

## Studies on Some Anionic Complexes of Cobalt(II), Nickel(II) and Copper(II): Part III

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A series of complexes of the type  $[LH_2][MCl_4L'_2]$ , where L = propylene diamine, M = Co(II), Ni(II) or Cu(II), L' = pyridine (Py),  $\gamma$ -picoline ( $\gamma$ -pic), quinoline (Qn), pyridine-N-oxide (Py-NO) and  $\gamma$ -picoline-N-oxide ( $\gamma$ -pic-NO) have been prepared and characterized on the basis of element analyses, molecular weight measurement, molar conductance, room temperature magnetic moment, infrared and electronic spectral data.

**Key Words:** Synthesis, Anionic complexes, Transition metals.

### INTRODUCTION

Several reports<sup>1-6</sup> 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<sup>7, 8</sup>, fifteen new complexes having the above formulae have been prepared and characterized in the present investigation.

### EXPERIMENTAL

All the chemicals used were of AR grade. 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 a Shimadzu-160 spectrophotometer. The conductance measurements were carried out in  $10^{-3}$  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.

**Preparation of the complexes of the type  $[LH_2][MCl_4]$ :** The complexes were prepared as reported earlier<sup>6, 7</sup>. To an ethanolic solution of propylene diamine, dilute HCl was added till the solution became acidic (pH *ca.* 5). The resulting solution was then added to an ethanolic solution of  $MCl_2$  (0.01 mol) and refluxed for 0.5 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,  $\gamma$ -picoline, quinoline or  $\gamma$ -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. The 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 propylenediamine (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 in 1 : 1 : 2 molar ratio and refluxed for 0.5 h.

## RESULTS AND DISCUSSION

The physical and analytical data are given in Table-1. 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 solutions in methanol medium ( $87-116 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) show that the compounds are 1 : 1 electrolytes.

TABLE-I  
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compound (Colour)	m.w. Calcd. (Found)	Analysis % Calcd. (Found)			$\Lambda_M$	$\mu_{\text{eff}}$ (B.M.)
		M	N	C		
[PDnH <sub>2</sub> ][CuCl <sub>4</sub> (Py) <sub>2</sub> ] (Blue)	437.871 (452.7)	14.51 (14.12)	12.79 (12.45)	35.65 (35.89)	106	1.91
[PDnH <sub>2</sub> ][CuCl <sub>4</sub> ( $\gamma$ -Pic) <sub>2</sub> ] (Light green)	465.925 (471.9)	13.63 (13.76)	12.02 (12.51)	38.66 (38.76)	99	1.89
[PDnH <sub>2</sub> ][CuCl <sub>4</sub> (Qn) <sub>2</sub> ] (Greenish black)	537.979 (549.65)	11.81 (12.03)	10.41 (10.64)	46.88 (46.77)	101	1.86
PDnH <sub>2</sub> [CuCl <sub>4</sub> (PyNo) <sub>2</sub> ] (Blue)	469.869 (485.2)	13.52 (13.71)	11.92 (12.01)	33.23 (33.44)	112	1.95
[PDnH <sub>2</sub> ][CuCl <sub>4</sub> ( $\gamma$ -PicNo) <sub>2</sub> ] (Light blue)	497.923 (576.42)	12.76 (12.89)	11.25 (11.4)	36.18 (36.57)	104	1.81
[PDnH <sub>2</sub> ][CoCl <sub>4</sub> ( $\gamma$ -Pic) <sub>2</sub> ] (bluish pink)	461.312 (488.9)	12.77 (12.96)	12.14 (12.96)	39.05 (39.18)	89	3.75
[PDnH <sub>2</sub> ][CoCl <sub>4</sub> (Py) <sub>2</sub> ] (Bluish pink)	433.258 (455.6)	13.60 (13.78)	12.93 (13.01)	36.03 (36.45)	96	3.49
[PDnH <sub>2</sub> ][CoCl <sub>4</sub> (Qn) <sub>2</sub> ] (Green)	533.366 (542.7)	11.04 (11.32)	10.50 (10.81)	47.29 (47.35)	116	3.52
[PDnH <sub>2</sub> ][CoCl <sub>4</sub> (PyNo) <sub>2</sub> ] (Blue)	465.256 (477.3)	12.66 (12.95)	12.04 (12.57)	33.56 (33.91)	102	3.33
[PDnH <sub>2</sub> ][CoCl <sub>4</sub> ( $\gamma$ -PicNo) <sub>2</sub> ] (Greenish blue)	493.31 (521.4)	11.94 (12.55)	11.35 (11.84)	36.52 (36.84)	87	3.65
[PDnH <sub>2</sub> ][NiCl <sub>4</sub> (Py) <sub>2</sub> ] (Light green)	433.015 (464.3)	13.55 (13.79)	12.93 (12.64)	36.05 (36.29)	114	2.78

Compound (Colour)	m.w. Calcd. (Found)	Analysis % Calcd. (Found)			$\Lambda_M$	$\mu_{\text{eff}}$ (B.M.)
		M	N	C		
[PDnH <sub>2</sub> ][NiCl <sub>4</sub> ( $\gamma$ -Pic) <sub>2</sub> ] (Dirty green)	461.069 (476.5)	12.72 (12.98)	12.15 (12.65)	39.07 (39.88)	95	2.35
[PDnH <sub>2</sub> ][NiCl <sub>4</sub> (Qn) <sub>2</sub> ] (Green)	533.123 (566.9)	11.00 (11.69)	10.50 (10.87)	47.31 (47.65)	103	2.41
[PDnH <sub>2</sub> ][NiCl <sub>4</sub> (PyNo) <sub>2</sub> ] (Dark green)	465.013 (487.1)	12.62 (12.99)	12.04 (12.55)	33.57 (33.86)	97	2.56
[PDnH <sub>2</sub> ][NiCl <sub>4</sub> ( $\gamma$ -PicNo) <sub>2</sub> ] (Bluish green)	493.067 (510.5)	11.90 (12.23)	11.36 (11.54)	36.53 (36.76)	111	2.48

**IR studies:** The assignment of important absorption bands is based on the study of IR spectrum of the free ligand and complexes. A peak observed at *ca.* 815 cm<sup>-1</sup> may be due to NH<sub>3</sub><sup>+</sup> rocking mode<sup>9</sup>. The  $\nu(\text{N—H})$  and  $\delta(\text{N—H})$  bands are identified in the ranges 3400–3020 and 1580–1450 cm<sup>-1</sup>, respectively<sup>10, 11</sup>. The bands at *ca.* 1630 and *ca.* 1580 cm<sup>-1</sup> due to pyridine,  $\gamma$ -picoline and quinoline suggest the coordination of the ligand to the metal ion through nitrogen atom<sup>12</sup>. The shifting of the  $\nu(\text{N—O})$  band of pyridine-N-oxide and  $\gamma$ -picoline-N-oxide from *ca.* 1215 to *ca.* 1190 cm<sup>-1</sup> and  $\delta(\text{N—O})$  band from *ca.* 850 to *ca.* 840 cm<sup>-1</sup> indicated its bonding to the metal ion through oxygen atom<sup>12</sup>.

**Magnetic and electronic spectral data:** The room temperature magnetic moment values of Cu(II), Ni(II) and Co(II) complexes are found to be 1.81–1.95, 2.35–2.78 and 3.33–3.75 B.M., respectively<sup>14</sup>. The Cu(II) complexes show a broad band around *ca.* 14500 cm<sup>-1</sup> which may be assigned to the transition<sup>15</sup>  ${}^2E_g \rightarrow 2T_{1g}$ . The Ni(II) complexes exhibit bands at 10750–10920, 15310–16400 and 26250–25000 cm<sup>-1</sup> corresponding to the transitions<sup>14</sup>,  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ ,  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$  and  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{P})$ , respectively. The Co(II) complexes exhibit bands at 9300–9500 and 16800–19850 cm<sup>-1</sup> corresponding to the transitions  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$  and  ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{P})$ , which correspond to those of octahedral complexes<sup>15</sup>. The ligand field parameters for Co(II) and Ni(II) complexes were calculated, which agreed with those of octahedral complexes<sup>14</sup> (Tables 2 and 3).

Magnetic and electronic spectral data suggest octahedral geometry for all the complexes.

TABLE-2  
LIGAND FIELD PARAMETERS OF THE ANIONIC  
COMPLEXES OF Co(II) COMPLEXES

S. No.	Compound	$\nu_1$	$\nu_2$	$\nu_2/\nu_1$	Dq	B	Dq/B	$\beta$	$\beta^0$ (%)
1.	[PDnH <sub>2</sub> ][CoCl <sub>4</sub> ( $\gamma$ -Pic) <sub>2</sub> ]	9500	16800	1.76	1046	551	1.89	0.568	43
2.	[PDnH <sub>2</sub> ][CoCl <sub>4</sub> (Py) <sub>2</sub> ]	9300	18700	2.01	1060	700	1.51	0.721	27
3.	[PDnH <sub>2</sub> ][CoCl <sub>4</sub> (Qn) <sub>2</sub> ]	9450	19150	2.02	1050	721	1.45	0.743	25
4.	[PDnH <sub>2</sub> ][CoCl <sub>4</sub> (PyNo) <sub>2</sub> ]	9420	19100	2.02	940	720	1.30	0.741	25
5.	[PDnH <sub>2</sub> ][CoCl <sub>4</sub> ( $\gamma$ -PicNo) <sub>2</sub> ]	9500	19850	2.08	1065	767	1.38	0.789	21

TABLE-3  
LIGAND FIELD PARAMETERS OF THE ANIONIC  
COMPLEXES OF Ni(II) COMPLEXES

Sl. No.	Compound	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_2/\nu_1$	Dq	B	Dq/B	$\beta$	$\beta^0$ (%)
1.	[PDnH <sub>2</sub> ][NiCl <sub>4</sub> ( $\gamma$ -Pic) <sub>2</sub> ]	10850	16390	26150	1.51	1085	685	1.51	0.648	35
2.	[PDnH <sub>2</sub> ][NiCl <sub>4</sub> (Py) <sub>2</sub> ]	10890	16310	26250	1.41	1089	688	1.58	0.650	35
3.	[PDnH <sub>2</sub> ][NiCl <sub>4</sub> (Qn) <sub>2</sub> ]	10800	16400	25000	1.51	1080	578	1.86	0.547	45
4.	[PDnH <sub>2</sub> ][NiCl <sub>4</sub> (PyNo) <sub>2</sub> ]	10750	16280	26190	1.51	1073	705	1.52	0.667	33
5.	[PDnH <sub>2</sub> ][NiCl <sub>4</sub> ( $\gamma$ -PicNo) <sub>2</sub> ]	10920	15310	26250	1.40	1092	682	1.60	0.645	35

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