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Studies on Some Anionic Complexes of Cobalt(II), Nickel(II) and Copper(II)—Part(II)

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A series of complexes of the type $[LH_2][MCl_4L'_2]$, where L = hexamethylenediamine; M = Co(II), Ni(II) or Cu(II). L′ = pyridine (Py), γ-picoline (γ-pic), quinoline (Qn), pyridine-N-oxide (Py-NO) and γ-picoline-N-oxide (γ-pic-NO) have been prepared and characterized on the basis of elemental analysis, molecular weight measurements, molar conductance room temperature magnetic moment, infrared and electronic spectral data.

INTRODUCTION

Several reports[1–6] have been made earlier on the isolation and characterization of anionic complexes of different transition metal ions involving different ligands. In continuation of our earlier works[7] fifteen complexes having the above formulae have been prepared and characterized in the present investigation.

EXPERIMENTAL

All the chemicals used were of A.R. grade.

Preparation of the complexes of the type $[LH_2][MCl_4]$

The complexes were prepared as reported earlier.[6, 7] To an ethanolic solution of hexamethylene diamine, dilute HCl was added till the solution became acidic (pH ~5). The resulting solution was then added to an ethanolic solution of MCl_2 (0.01 mol) and refluxed for $\frac{1}{2}$ h. The volume of the resulting solution was reduced over a water bath and kept overnight. The crystalline, coloured compound that separated out was filtered, washed with ethanol-ether and dried in vacuum.

Preparation of the anionic complexes of the type $[LH_2][MCl_4L_2']$

Ethanolic solutions of pyridine, γ-picoline, quinoline or γ-picoline-N-oxide were added to the solution (0.01 mol) of $[LH_2][MCl_4]$ in ethanol with constant stirring. The mixture was refluxed for 1 h. Volume of the resulting solution was reduced to half the original volume and kept overnight. The separated compound was washed with ethanol-ether and dried in vacuum. The complexes with pyridine and pyridine-N-oxide were prepared as follows: the ethanolic solution of hexamethylenediamine (0.01 mol) was acidified (pH *ca.* 5) with dilute HCl. The resulting solution was then added to an ethanolic solution of MCl_2 and ethanolic solution of pyridine or pyridine-N-oxide in 1 : 1 : 2 molar ratio and refluxed for $\frac{1}{2}$ h.

The elemental analyses were carried out by standard methods. IR spectra were recorded on a Shimadzu-480 spectrophotometer and the electronic spectra (in 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 Gouy's balance. Diamagnetic corrections were made by Pascal's constant. The molecular weights were determined by Rast's camphor method.

RESULTS AND DISCUSSIONS

The physical and analytical data are given in Table-1.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compound (Colour)	Mol. wt. Found (Calcd.)	Analysis % Found (Calcd.)			Λ_M	μ_{eff} (B.M.)
		M	N	C		
$[HMDnH_2][CuCl_4(Py)_2]$	491.8	13.23	11.74	29.57	96	1.99
(blue)	(481.5)	(13.18)	(11.63)	(29.49)		
$[HMDnH_2][CuCl_4(\gamma\text{-Pic})_2]$	512.7	12.55	11.20	27.91	113	1.81
(light blue)	(509.5)	(12.46)	(10.99)	(27.87)		
$[HMDnH_2][CuCl_4(Qn)_2]$	570.2	11.12	9.74	24.56	108	1.93
(greenish black)	(581.5)	(10.92)	(9.63)	(24.41)		
$[HMDnH_2][CuCl_4(PyNO)_2]$	528.6	12.41	11.12	27.71	102	1.88
(light green)	(513.5)	(12.36)	(10.90)	(27.65)		
$[HMDnH_2][CuCl_4(\gamma\text{-PicNO})_2]$	555.9	11.86	10.41	26.33	99	1.86
(light green)	(541.5)	(11.72)	(10.34)	(26.22)		
$[HMDnH_2][CoCl_4(Py)_2]$	487.9	12.44	11.81	30.13	114	3.26
(dark blue)	(476.93)	(12.35)	(11.74)	(29.17)		
$[HMDnH_2][CoCl_4(\gamma\text{-Pic})_2]$	512.86	11.72	11.13	28.23	84	3.24
(shining green)	(504.93)	(11.67)	(11.09)	(28.12)		
$[HMDnH_2][CoCl_4(Qn)_2]$	596.3	10.36	9.44	24.82	90	3.71
(bluish pink)	(576.93)	(10.27)	(9.70)	(24.61)		
$[HMDnH_2][CoCl_4(PyNO)_2]$	525.5	11.88	11.17	28.12	112	3.68
(bluish pink)	(508.93)	(11.57)	(11.00)	(27.90)		
$[HMDnH_2][CoCl_4(\gamma\text{-PicNO})_2]$	540.8	10.82	10.56	26.78	87	3.59
(blue)	(536.93)	(10.97)	(10.42)	(26.44)		
$[HMDnH_2][NiCl_4(Py)_2]$	482.6	12.46	11.90	29.81	120	2.58
(light green)	(476.70)	(12.31)	(11.74)	(29.78)		
$[HMDnH_2][NiCl_4(\gamma\text{-Pic})_2]$	522.71	11.78	11.13	28.41	98	2.40
(light green)	(504.70)	(11.63)	(11.09)	(28.13)		
$[HMDnH_2][NiCl_4(Qn)_2]$	598.2	10.29	9.83	24.73	85	2.86
(dirty green)	(576.70)	(10.17)	(9.71)	(24.62)		
$[HMDnH_2][NiCl_4(PyNO)_2]$	531.9	11.69	11.35	28.08	116	2.34
(dark green)	(508.70)	(11.53)	(11.00)	(27.91)		
$[HMDnH_2][NiCl_4(\gamma\text{-PicNO})_2]$	547.2	11.07	10.55	26.68	108	3.18
(green)	(536.70)	(10.93)	(10.43)	(26.45)		

Analytical data are in good agreement with the proposed formulation of the complexes. All the complexes are crystalline, coloured and stable having high melting point above 200°C. The molecular weight measurement data indicate the complexes to be monomeric in nature. The molar conductance values of 10^{-3} M solution in methaol medium (84–120 ohm^{-1} cm^2 mol^{-1}) show that the compounds are 1:1 electrolytes.

IR studies: The assignment of important absorption bands is based on the study of IR spectrum of the free ligand and the complexes. A peak observed at 815 cm^{-1} may be due to NH_3^+ rocking mode[8]. The ν(N—H) and δ(N—H) bands are identified in the ranges 3400–3020 and 1580–1450 cm^{-1} respectively[9, 10]. The bands at *ca.* 1630 and 1580 cm^{-1} due to pyridine, γ-picolone and quinoline suggest the coordination of the ligand to the metal ion through nitrogen atom[11]. The shifting of the ν(N—O) band of pyridine-N-oxide and γ-picoline-N-oxide from *ca.* 1215 to *ca.* 1190 cm^{-1} and δ(N—O) band from 850 to 840 cm^{-1} indicated its bonding to the metal ion through oxygen atom[12].

Magnetic and Electronic spectral data: The room temperature magnetic moment values of Cu(II), Ni(II) and Co(II) complexes are found to be 1.81–1.99, 2.34–3.18 and 3.24–3.71 B.M. respectively[13]. The Cu(II) complexes show a broad band around 14500 cm^{-1} which may be assigned to the transition[14] $^2E_g \rightarrow {}^2T_{1g}$. The Ni(II) complexes exhibit bands at 10800, 16400 and 22000 cm^{-1} corresponding to the transitions[14] $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$ respectively. The Co(II) complexes exhibit bands at 9500 and 16000 cm^{-1} corresponding to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ which correspond to that of octahedral complexes[14]. Magnetic and electronic spectral data suggest octahedral geometry for all the complexes.

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