

# Notes

## Complexes of Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) and Mercury(II) with 1,2-Diphenyl-2 (2'-pyridylimino)ethanol

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**M**ETAL complexes with multidentate ligands evoked a lot of interest in recent years<sup>1-4</sup>. The present paper deals with the synthesis of a new polydentate ligand 1,2-diphenyl-2 (2'-pyridylimino) ethanol and its complexation behaviour with Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Hg<sup>II</sup> ions.

### Experimental

All the chemicals were of A.R. grade. The Schiff base 1,2-diphenyl-2-(2'-pyridylimino)ethanol was prepared by refluxing benzoin (0.1 mol) with 2-aminopyridine (0.1 mol) in ethanol over a water-bath for 2 h. Light yellow needle-shaped crystals of the Schiff base separated out on cooling. It was then filtered, washed with ethanol, dried and recrystallised from 95% ethanol (Found: C, 78.42; H, 5.23; N, 9.7. C<sub>19</sub>H<sub>16</sub>ON<sub>2</sub> calcd for: C, 79.16; H, 5.5; N, 9.7%). The metal complexes were synthesised by reacting metal chlorides with the ligand solution in ethanol. Then concentrated ammonia was added dropwise with stirring (pH 7), when the metal complexes separated out. These were then filtered, washed with ethanol and finally with ether and dried in vacuum.

Metal contents were determined by EDTA method after decomposing the complexes and nitrogen was determined by microanalytical method

(Table 1). Conductances were measured using 0.001 M solutions of the complexes in dimethylformamide. Room temperature magnetic moments of the complexes were determined by Gouy method using cobalt mercury thiocyanate as calibrant. IR spectra (KBr) were recorded with Perkin-Elmer 557 and Polytech FIT-IR spectrophotometers. Electronic spectra (nujol) were recorded with a Higer-Watt uvispeck spectrophotometer. The molecular weight was determined by Rast method using camphor as solvent.

### Results and Discussion

Co<sup>II</sup> complex was yellowish green, Ni<sup>II</sup> complex light green, the Cu<sup>II</sup> complex green and Zn<sup>II</sup>, Cd<sup>II</sup> and Hg<sup>II</sup> complexes were white. Low conductance (Table 1) of the complexes indicated their non-electrolytic nature. The  $\nu_{\sigma-N}$  ir band of the ligand appearing at 1 660 cm<sup>-1</sup> was found to be shifted to ~ 1 600 cm<sup>-1</sup> indicating the coordination of the azomethine nitrogen to the metal ions<sup>5</sup>, which was further supported by the presence of  $\nu_{M-N}$  at ~ 390 cm<sup>-1</sup> in the far-ir spectra of the complexes. The free ligand showed  $\nu_{\sigma-O}$  and  $\nu_{\sigma-N}$  of the pyridine ring in the regions 1 590 (band I), 1 570 (band II), 1 485 (band III) and 1 445 cm<sup>-1</sup> (band IV). The spectra of Co<sup>II</sup> and Ni<sup>II</sup> complexes exhibited various changes consistent with pyridine nitrogen coordination<sup>6,7</sup>. This mode of bonding was further confirmed by the presence of  $\nu_{M-N}$  (pyridine) band at 290 and 280 cm<sup>-1</sup> for Co<sup>II</sup> and Ni<sup>II</sup> complexes, respectively<sup>8,9</sup>. The  $\nu_{O-H}$  band of the ligand was observed at 3 450 cm<sup>-1</sup> as a broad band, and a band of medium intensity at 2 900 cm<sup>-1</sup> was ascribed to intramolecular O—H...N hydrogen bonding. Absence of these bands in the spectra of the complexes indicated bonding of phenolate oxygen atom to the metal ions. The sharp band at 1 250 cm<sup>-1</sup> for the free ligand could

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF LIGAND AND COMPLEXES

Compd.*	M p. °C	Analysis % : Found/(Calcd)		$\mu_{eff}$ B.M.	$\Delta\epsilon$ Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Mol. wt. : Found/ (Calcd)
		Metal	N			
LH	132	—	9.57 (9.72)	—	—	—
[Co <sub>2</sub> L <sub>2</sub> Cl <sub>2</sub> ]	250	15.25 (15.40)	7.21 (7.32)	2.85	4.0	751 (754)
[Ni <sub>2</sub> L <sub>2</sub> Cl <sub>2</sub> ]	250	15.27 (15.36)	7.24 (7.32)	2.3	3.5	752 (763)
[CuL <sub>2</sub> ]	242	9.85 (9.92)	4.13 (4.37)	1.75	4.5	—
[ZnL <sub>2</sub> ]	243	10.08 (10.19)	4.25 (4.36)	—	5.2	—
[CdL <sub>2</sub> ]	150	16.24 (16.32)	4.00 (4.06)	—	6.4	—
[HgL <sub>2</sub> ]	145	25.62 (25.83)	3.51 (3.60)	—	5.5	—

\*L = C<sub>19</sub>H<sub>16</sub>ON<sub>2</sub>.

be ascribed to  $\nu_{C-O}$ . Decrease in this frequency by 20–25  $\text{cm}^{-1}$  in  $\text{Cu}^{II}$ ,  $\text{Zn}^{II}$ ,  $\text{Cd}^{II}$  and  $\text{Hg}^{II}$  complexes indicated the enolic oxygen coordination to the metal ions. But in the case of  $\text{Co}^{II}$  and  $\text{Ni}^{II}$  complexes, a positive shift by 35–45  $\text{cm}^{-1}$  was observed

due to the formation of  $\text{M} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{M}$  bridge. The

bonding of enolic oxygen atom to the metal ions was further confirmed by the appearance of the  $\nu_{M-O}$  band at  $\sim 450 \text{ cm}^{-1}$ . The band at  $\sim 190 \text{ cm}^{-1}$  in case of  $\text{Co}^{II}$  and  $\text{Ni}^{II}$  complexes was ascribed to  $\nu_{M-O}$  vibration<sup>10,11</sup>.

The visible electronic spectrum of  $\text{Cu}^{II}$  complex exhibited bands at 15 000, 18 300 and 27 000  $\text{cm}^{-1}$ . The band at 18 300  $\text{cm}^{-1}$  is diagnostic of square-planar configuration<sup>12</sup>.  $\mu_{eff}$  value of 1.75 B.M. for the  $\text{Cu}^{II}$  complex corresponds to one unpaired electron. The magnetic moment of  $\text{Co}^{II}$  complex was 2.85 B.M. Electronic spectrum of the complex showed only one absorption band at 19 500  $\text{cm}^{-1}$ . The intensity of the band is nearer to that of an octahedral complex. But analytical, conductance, low magnetic moment and molecular weight data (Table 1) suggest the complex to be dimeric pentacoordinated, which was in conformity with earlier observation<sup>13</sup>. The  $\text{Ni}^{II}$  complex exhibited two absorption bands at 25 400 and 20 400  $\text{cm}^{-1}$  attributable to  ${}^3B_1 \rightarrow {}^3E^{II}$  and  ${}^3B_1 \rightarrow {}^3E^{III}$  transitions in conformity with the earlier reports<sup>14,15</sup> on pentacoordinated complexes supported by the molecular weight data. The  $\mu_{eff}$  value of 2.3 B.M. for the  $\text{Ni}^{II}$  complex could be attributed to partial quenching of paramagnetism due to spin-spin interaction.

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#### Stability Constants of some Bivalent Transition Metal Chelates of Salicylidene Sulphanilamide†

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LITERATURE survey reveals that no equilibrium study has been made on the formation of  $\text{Mn}^{II}$ ,  $\text{Co}^{II}$ ,  $\text{Ni}^{II}$ ,  $\text{Cu}^{II}$  and  $\text{Zn}^{II}$  complexes with the Schiff base ligand salicylidene sulphanilamide (SASUD). The present communication describes the results of potentiometric study of these systems in 50% (v/v) aqueous ethanol medium in different ionic strengths at 42° ( $\mu=0.1, 0.05, 0.01 \text{ M KNO}_3$ ) and at 32° ( $\mu=0.1 \text{ M KNO}_3$ ).

#### Experimental

A. R. grade or purified chemicals were used in the study.

*Preparation of the ligand (SASUD)*: The Schiff base salicylidene sulphanilamide (SASUD) was prepared by refluxing an ethanolic mixture of salicylaldehyde (0.01 M) and sulphanilamide (0.01 M) on a water-bath for 2 h. The resulting yellow solution on cooling yielded bright yellow crystals of SASUD, which were collected by filtration and washed with ethanol. The crude product was recrystallised from ethanol and preserved in a vacuum desiccator. The purity of the sample was checked by elemental analysis and melting point determination. Solutions of the metal nitrates (0.01 M) were made in 0.1 M  $\text{HNO}_3$  and the estimation of the metal ions was done as described earlier<sup>1</sup>. A ECL 5651 digital pH meter (accuracy  $\pm 0.01$  pH unit) with a glass electrode assembly was used for the study.

Equilibrium study involved pH titration of 50 ml solution containing known amounts of SASUD with known amount free  $\text{HNO}_3$  in the absence and in the presence of known amounts of metal nitrate

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