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NOTE

Studies on Some Anionic Complexes of Co(II), Ni(II) and Cu(II)

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A series of complexes of the type $[LH_2]\,[MCl_4L'_2]$ where L = *o*-phenylene diamine (*o*-PDn) or diethylene diamine (Den); M = Co(II), Ni(II) and Cu(II); L'-pyridine, γ-picoline and quinoline have been isolated in non-aqueous medium. The compounds were characterised on the basis of their elemental analyses, molecular weight, conductivity, magnetic moment, infrared and electronic spectral data.

Several reports[1–5] have been made earlier on the isolation and characterization of anionic complexes of different transition metal ions involving different cations. Under the present investigation an attempt has been made to study the preference and stabilization of co-ordination number and stereochemistry of eighteen different complexes of Co(II), Ni(II) and Cu(II) when provided with nitrogen donor neutral monodentate ligands.

All the chemicals used were of AR grade.

Preparation of the complexes $[LH_2][MCl_4]$: To an ethanolic solution (0.01 mol) of *o*-phenylene diamine and diethylene diamine, dilute HCl was added till the solution became acidic (pH *ca.* 5). The resulting solution was added to an ethanolic solution of MCl_2 (0.01 mol) and refluxed for $\frac{1}{2}$ h. The solution was slightly evaporated over the water bath and kept overnight. The crystalline coloured compound that separated was filtered, washed with ethanol, ether and dried in vacuum.

Preparation of the complexes $[LH_2][MCl_4L'_2]$: To an ethanolic solution (0.01 mol) of $[LH_2][MCl_4]$, an ethanolic solution (0.02 mol) of pyridine, γ-picoline and quinoline was added with constant stirring. The mixture was refluxed for $\frac{1}{2}$–1 h. The solution was slightly evaporated over a water bath and kept overnight. The resulting complexes were filtered, washed with ethanol followed by ether and dried in vacuum.

Metals were estimated by standerd methods. IR spectra were recorded on a Shimadzu-480 spectrophotometer and electronic spectra (methanol) on Shimadzu 160-A spectrophotometer. The conductance measurements were carried out in *ca.* 10^{-3} M solution of methanol with Systronics-303 direct reading conductivity

meter. Magnetic susceptibility measurements were carried out at room temperature by a Gouy balance. Diamagnetic corrections were made by Pascal's constant. The molecular weights were determined by Rast's camphor method.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF COMPLEXES

Compounds (colour)	m.w. Found (Calcd.)	Analysis % Found (Calcd)			μ_{eff} (B.M.)
		M	N	Cl	
[o-PDnH$_2$][CuCl$_4$(Py)$_2$] (green)	481.80 (473.50)	13.53 (13.41)	11.99 (11.82)	30.05 (29.98)	2.03
[o-PDnH$_2$][CuCl$_4$(γ-pic)$_2$] (greenish black)	521.30 (501.50)	12.78 (12.66)	11.28 (11.16)	28.53 (28.21)	2.11
[o-PDnH$_2$][CuCl$_4$(Qn)$_2$] (dark green)	564.80 (583.50)	11.19 (11.07)	9.83 (9.76)	24.63 (24.76)	2.97
[o-PDnH$_2$][CoCl$_4$(Py)$_2$] (shining black)	479.20 (468.93)	12.71 (12.56)	11.89 (11.94)	30.35 (30.28)	2.73
[o-PDnH$_2$][CoCl$_4$(γ-pic)$_2$] (black)	510.31 (496.93)	11.93 (11.85)	11.35 (11.26)	28.61 (28.57)	3.81
[o-PDnH$_2$][CoCl$_4$(Qn)$_2$] (light violet)	585.89 (568.93)	10.41 (10.35)	9.96 (9.84)	25.01 (24.95)	3.39
[o-PDnH$_2$][NiCl$_4$(Py)$_2$] (green)	488.23 (468.70)	12.69 (12.52)	12.13 (11.94)	30.38 (30.29)	2.68
[o-PDnH$_2$][NiCl$_4$(γ-pic)$_2$] (brown)	520.38 (496.70)	11.95 (11.81)	11.39 (11.27)	28.72 (28.58)	2.93
[o-PDnH$_2$][NiCl$_4$(Qn)$_2$] (light green)	573.25 (568.70)	10.44 (10.32)	9.96 (9.84)	25.13 (24.96)	3.05
[DenH$_2$][CuCl$_4$(Py)$_2$] (pea green)	478.41 (453.50)	14.11 (14.00)	12.42 (12.34)	31.51 (31.31)	1.88
[DenH$_2$][CuCl$_4$(γ-pic)$_2$] (blue)	498.30 (481.50)	13.27 (13.18)	11.78 (11.63)	29.51 (29.49)	1.96
[DenH$_2$][CuCl$_4$(Qn)$_2$] (light green)	572.80 (553.50)	11.58 (11.47)	10.29 (10.11)	25.73 (25.65)	2.09
[DenH$_2$][CoCl$_4$(Py)$_2$] (dark blue)	462.75 (448.93)	13.29 (13.12)	12.53 (12.47)	31.71 (31.63)	3.65
[DenH$_2$][CoCl$_4$(γ-pic)$_2$] (light green)	491.81 (476.93)	12.41 (12.35)	11.88 (11.74)	29.93 (29.77)	3.28
[DenH$_2$][CoCl$_4$(Qn)$_2$] (dirty green)	564.32 (548.93)	10.89 (10.73)	10.32 (10.20)	25.93 (25.86)	3.54
[DenH$_2$][NiCl$_4$(Py)$_2$] (dark blue)	456.43 (448.70)	13.12 (13.08)	12.51 (12.48)	31.73 (31.64)	2.54
[DenH$_2$][NiCl$_4$(γ-pic)$_2$] (light green)	499.60 (476.70)	12.45 (12.31)	11.69 (11.74)	29.88 (29.78)	3.26
[DenH$_2$][NiCl$_4$(Qn)$_2$] (greenish blue)	568.98 (548.70)	10.75 (10.69)	10.32 (10.20)	25.93 (25.87)	3.12

The compounds formed are microcrystalline in nature and are quite stable. The analytical data (Table-1) are in consistence with the formulation of the compounds. The molar conductance values in methanol (91–120 ohm^{-1} cm^2 mol^{-1}) show that the compounds are 1:1 electrolytes. The molecular weight measurements indicate all the compounds to be monomeric in nature.

IR spectra: Involvement of cations in the complexes is well substantiated by the IR spectrum of the complexes. The IR spectra of the complexes exhibit bands in the range 3270–3100 and 2860–2770 cm^{-1} which may be assigned to the first overtone or combination bands of the deformation vibration in the region 1600–1500 cm^{-1} and CH_2 and CH and NH_3^+ stretching vibrations respectively[6,7]. Besides, a band at 2575 cm^{-1} attributed to the combination bands involving fundamentals of NH_3^+ deformation vibration has been obtained. The weak peaks observed at 280–270 cm^{-1} may be assigned to ν(M—Cl)[8]. The bands at *ca.* 1630 and *ca.* 1580 cm^{-1} due to pyridine, γ-picoline and quinoline suggest the cordination of the ligand through nitrogen atom.[9]

The Cu(II) complexes have normal magnetic moment values in the range 1.88–2.11.[10] The electronic spectra of the Cu(II) complexes show the broad band around 14800 cm^{-1} which may be assigned to $^2E_g \rightarrow {}^2T_{1g}$ in an octahedral field[11] The Ni(II) complexes have magnetic moment values between 2.54–3.26 B.M.[10] The electronic spectra of Ni(II) complexes show three well resolved bands at 12900 (ν_1), 15300 (ν_2) and 22200 (ν_3) cm^{-1} assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively under an octahedral environment around Ni(II) ion. The Co(II) complexes have magnetic moment values of 3.28–3.81 B.M. expected for high spin octahedral Co(II)[10] and two bands at 9500 and 16800 cm^{-1} which may be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ respectively which suggest octahedral geometry[11]

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