Asian Journal of Chemistry Vol. 9, No. 4 (1997), 652–657

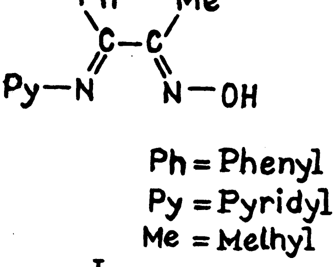
Cobalt(II), Nickel(II) and Copper(II) Complexes with 1-Pyridylimino-1-Phenyl-2-Hydroxyiminopropane

H.C. RAI*, HARISH KUMAR and AMARESH KUMAR
Department of Chemistry
L.S. College, Muzaffarpur-842 001, India

A series of complexes having the formula $[M(HL)_2(H_2O)_2]X_2$ where M = Co(II), Ni(II) or Cu(II); X = Cl^-, Br^- and HL = 1-pyridylimino-1-phenyl-2-hydroxyiminopropane has been synthesized by allowing the ligand and the metal salts to react in the 2 : 1 molar ratio in an ethanolic medium. Besides this, another series of complexes of the type ML_2 has been synthesized by allowing the ligand and metal acetates to react in the molar ratio 2 : 1 in an aqueous medium made alkaline with NH_4OH. The complex CuL_2, when allowed to react with CuX_2 salts, gives another series of binuclear complexes having the formula $Cu_2L_2X_2$ [X = Cl^-, Br^-]. The characterization of the complexes has been done on the basis of elemental analyses, magnetic moment, conductance and spectral studies.

INTRODUCTION

Metal complexes of monoximes and their derivatives have been extensively studied in recent years[1–8] due to their capabilities to form organometallic and encapsulation compounds. This prompted us to prepare metal complexes with the ligand obtained by the condensation of 2-aminopyridine and 1-phenyl-1,2-propanedione-2-oxime. This promising ligand (I) acts in a bidentate manner to form two series of complexes having the formulae $[M(HL)_2(H_2O)_2]X_2$ and ML_2 when it is allowed to react with metal salts in the molar ratio 2 : 1 in thanolic and aqueous (basic) media respectively. The complexes CuL_2 further react in an ethanolic medium with CuX_2 salts to give yet another series of binuclear complexes of the type $[Cu_2L_2X_2]$ (X = Cl^-, Br^-).



I

EXPERIMENTAL

All the chemicals used were BDH or E. Merck reagents except 1-phenyl-1,2-propanedione-2-oxime which was an Aldrich reagent. Bromide salts of cobalt(II), nickel(II) and copper(II) were prepared by dissolving the respective metal carbonates in the minimum volume of hydrobromic acid followed by crystallization.

Preparation of the ligand, HL

The ligand 1-pyridylimino-1-phenyl-2-hydroxyiminopropane was synthesized by the method reported earlier[4] [m.p. = 172 ± 2°C, yield = 55%].

Preparation of the complexes

A similar procedure was used for the preparation of all the complexes. The preparation of one typical complex is described below for each of the series of complexes.

TABLE-1
ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRAL AND CONDUCTIVITY DATA OF METAL COMPLEXES OF 1-PYRIDYLIMINO-1-PHENYL-2-HYDROXYIMINOPROPANE WITH COBALT(II), NICKEL(II) AND COPPER(II)

Complexes (Colour)	% Analysis, Found (Calcd.)			μ_{eff} (B.M.)	λ_{max} (electronic) cm^{-1}	Λ_m ($ohm^{-1}cm^2$ mol^{-1})
	M	N	Halogen			
$[Co(HL)_2(H_2O)_2]Cl_2$ (light violet)	9.20 (9.16)	13.12 (13.04)	11.00 (11.02)	4.80	25,200	116
$[Co(HL)_2(H_2O)_2]Br_2$ (pink)	8.00 (8.05)	11.39 (11.45)	12.78 (12.83)	4.82	25,400	118
$[CoL_2]$ (red)	10.98 (11.03)	15.60 (15.70)	—	2.00	22,200	15
$[Ni(HL)_2(H_2O)_2]Cl_2$ (blue)	9.02 (9.16)	13.00 (13.04)	10.97 (11.02)	3.26	25,700, 15,100	122
$[Ni(HL)_2(H_2O)_2]Br_2$ (bluish violet)	7.99 (8.05)	11.48 (11.45)	21.60 (21.83)	3.18	26,000, 15,000	120
$[NiL_2]$ (yellow)	11.00 (11.03)	15.60 (15.70)	—	Diamag.	19,000	16
$[Cu(HL)_2(H_2O)_2]Cl_2$ (deep red)	9.76 (9.79)	12.88 (12.95)	10.88 (10.95)	1.88	14,800	125
$[Cu(HL)_2(H_2O)_2]Br_2$ (greyish red)	8.59 (8.61)	11.28 (11.39)	24.00 (24.40)	1.85	14,700	127
$[CuL_2]$ (green)	11.65 (11.77)	15.52 (15.57)	—	1.75	14,500	18
$[Cu_2L_2Cl_2]$ (green)	18.78 (18.84)	12.40 (12.46)	10.48 (1053)	1.76	12,000, 17,100	22
$[Cu_2L_2Br_2]$ (brownish green)	16.55 (16.64)	10.98 (11.00)	23.48 (23.59)	1.81	12,500, 17,500	25

Bis-(1-pyridylimino-1-phenyl-2-hydroxyiminopropane)diaquo-nickel(II) chloride $[Ni(HL)_2(H_2O)_2]_2Cl_2$: The Ni(II) chloride solution (0.01 mol) in absolute ethanol was mixed with a warm ethanolic solution of the ligand (0.02 mol) and the mixture was shaken vigorou sly. The colour of the solution changed immediately to blue. The solution, on standing, gave a blue crystalline product which was filtered, washed with ethanol and solvent ether and dried *in vacuo.*

Bis-(1-pyridylimino-1-phenyl-2-hydroxyiminopropane)copper(II) $[CuL_2]$: An ethanolic solution of the ligand (0.02 mol) was treated with a few mL of sodium acetate solution and an aqueous solution of cupric acetate monohydrate (0.01 mol) was added to it with vigorous shaking. A green crystalline product was obtained which was filtered, washed with ether and dried *in vacuo.*

Dichloro-bis-(1-pyridylimino-1-phenyl-2-hydroxyiminopropane)dicopper(II) $[Cu_2L_2Cl_2]$: Bis-(1-pyridylimino-1-phenyl-2-hydroxyiminopropane)copper(II) (0.01 mol) was dissolved in ethanol and to it, an ethanolic solution of cupric chloride (0.01 mol) was added with constant stirring. A greyish-green crystalline solid was obtained which was filtered, washed with ether and dried *in vacuo.*

Elemental analyses were done using standard procedures.[9] The infrared spectra of the complexes were recorded on a Beckman IR-20 spectrophotometer. Magnetic moments were measured by the Gouy method using $Hg[Co(CNS)_4]$ as the calibrant. Conductivity measurements were made on a systronic conductometer Model 303 using dimethyl sulphoxide as a solvent. Analytical, spectral, conductance and magnetic moment data are recorded in Table-1.

RESULTS AND DISCUSSION

Infrared spectra: The infrared spectrum of the ligand shows a strong band at 3310 cm^{-1} and a medium one at 3320 cm^{-1} which have been assigned to the symmetric and asymmetric stretching vibrations of the —N—OH group. It also exhibits a sharp band at 1660 cm^{-1} which has been assigned to the $\nu(C{=}N)$ mode of the oxime group. Two bands at 1610 and 1545 cm^{-1} have been ascribed to the ring breathing mode of the pyridine nucleus. The ligand shows a characteristic group of bands for the phenyl ring vibrations.

In the lower energy region, the ligand shows bands at 1005, 790 and 770 cm^{-1}. The band at 1005 cm^{-1} has been assigned to the ν(N—O) vibrations of the oxime mode of the ligand.[1, 5]

The complexes of the type $[M(HL)_2(H_2O)_2]X_2$ show a broad band centred at 3300 cm^{-1} assignable to ν(O—H) mode of the N—O—H group, the broadening may be due to coupling with ν(O—H) of coordinated water molecules. The presence of this band in these complexes indicates existence of the ligand in its neutral form. Significantly, this band is absent in the spectra of the complexes of the type ML_2 or $Cu_2L_2X_2$, where deprotonation has taken place during coordination of the ligand with the metal ions.

A band present at 1660 cm^{-1} in the ligand is considerable lowered (1635–1600 cm^{-1}) in the spectra of all the three series of complexes, namely $[M(HL)_2(H_2O)_2]X_2$, ML_2 and $Cu_2L_2X_2$ indicating involvement of the exocyclic

C=N group in complex formation. The lowering is more in the complexes $Cu_2L_2X_2$ in comparison to that in $[M(HL)_2(H_2O)_2]X_2$.

The characteristic pyridine ring vibrations do not show any appreciable perturbation, thus clearly indicating non-participation of the pyridine nitrogen in coordination. The ν(N—O) band of the ligand at 1005 cm^{-1} is almost unperturbed in the complexes (1000–995 cm^{-1}); the slight lowering is due to involvement of adjacent C=N group in coordination in the spectra of the complexes of the type $[M(HL)_2(H_2O)_2]X_2$. But the band appears at a higher frequency (1025 cm^{-1}) in the complex ML_2 indicating deprotonation of NOH group. It appears in the lower frequency region (985–975 cm^{-1}) in the complexes $Cu_2L_2X_2$ indicating formation of new links between the copper(II) inner complexes (CuL_2) and copper(II) salts (CuX_2) through oxygen atom of the N—O group. A new band, however, appears in all the bis-(aquo) complexes around 865 cm^{-1} which is characteristic vibration of the coordinated water molecules. A few sharp and intense additional bands recorded in the spectra of $Cu_2L_2X_2$ in the far infrared region 600–400 cm^{-1} are believed to arise due to ν(Cu—Cl) or ν(Cu—Br) vibrational modes and support coordination of the anions Cl^- and Br^- to Cu-atom.

On the basis of above discussion, complexes $[M(HL)_2(H_2O)_2]X_2$, ML_2 and $Cu_2L_2X_2$ may be assigned the structures II, III and IV, respectively. These structures are supported by magnetic moment, electronic spectral and conductivity data as discussed in the following paragraphs.

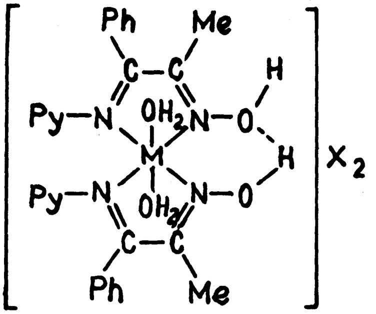
Magnetic moment, Electronic spectra and Conductivity data

During the course of the present investigation, it has been found (Table-1) that the copper(II) complexes of the type $[Cu(HL)_2(H_2O)_2]X_2$ have magnetic moment values in the range 1.85–1.95 B.M., which is usually observed for octahedral copper(II) complexes.[10] Visible spectra of the complexes show a broad band spanning the region 15,000–14,500 cm^{-1}. This band may arise due to $^2E_g \rightarrow {}^2T_{2g}$ transition in an octahedral field.

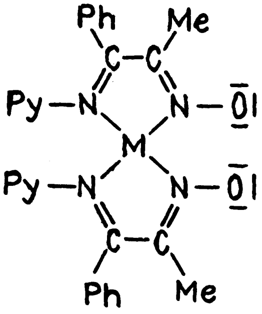
The binuclear complexes of copper(II) of the type $Cu_2L_2X_2$ show two broad ligand field bands in the regions 12,800–12,000 and 18,000–17,000 cm^{-1} and have magnetic moments in the region 1.70–1.90 B.M. Both the electronic spectral bands seem to be due to the same d–d transition differing in energy due to the presence of different ligand fields.[10] The high energy band may be due to the chromophore, CuN_4 in D_{4h} symmetry while the low energy band may be due to the chromophore, CuO_2X_2 and a lower symmetry[11] such as C_2. Alternatively, the two bands might also be due to difference in coodination numbers of copper(II) ions and possibility of complexes having a polymeric structure (V) cannot be ruled out.[12]

A single broad band in the electronic spectrum of the complex CuL_2, centred at 14,500 cm^{-1}, has been attributed to the ligand field band due to the chromophore CuN_4.

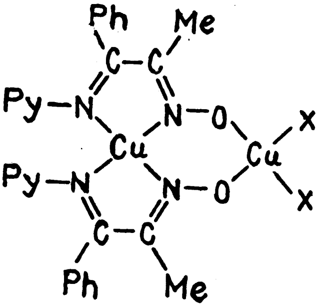
The nickel(II) complexes of the type $[Ni(HL)_2(H_2O)_2]X_2$ have magnetic moment values in the region 3.15–3.35 B.M. at room temperature. These values are typical of a nickel(II) ion in an octahedral environment. The two typical bands occurring at 26,000 and 15,000 cm^{-1} are due to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(P)$



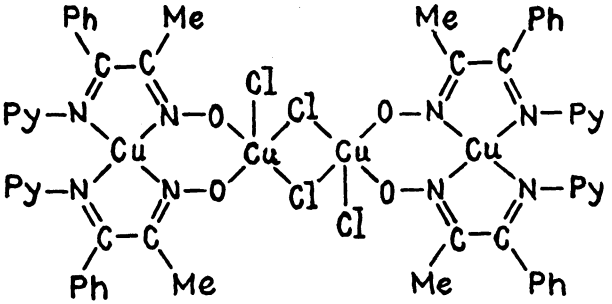
II



III



IV



V

and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ respectively in an octahedral field. The nickel(II) complex NiL_2 is diamagnetic and its spectrum consists of a broad band centred at 19,000 cm^{-1}. This suggests a planar environment around nickel(II) with the chromophore NiN_4. The cobalt(II) complexes of the type $[Co(HL)_2(H_2O)_2]X_2$ possess magnetic moment values in the range 4.75–4.85 B.M. at 25°C, which are typical of cobalt(II) ion in an octahedral environment. A broad band centred at 25,000 cm^{-1} is observed in the electronic spectra of the complexes and it supports octahedral stereochemistry. Broadness is most presumably due to superimposition of two to three bands. Cobalt(II) complex CoL_2 has magnetic moment of 2.0 B.M. with a broad electronic spectral band centred at 22,000 cm^{-1} indicating planar environment of the ligand atoms around cobalt(II) ion.

All the metal complexes are insoluble in water but soluble in DMSO and DMF on warming. The molar conductance values of the complexes of the type $[M(HL)_2(H_2O)_2]X_2$ in DMSO (10^{-3} M) lie in the range 115–130 ohm^{-1} cm^2 mol^{-1} and are typical of 1 : 2 electrolytes. The complexes of the type ML_2 and $[Cu_2L_2X_2]$ have negligible conductance values showing non-electrolytic nature of these complexes.

ACKNOWLEDGEMENTS

The authors are thankful to Professor Mithilesh Sharma, the Principal, L.S. College, Muzaffarpur for providing laboratory facilities and the University Grants Commission, New Delhi for providing a Research Fellowship to one of them (Amaresh Kumar).

REFERENCES

1. H.C. Rai, J. Chakrabarti and B. Sahoo, *Indian J. Chem.*, **18A**, 242 (1979).
2. Bhagirathi Sahoo, J. Chakrabarti and B. Sahoo, *Indian J. Chem.*, **23A**, 209 (1984).
3. Bijay K. Mahapatra and B. Sahoo, *Indian J. Chem.*, **24A**, 653 (1985).
4. Bimanesh Sur, S.K. Nandi, B. Banerjee and S. Roy Choudhary, *Indian J. Chem.*, **24A**, 1061 (1985).
5. H.C. Rai, Jaya Tiwary, Ranjana Prakash and Susan, *Indian J. Chem.*, **27A**, 421 (1988).
6. H.C. Rai, Ramesh Kumar, S.N. Vidyarthi and Balmiki Singh, *Indian J. Chem.*, **27A**, 886 (1988).
7. H.C. Rai, Ramesh Kumar, U.N. Sharma and S.S. Ojha, *Indian J. Chem.*, **29A**, 796 (1990).
8. H.C. Rai and S.P. Chaudhary, *Asian J. Chem.*, **8**, 628 (1996).
9. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham, Vogel's Textbook of Quantitative Inorganic Analysis, Longman, London (1982).
10. H.B. Gray and R.L. Carlin (ed.), in: Transition Met. Chem., Marcel-Dekker, New York, p 1 (1969).
11. E. Sinn and C.M. Harris, *Coord. Chem. Rev.*, **4**, 361 (1969).
12. A.A.G. Tomlinson and B.J. Hathaway, *J. Chem. Soc.*, 1905 (1968).

(*Received*: 13 January 1997; *Accepted:* 2 June 1997) AJC-1270