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Polymetallic Complexes, Part LXI: Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with ONO and OOO Donor Tridentate Ligands

BIPIN B. MAHAPATRA*, M.K. RAVAL and AJAYA K. BEHERA
Department of Chemistry
G.M. Autonomous College, Sambalpur-768 004, India

Twelve metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with tridentate ONO donor ligand, N-[phenacyl(phenylmethyl)]-anthranilic acid and OOO donor tridentate ligand, 2-carboxy[phenyl-phenacyl(phenylmethyl)]ether have been synthesized. The complexes of first two metal ions are suggested to be octahedral and the complexes with rest are tetrahedral in configuration. The characterisation of the complexes is made basing upon analytical, conductance, magnetic susceptibility measurement, IR, electronic and ESR spectral data. All the complexes are dimeric in nature, the dimerisation is achieved through the bidentate carboxylate group.

INTRODUCTION

In our programme of preparing polynuclear metal complexes using polydentate (bi-, tri-, tetra- and hexadentate) ligands[1], the present paper reports the synthesis of two ONO and OOO donor tridentate monobasic ligands and their twelve dimeric metal complexes.

EXPERIMENTAL

Preparation of N-[phenacyl-(phenylmethyl)]anthranilic acid: A mixture of benzalacetophenone (0.05 mol) and anthranilic acid (0.05 mol) and pyridine (15 mL) was refluxed on a water bath for 6 h. The mixture was then poured into ice-cold water (150 mL) and acidified with conc. HCl (10 mL). The solid compound separated out was then filtered and dried on exposure to air.

The other ligand 2-carboxy[phenyl-phenacyl(phenylmethyl)]ether was prepared in a similar procedure by refluxing benzalacetophenone with salicylic acid. Both the ligands can be represented by Fig. 1.

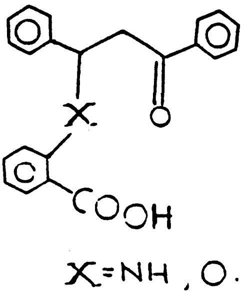


Fig. 1

Preparation of the complexes: The metal chlorides in ethanol were reacted with the ligands dissolved in ethanol in 1 : 1 molar ratio. The reaction mixture was refluxed over a heating mantle for 3 h. On cooling, conc. NH_4OH was added dropwise with constant stirring when the metal chelates separated out immediately. These were then filtered, washed with ethanol, ether and dried under reduced pressure.

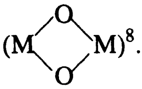
RESULTS AND DISCUSSION

The complexes isolated have the compositions $[M_2L_2/L'_2(H_2O)_4]$ and $[M'_2L_2/L'_2]$ where M = Co(II), Ni(II), M′ = Cu(II), Zn(II), Cd(II), Hg(II); LH = N-[phenacyl-(phenylmethyl)]anthranilic acid; L′ H = 2-carboxyphenyl-[phenacyl-(phenylmethyl)]ether. All the complexes are amorphous in nature, have high melting points and are insoluble in common organic solvents but sparingly soluble in dimethylformamide. The complexes are found to be non-electrolytes as the Λ_M values of the complexes in DMF are very low (3.5–4.7 Ω^{-1} cm^2 mol^{-1}).

In the IR spectra of the ligands, the band at 1665 cm^{-1} due to the ν(C═O) shifts to lower frequency region by 5–10 cm^{-1} in the spectra of the metal complexes indicating oxygen coordination of the carbonyl group. In the ligands the $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ stretches of the carboxylate group appears at 1565 cm^{-1} and 1430 cm^{-1} (LH) and 1565 cm^{-1} and 1440 cm^{-1} (L′ H) respectively. In the metal complexes these bands are observed in the range 1600–1595 cm^{-1} and 1490–1480 cm^{-1} respectively. The energy difference ($\Delta\nu$ = 110–115 cm^{-1}) between $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ stretching vibrations indicates the bidentate nature of the carboxylate group[2]. The band appearing at 3050 cm^{-1} in the ligand (LH) can be assigned to ν(NH) vibration and its decrease of *ca.* 30–50 cm^{-1} in the metal chelates shows the bonding of secondary nitrogen atom to the metal ions.

The ν(C—O—C) band in the ligand (L′ H) appears 1070 cm^{-1} which has been shifted down to lower frequency region by 5–10 cm^{-1} in the metal complexes showing thereby the involvement of etherial oxygen atom to the metal ions. The occurence of broad bands at *ca.* 3450 cm^{-1} followed by a sharp peak at *ca.* 860–810 cm^{-1} in case of cobalt and nickel complexes indicates the presence of coordinated water molecules[3]. The bands appearing at *ca.* 485 cm^{-1} and 410 cm^{-1} in the complexes assignable[4] to ν(M—O) and ν(M—N) vibrations respectively suggest the bonding of metal ions with the oxygen and nitrogen atoms of the ligand (LH) and the oxygen atoms of the other ligand (L′ H).

The cobalt complexes exhibit four electronic spectral bands at *ca.* 8,810 cm^{-1}, 17,790 cm^{-1}, 20,480 cm^{-1} and 28,560 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) \rightarrow {}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ and CT transitions respectively. The ratio ν_2/ν_1 of the complexes is calculated as 2.01 and 2.02 which lies in the normal range of octahedral Co(II) complexes[5]. The Ni(II) complexes exhibit four bands at *ca.* 10,120 cm^{-1}, 17,240 cm^{-1}, 23,475 cm^{-1} and 30,290 cm^{-1} assignable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \rightarrow {}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ and CT transitions indicating an octahedral structure. The ratio ν_2/ν_1 of the complexes has been found out to be 1.70 and 1.67 in agreement with the majority of the octahedral complexes[6] (1.60–1.82). The Cu(II) complexes exhibit a band in the range 17,850–18,050 cm^{-1} characteristic of a square-planar structure[7].

The sub-normal magnetic moments observed in case of Co(II), Ni(II) and Cu(II) complexes at *ca.* 2.85 B.M., 2.73 B.M. and 1.54 B.M. respectively indicate the presence of antiferromagnetic exchange interaction between the metal ions in a dinuclear structure ()[8].

The ESR spectrum of the copper complex [Cu_2L_2] is found to be silent indicating strong exchange interactions between Cu(II)—Cu(II) ions in the unit cell. The Zn(II), Cd(II) and Hg(II) complexes are suggested to be dinuclear tetrahedral on the basis of analytical and IR spectral data.

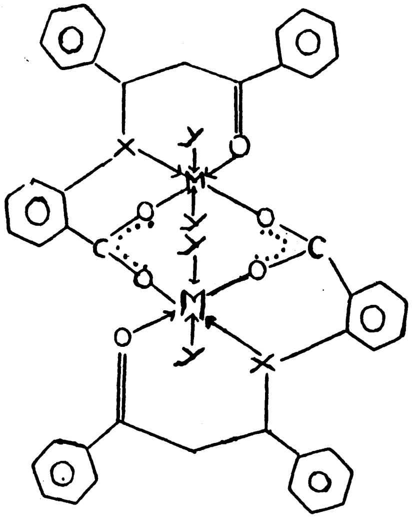
TABLE-1—ANALYSIS AND IR SPECTRAL DATA (cm^{-1}) OF THE COMPLEXES

Compound/ colour	% Analysis (found/calcd.)				ν(C=O)	ν_{asym}(COO$^-$)	ν(M—O)
	M	C	H	N	ν(NH)	ν(C—O—C)	ν(M—N)
LH	—	76.10	5.20	3.80	1665	1565	—
(brown)		(76.52)	(5.50)	(4.05)	3050	—	
L′H	—	75.80	5.10	—	1662	1565	—
(yellow)		(76.30)	(5.20)		—	1070	
[$Co_2L_2(H_2O)_4$]	13.20	59.60	4.90	3.00	1655	1600	485
(grey)	(13.41)	(60.15)	(5.01)	(3.18)	3020	—	405
[$Co_2L'_2(H_2O)_4$]	13.10	59.70	4.50	—	1655	1595	480
(light red)	(13.38)	(60.01)	(4.77)		—	1060	410
[$Ni_2L_2(H_2O)_4$]	13.20	59.80	4.80	2.90	1660	1595	480
(grey)	(13.38)	(60.17)	(5.01)	(3.19)	3010	—	405
[$Ni_2L'_2(H_2O)_4$]	13.20	59.50	4.40	—	1655	1600	480
(green)	(13.35)	(60.04)	(4.77)		—	1065	410
[Cu_2L_2]	15.40	64.50	4.20	3.30	1655	1595	475
(green)	(15.58)	(64.78)	(4.41)	(3.43)	3000	—	405
[$Cu_2L'_2$]	15.20	64.20	3.80	—	1552	1600	485
(green)	(15.54)	(64.62)	(4.16)		—	1060	410
[Zn_2L_2]	15.50	64.20	4.20	3.20	1660	1600	440
(brown)	(15.89)	(64.54)	(4.40)	(3.42)	3020	—	405
[$Zn_2L'_2$]	15.60	64.10	4.10	—	1665	1600	485
(brown)	(15.85)	(64.39)	(4.14)		—	1060	410
[Cd_2L_2]	24.20	57.40	3.70	2.90	1660	1595	485
(brown)	(24.62)	(57.84)	(3.94)	(3.06)	3010	—	405
[$Cd_2L'_2$]	24.10	57.20	3.60	—	1652	1600	480
(white)	(24.57)	(57.71)	(3.79)		—	1065	410
[Hg_2L_2]	36.50	48.10	3.10	2.40	1653	1595	485
(grey)	(36.82)	(48.48)	(3.30)	(2.57)	3020	—	405
[$Hg_2L'_2$]	36.50	47.70	3.10	—	1654	1595	480
(white)	(36.75)	(48.39)	(3.11)		—	1060	410

LH = N-[phenacyl(phenylmethyl)]anthranilic acid

L′H = 2-[carboxyphenyl-phenacyl(phenylmethyl])ether

Hence both the compounds behave as tridentate chelating ligands with $\widehat{O}\widehat{N}\widehat{O}$ and $\widehat{O}\widehat{O}\widehat{O}$ donor atoms. The tentative structure of the complexes can be represented by Fig. 2.



M = Co(II), Ni(II).
–y = H_2O
M = Cu(II), Zn(II), Cd(II), Hg(II)
y = Nil.

Fig. 2

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