + L	370(12), 610(7), 990(9)	10,101
	mull	590, 980	10,204
$NiL_3(ClO_4)_2$[a]	water	380(7), 640(4), 1030(5)	9,708
$NiL_2(SCN)_2$[b]	mull	540, 930	10,753
$NiL_3(NO_3)_2$[a]	water	380(9), 645(5), 1045(7)	9,569
	water + L	370(12), 620(7), 1025(9)	9,756
CuL_2Cl_2[c]	water	760(131)	–
	mull	690	–
CuL_2Br_2[c]	water	740(160)	–
CuL_2SO_4[c]	water	750(143)	–
$CuL_2(ClO_4)_2$[c]	water	740(120)	–
$PdLCl_2$[b]	mull	400 sh	–

[a] Mull spectra could not be taken due to high hygroscopic nature of the complex.

[b] Solution spectra could not be taken due to insoluble character of the complex.

[c] Complex decomposes with excess ligand.

to the change in the spectral medium is generalised as:

Mull ≥ Aqueous solution > Aqueous solution
+
Excess ligand

In the case of Ni(II) this phenomenon probably indicates that NiL_3X_2 exists as: $NiL_3X_2 + 2H_2O \leftrightharpoons [NiL_2(H_2O)_2]X_2 + L$ in aqueous solution. Excess ligand retards solvation. On the other hand the spectroscopic difference observed between solutions of chromium(III) complexes in the presence and absence of an excess of ligand is not due to the equilibrium as presumably expected for nickel(II) complexes because such equilibria for chromic complexes are extraordinarily slow to establish with half-lives at room temperature in neutral solution of years. Therefore, it is difficult to comment on the spectroscopic differences observed for chromium(III) complexes. Cobalt(II) bis complexes in aqueous solution probably form an equilibrium[19,20] $[CoL_2X_2] + 2H_2O \rightleftharpoons [CoL_2(H_2O)_2]^{+2} + 2X^-$. Excess ligand probably forms two types of equilibria: 1) $[CoL_2(H_2O)_2]^{+2} + L \rightleftharpoons [CoL_3]^{+2}$ and 2) $[CoL_2(H_2O)_2]^{+2} + 2X^- + L \rightleftharpoons [CoL_2X_2] + L$. This type of solution[19,20] is supported by 10 Dq values[21] (Table 2) which place the ligand (L) very close to water and ammonia.[22]

The i.r. spectrum (4000–650 cm^{-1}) of the ligand is identical with the observation made by Mashima.[23] In our present studies the most significant changes comparing the i.r. spectra of the complexes and free ligand are the negative shift of the amide I band appearing at 1600 cm^{-1} (for free ligand at ~1674 cm^{-1}), the positive shift of β-NH_2 appearing at ~1660 cm^{-1} (for free ligand at ~1632 cm^{-1}) amide II at ~1510 09 cm^{-1} (for free ligand at ~1488 cm^{-1}) and amide III at ~1260 cm^{-1} (for free ligand at ~1233 cm^{-1}). In the 3μ region the ν NH_2 and ν NH bands are split and highly resolved. The above facts indicate that coordination occurs through carbonyl oxygen and the terminal nitrogen of the amino group in the metal complexes. This type of observation is not noticed in the works reported by this laboratory.[1–5] But the works of Kharitanov *et al.*,[8] Agarwal *et al.*[9–11] and Saha *et al.*[12] support the observation made in our present study. I.r. spectra of thiocyanate complexes usually show three bands ν(CN), ν(CS) and δ(NCS). From the i.r. spectra of $NiL_2(SCN)_2$ and $CoL_2(SCN)_2$ only the ν(CN) band is identified properly and the identification of other two bands is very difficult as these are obscured by the presence of ligand bands in the same region. In general the CN stretching frequency is lower in N-bonded complexes than in S-bonded complexes.[24,25] The nickel(II) thiocyanate complex shows ν(CN) at 2118 cm^{-1} and the cobalt(II) thiocyanate complex shows the same band at 2090 cm^{-1}. This observation probably indicates that thiocyanate coordination occurs through nitrogen in the case of cobalt(II) and through sulphur in the case of nickel(II) which may be the cause of its insoluble character. Complexes having water molecule are supported by both i.r. spectra and thermal analyses.

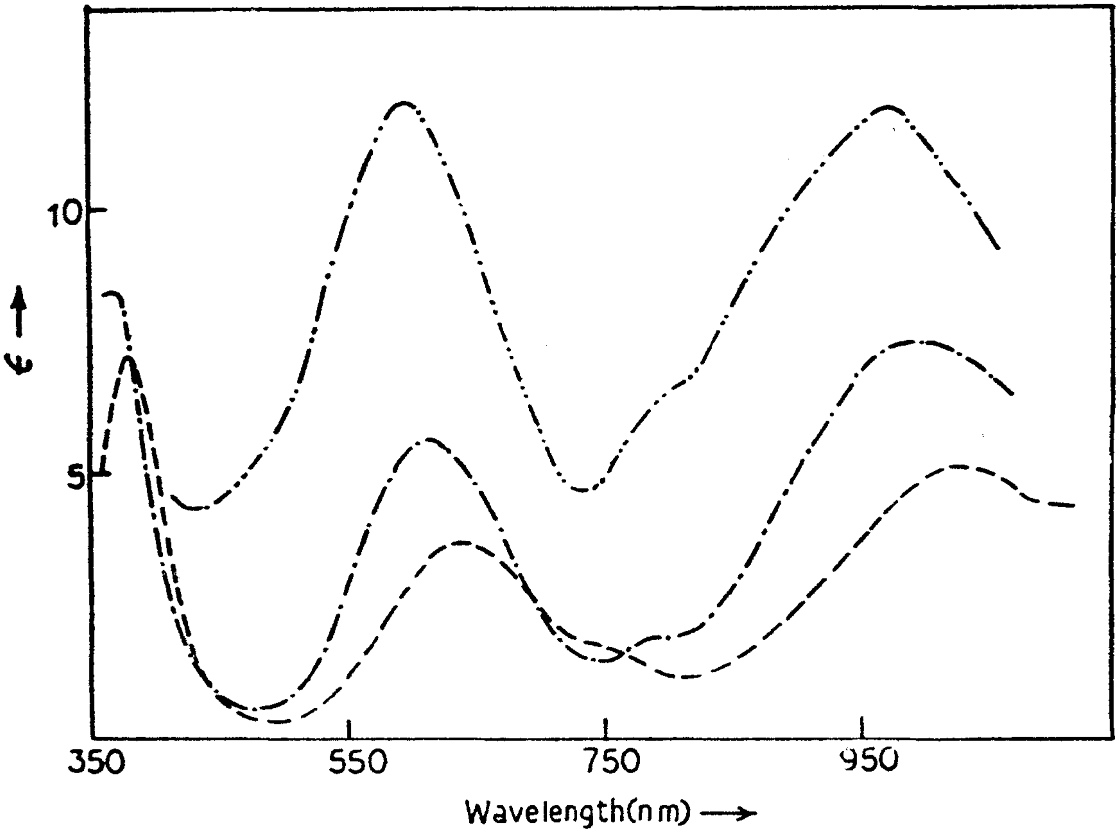

FIGURE 1 Electronic spectra of $NiL_3Br_2 \cdot H_2O$ in water (— — —), water + excess ligand (— · — · —) and in mull (arbitrary absorbance) (— · · — · · —).

Far-i.r. spectra of CoL_2Cl_2, CoL_2Br_2, CuL_2Cl_2 and $PdLCl_2$ have been taken. Far-i.r. spectra of CoL_2Cl_2 and CoL_2Br_2 are almost identical except one band in lower frequency region. We assign ν(M–Cl) at 220 cm^{-1} and ν(M–Br) at 162 cm^{-1} following the studies on nickel complexes reported by Saito *et al.*[26] The position of ν(M–X) also supports the octahedral geometry as well as terminally coordinated halide ion. The far-i.r. spectrum of $PdLCl_2$ shows two split bands at 378 cm^{-1} and 362 cm^{-1}. These bands indicate terminal coordination[27] of halide ions which are in *cis* configuration.[28] In the case of CuL_2Cl_2 the metal halogen band is absent[26] which supports the tetra-coordinated planar configuration. Far-i.r. spectra support metal oxygen (for ν(Co–O),[29] 334 cm^{-1}; ν(Cu–O),[30] 354 cm^{-1}; ν(Pd–O), 434 cm^{-1}) as well as metal nitrogen (for ν(Cu–N),[30] 470 cm^{-1}; ν(Co–N),[31] 410 cm^{-1}; ν(Pd–N),[32] 460 cm^{-1}) coordination.

The magnetic moments (Table I) of cobalt(II) and nickel(II) are characteristic of high spin octahedral configuration. The magnetic moment of $CoL_2(SCN)_2$ is 4.0 but the color and spectral characteristics are in favour of octahedral configuration. Magnetic data also reveal that Cr(III), Mn(II) and Fe(II) complexes are high spin octahedral complexes.

Molar conductance values in aqueous solution show a 1 : 3 electrolyte for the chromium(III) complex and 1 : 2 electrolytes for the rest (Table I). Conductance data of MnL_2Cl_2, MnL_2SO_4, FeL_2Cl_2 and CoL_2X_2 ($X = Cl^-$, Br^-, I^-, SCN^-) in aqueous solution do not indicate anion coordination to the metal. It is evident from magnetic data, i.r. and mull spectra, however, that the anions are coordinated to the metal ion. Electronic spectra in solution support the 1 : 2 electrolytic behaviour of the complexes. Conductance data of cobalt(II) bis complexes in aqueous solution with excess ligand do not vary (Table I). This observation indicates that cobalt(II) bis complex forms tris rather than non-solvated bis in aqueous solution with excess ligand. Unfortunately, the conductance and i.r. data do not allow any structural conclusions to be drawn for ML_2SO_4 (M = Zn or Cd).

It is generally expected that with a ligand (L) of this class, where one end is not the same as the other, there is, in any geometry around the metal, the possibility of geometrical isomerism, of the *cis-trans* type. But thin layer chromatography of the soluble complexes shows that they exist as only one isomer. The electronic spectra reported in Table II do not clearly indicate which configurations are possessed by the complexes. Therefore, it is difficult to suggest the exact configuration (*cis* or *trans*) without crystal structure determinations.

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