

Complexes of 2-Hydroxyimino-3-(2'-iminopyridyl)-butane with Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) & Mercury(II)

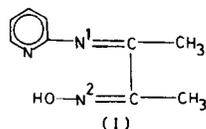
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The schiff base 2-hydroxyimino-3-(2'-iminopyridyl)-butane (HL), having two imino nitrogens, a pyridine nitrogen and an oxygen as potential donor sites, has been synthesised. Metal(II) sulphate complexes of the general formula $[M(HL)_2(H_2O)_2]SO_4$ where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been prepared and characterised on the basis of elemental analyses and magnetic, conductance and spectral studies.

Diacetyl monooxime and its various derivatives have been extensively used as biologically active complexing agents and analytical reagents¹⁻⁶. Monooximes show interesting ligating behaviour. It has been observed that in the dioximes as well as in monooximes coordination occurs through two imino nitrogens only and not through oxygen⁷⁻⁹. Keeping this in view, we have synthesised 2-hydroxyimino-3-(2'-iminopyridyl)-butane (I, HL) and investigated its coordination behaviour; the ligand has two imino nitrogens, one pyridine nitrogen and an oxygen as the potential coordination sites.



All the chemicals used were of AR grade. The ligand (HL) was synthesised by refluxing for 3 hr a 1:1 (molar) mixture of 2-aminopyridine and diacetyl monooxime dissolved in ethanol. The solution was concentrated and the crude product so obtained was washed with water-ethanol mixture and recrystallised several times from ethanol before use. All the analyses were performed following the conventional methods. The UV, visible and infrared spectra were recorded on Shimadzu 210 A UV, Cary 17D and Perkin-Elmer Model 21 spectrophotometers respectively. The magnetic measurements were carried out using the Gouy method. The conductances were measured on a Philips PR 9500 conductivity bridge. Sublimed camphor was used for the determination of molecular weights by Rast's method.

The Co(II), Ni(II) and Cu(II) complexes were

prepared by mixing ethanolic solution of the ligand with aqueous solution of the metal sulphate in the molar ratio 2.5:1. The mixture was heated on a water-bath for 30 min and cooled. On making the solution ammoniacal, precipitate appeared. The precipitate obtained was filtered under suction, washed with water, ethanol and dried *in vacuo* over fused $CaCl_2$. The filtrate in the case of Ni(II) complex, on further concentration and addition of ammonia, gave a light-green precipitate which was found to be different from the first compound (red). This was filtered, washed and dried as before.

The Zn(II) and Cd(II) complexes were prepared in the same way except the fact that before adding ammonia, ammonium chloride (1 g) was added to each of the solution and then pH was raised to 7.5-8.0. The precipitates were collected, washed and dried as done earlier.

The Hg(II) complex was prepared in the cold by simply mixing the aqueous solution of the metal sulphate with an ethanolic solution of the ligand in the same molar ratio as mentioned before. The precipitate was collected, washed and dried in the usual way.

Characterisation of the ligand

The UV spectrum of the ligand in methanol shows two absorption bands at 235 and 290 nm which may be assigned to $\pi-\pi^*$ transitions of pyridine ring⁷. The slight blue shift may be caused by intra-ligand hydrogen bonding involving H atom of the oxime group and pyridine nitrogen.

The ¹H NMR spectrum of the ligand in $CDCl_3$ showed two triplets at δ 2.0 and 2.5 indicating the presence of two methyl groups in the ligand. Their non-equivalent nature caused the splitting of the two $-CH_3$ proton signals ($J=0.5$ Hz). The signals for C-H protons in the pyridine ring at α -, and β -positions appeared as a doublet at δ 8.1 and a pair of quadruplets around δ 7.5 and 6.6 respectively¹⁰. The $>N-OH$ proton showed a weak and broad signal between δ 10.5 and 11.0. The broadening is due to the intramolecular H-bonding with pyridine nitrogen.

The IR spectrum of the ligand showed a strong band at 3300 cm^{-1} and a medium one at 3200 cm^{-1} which may be assigned to symmetric and antisymmetric stretching vibrations of $-O-H$ of $N-OH$ group¹¹. The ligand exhibited a sharp band at 1660 cm^{-1} which may be due to $\nu C=N$ mode of the oxime group^{12,13}. Two bands at 1610 and 1560 cm^{-1} have been ascribed to the ring breathing mode of the pyridine nucleus¹⁴.

In the lower region, the ligand showed bands at 980,

Table 1—Analytical Data, Magnetic Moment & Molar Conductance Values of the Metal Complexes of 2-Hydroxyimino-3-(2'-iminopyridyl)-butane (HL)

Complex	Colour	Molec. wt	Found (Calc.), %				$\mu_{\text{eff.}}$ (B.M.) at 25°C	Λ_M (ohm ⁻¹ mol ⁻¹ cm ²)
			M	N	C	SO ₄		
[Co(HL) ₂ 2H ₂ O]SO ₄	Pink	544.9	10.8 (10.59)	15.2 (15.41)	39.00 (39.64)	17.8 (17.62)	4.84	91.6
[Ni(HL) ₂ 2H ₂ O]SO ₄	Light-green	544.4	11.2 (10.79)	15.6 (15.42)	39.10 (39.65)	17.74 (17.62)	3.21	81.2
[Ni(HL) ₂]SO ₄	Red	508.7	11.40 (11.53)	16.32 (16.51)	42.80 (42.46)	18.60 (18.87)	Diamagnetic	104.1
[Cu(HL) ₂ 2H ₂ O]SO ₄	Dark-green	549.5	11.33 (11.56)	16.63 (15.28)	39.7 (39.30)	17.2 (17.47)	1.94	96.7
[Zn(HL) ₂ 2H ₂ O]SO ₄	White	551.3	11.93 (11.84)	15.7 (15.23)	38.7 (39.18)	17.58 (17.41)	Diamagnetic	111.3
[Cd(HL) ₂ 2H ₂ O]SO ₄	White	598.4	18.5 (18.78)	13.7 (14.03)	36.9 (36.09)	15.87 (16.04)	Diamagnetic	106.9
[Hg(HL) ₂ 2H ₂ O]SO ₄	White	686.5	28.75 (29.21)	12.11 (12.35)	31.40 (31.09)	14.26 (13.98)	Diamagnetic	99.7

780 and 770 cm⁻¹. Of these, the 980 cm⁻¹ band has been assigned to the $\nu\text{N}-\text{O}$ vibration of the oxime group¹⁵ and the last two to the $-\text{CH}$ deformation mode of the ligand.

Characterisation of the metal complexes

All the metal complexes are insoluble in water and ethanol but are soluble in DMSO and DMF on warming. The molar conductance values of the complexes in DMSO (10⁻³ M) lie between 85 and 100 ohm⁻¹ cm² mol⁻¹ (Table 1) which are typical of 1:1 electrolytes.

Since the complexes are insoluble in common organic solvents, their reflectance spectra were recorded. The bis(aquo)cobalt(II) complex exhibited three bands at 25,640, 19,230 and 17,860 cm⁻¹. Of these the first has been assigned to metal \rightarrow ligand charge-transfer because of its high intensity. The band at 19,230 cm⁻¹ is assigned to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ for Co(II) ion in octahedral environment. The 17,860 cm⁻¹ band is assigned to the transition ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$. These transitions together with a magnetic moment value of 4.84 B.M. (25°C), which is typical of octahedral Co(II) ion, clearly suggest an octahedral stereochemistry for the Co(II)¹⁶⁻¹⁹ complex.

The bis(aquo)nickel(II) complex has a magnetic moment value of 3.21 B.M. which is again typical of a Ni(II) ion in octahedral environment¹¹⁻¹⁹. This is further supported by the electronic spectral data of the complex. Two typical bands occurring at 26,320 and 15,630 cm⁻¹ are due to the transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in octahedral field^{11,20,28,21}. Thus, the green Ni(II) complex may possibly have an octahedral stereochemistry.

The red anhydrous Ni(II) complex is diamagnetic and exhibits a high intensity metal-ligand C.T. band at 24,390 cm⁻¹ and a split band around 18,870 cm⁻¹. The second band is due to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition^{12,22-24}, which is usually observed in Ni(II) complexes with square-planar geometry.

The bis(aquo)copper(II) complex has a magnetic moment value of 1.91 B.M. which is usually observed for octahedral Cu(II) complexes. Its visible spectrum shows a broad band spanning the region 14,930 to 14,290 cm⁻¹. This band may arise from ${}^2E_g \rightarrow {}^2T_{2g}$ transition^{23,24} in octahedral field.

The bis(aquo) complexes of Zn(II), Cd(II) and Hg(II) are all diamagnetic and the elemental analyses and the IR spectral data strongly suggest octahedral stereochemistry for these complexes also.

In the higher frequency region, the IR spectra of the complexes are rather diffused and broadened. The broadening may be caused by the appearance of $\nu\text{O}-\text{H}$ of coordinated water molecules. Except in the case of the red Ni(II) complex, these vibrations appear as a broad band between 3550 and 3530 cm⁻¹. The $\nu\text{O}-\text{H}$ modes of the oxime group at 3300 and 3200 cm⁻¹ are, however, not disturbed at all, showing the non-involvement of the group in complexation reactions.

A band present at 1660 cm⁻¹ in the ligand is considerably lowered (1630-1620 cm⁻¹) in the spectra of the complexes showing the involvement of the exocyclic C=N group in complex formation. The characteristic pyridine ring vibrations do not show any appreciable perturbation thus clearly indicating non participation of the pyridine nitrogen in coordination.

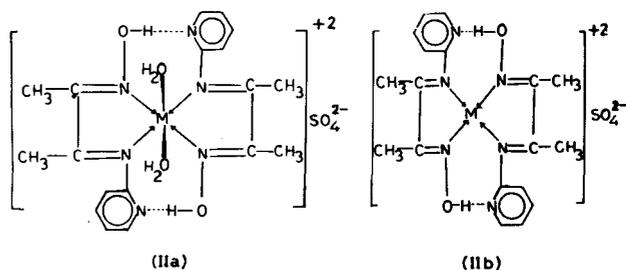
A new band, however, appears in all the metal complexes around 1120-1150 cm⁻¹, which is the characteristic vibration of the anionic SO₄²⁻ ion²⁵. The

$\nu\text{N}-\text{O}$ in the ligand is not shifted appreciably on complexation, thus excluding the possibility of its coordination. A new band, however, appears in all the (bis)aquo complexes around 860 cm^{-1} which is characteristic vibration of the coordinated water molecule²⁶.

Analytical data (Table 1) of the metal complexes together with other experimental evidences strongly suggest the general formulation of the bis(aquo) complexes as $[\text{M}(\text{HL})_2(\text{H}_2\text{O})_2]\text{SO}_4$ and of the red anhydrous Ni(II) complex as $[\text{Ni}(\text{HL})_2]\text{SO}_4$, where HL is the ligand 2-hydroxyimino-3-(2'-iminopyridyl)-butane and M is the divalent metal ion. The experimental data also support the neutral bidentate nature of the ligand. The existence of coordinated water molecules in the bis(aquo) complexes is evident from the IR spectral data and also from thermal analysis. The bis(aquo) complexes are stable upto 110°C after which they start losing mass. This mass loss continues up to 150°C and corresponds to the loss of two water molecules. After 150°C , the anhydrous complexes start decomposing.

In all probability the possible coordination sites are N_1 and N_2 atoms of exocyclic imino group which would give rise to a five-membered chelate ring. This is supported by IR data which show considerable lowering of $\nu\text{C}=\text{N}$ frequency on complexation. That SO_4^{2-} does not participate in complexation is evident from the conductance as well as IR spectral data.

Considering the steric nature of the ligand, it is probable that two ligand molecules are arranged around the metal ion in *trans* octahedral arrangement. The H atom of the $>\text{N}-\text{OH}$ group of one molecule is probably H-bonded to the pyridine nitrogen of the other. Such a possibility is supported by spectral data and also by the molecular models of the complexes. Structure(II) is tentatively assigned to the aquo complexes. The anhydrous red Ni(II) complex has a square-planar stereochemistry as supported by its spectral and magnetic moment data. A *trans* planar arrangement of the ligand around the metal ion as shown in structure IIb is suggested for this complex.



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