

Co(II), Ni(II) and Cu(II) Chelates of Bis-9,10-Phenanthroquinonedioxime and their Nitrogen-Donor Adducts with NH₃ and Pyridine

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Metal chelates of 9,10-phenanthroquinonedioxime with Co(II), Ni(II) and Cu(II) of the types $M(HL)_2$ [$M = Co(II), Ni(II)$ and $Cu(II)$], $H_2L = 9,10$ -phenanthroquinonedioxime where H = dissociable oximate proton have been synthesised by allowing ethanolic solutions of metal salts to react with solution of the ligand in tetrahydrofuran in the molar ratio 1 : 2. They produce another series of metal chelates of the type $[M(HL)_2X_2]$ ($X = NH_3$ or pyridine) when their solution was treated with ammonia or pyridine. I,R spectrum suggests coordination of the ligand with metal ions through azomethine nitrogen in bidentate manner. Electronic spectral and magnetic moment studies indicate complexes of the type $[M(HL)_2]$ to be square planar and those of the type $[M(HL)_2X_2]$ to be octahedral in nature.

INTRODUCTION

Metal complexes with oximes have received much attention during recent years¹⁻⁵ as the bis complexes with Co(II), Ni(II) and Cu(II) and tris complexes with Fe(II)/(III) and Co(III) have been found to be excellent ligands capable of coordinating further through unused oxygen donor atoms to give homo and hetero polynuclear encapsulated and macrocyclic metal complexes.

In continuation of earlier work in the field^{6,7}, we report here, isolation and characterisation of a series of Co(II), Ni(II) and Cu(II) complexes with 9,10-phenanthroquinone dioxime along with nitrogen donor adducts with ammonia or pyridine.

EXPERIMENTAL

All the chemicals used were BDH reagents except phenanthroquinone which was an Aldrich reagent.

Preparation of the dioxime of 9,10-phenanthroquinone, H₂L

1 g 9,10-phenanthroquinone were dissolved in 7 mL of glacial acetic acid in a hard glass test tube and allowed to react with solution of 1 g hydroxylamine

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hydrochloride dissolved in 10% sodium acetate solution. The mixture was shaken for 5 min when a yellow precipitate was obtained. It was filtered and washed with water, dried and recrystallised with alcohol. The melting point was found to be $200 \pm 2^\circ\text{C}$ (analysis was within 1% of the formulation).

Preparation of the Complexes

Similar procedures have been adopted for the preparation of the complexes. A representative description is given.

Preparation of Bis-(9,10-Phenanthroquinonedioximato) copper (II) complex $[\text{Cu}(\text{HL})_2]$

9,10-Phenanthroquinonedioxime 10.232 g (M/1000) dissolved in hot tetrahydrofuran (12 mL) was mixed with ethanolic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.170 g, M/100) when a green precipitate with yellow tinge was obtained. The whole mixture was then refluxed on a water bath for 45 min. The mixture was cooled, filtered and washed with tetrahydrofuran and then with ethyl alcohol to remove excess of metal. Dark green crystals with a yellow tinge were obtained. This complex was soluble in acetone and dimethylformamide and insoluble in water and ethanol. The compound was stable below 270°C and above this temperature, decomposition started. The complex was paramagnetic and $\mu_{\text{eff}} = 1.81$ B.M. Acetone solutions of complexes show maximum absorption at $19,505 \text{ cm}^{-1}$.

The analysis corresponds to the formula $\text{Cu}(\text{C}_{14}\text{H}_9\text{N}_2\text{O}_2)_2$.

Co(II) and Ni(II) complexes of the type $[\text{M}(\text{HL})_2]$ were synthesised using similar procedure replacing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$.

For the preparation of nitrogen donor adducts of the type $[\text{M}(\text{HL})_2\text{X}_2]$ [$\text{X} = \text{NH}_3$ or pyridine] tetrahydrofuran solution of the complexes $\text{M}(\text{HL})_2$ was treated with little quantity of liquor ammonia or pyridine followed by refluxing of the solution for 3–4 h on water bath for NH_3 complex and for 1 h for pyridine complex.

The complexes were analysed using standard procedures⁸ such as copper iodometrically, nickel as bis-dimethyl glyoximatonickel(II) and carbon, hydrogen and nitrogen by semimicro combustion methods. Analytical data along with colour and magnetic moment data have been given in Table-1.

The infrared spectra of the ligand as well as metal(II) complexes were recorded on Beckman IR-20 spectrophotometer and data have been given in Table-2. The conductivity measurements were made on a Systronic conductometer model 303 using dimethylsulphoxide as a solvent. Magnetic moments were measured by the Gouy method using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as the calibrant.

The absorption spectra of dimethyl sulphoxide solution of the complexes were recorded on a Cary-2390 spectrophotometer and data have been given in Table-2.

RESULTS AND DISCUSSION

The infrared spectra of the ligand exhibit sharp and strong peaks at 3200 cm^{-1} , 1680 cm^{-1} , 1590 cm^{-1} , and 1190 cm^{-1} which can be assigned to $\nu(\text{O—H})$, $\nu(\text{C=N})$ oxime, $\delta(\text{O—H})$ and $\nu(\text{N—O})$.

TABLE-1
ANALYTICAL MAGNETIC MOMENT, ELECTRONIC SPECTRA AND
CONDUCTIVITY DATA FOR METAL COMPLEXES OF BIS 9,10-
PHENANTHROQUINONEDIOXIME WITH COBALT(II),
NICKEL(II) AND COPPER(II)

Complexes (Colour)	%Analysis found (calcd.)				μ_{eff} (B.M)	λ_{max} (elect.) cm^{-1}	Λ_{m} $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
	M	C	H	N			
H ₂ L	—	70.46 (70.58)	4.14 (4.20)	11.69 (11.76)			
Co(HL) ₂ (Green)	10.99 (11.05)	62.96 (63.05)	3.49 (3.56)	14.43 (14.50)	1.99	21008	21
Ni(HL) ₂ (Blue)	10.99 (11.05)	62.96 (63.05)	3.29 (3.38)	10.42 (10.51)	2.97	24500	22
Cu(HL) ₂ (Dark green)	11.72 (11.81)	62.43 (62.63)	3.26 (3.26)	10.35 (10.41)	1.18	19905	20
[Co(HL) ₂ (NH ₃) ₂] (Deep red)	10.29 (10.38)	59.19 (59.27)	4.19 (4.23)	14.76 (14.81)	4.73	15600	23
[Co(HL) ₂ (Py) ₂] (Black green)	8.26 (8.32)	65.91 (66.00)	3.93 (4.05)	12.02 (12.11)	4.95	15400	24
[Ni(HL) ₂ (NH ₃) ₂] (Yellow)	10.26 (10.34)	59.21 (59.30)	4.18 (4.23)	14.79 (14.86)	2.83	23700	27
[Ni(HL) ₂ (Py) ₂] (Greenish yellow)	8.37 (8.48)	66.04 (66.17)	3.96 (4.05)	12.04 (12.06)	2.88	23600	28
[Cu(HL) ₂ (NH ₃) ₂] (Green)	11.04 (11.11)	58.67 (58.79)	4.09 (4.19)	14.58 (14.69)	1.91	14998	29
[Cu(HL) ₂ (Py) ₂] (Green)	9.04 (9.13)	65.49 (65.56)	3.96 (4.02)	11.98 (12.07)	1.98	15020	30

TABLE-2
INFRARED SPECTRA (cm^{-1}) OF THE LIGAND H₂L AND METAL
COMPLEXES OF BIS-9,10-PHENANTHROQUINONEDIOXIME

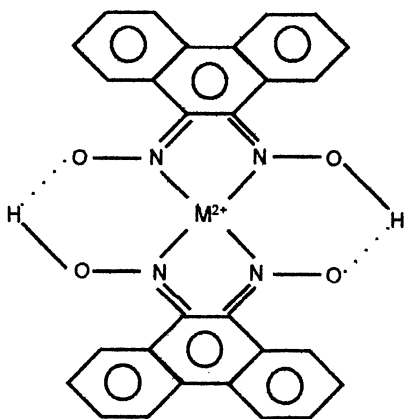
S.N.	Ligand/Complexes	$\nu(\text{O—H})$	$\delta(\text{O—H})$	$\nu(\text{C=N})$	$\nu(\text{N—O})$	$\nu(\text{M—N})$
1.	H ₂ L	3200s	1460b	1680s	1190m	—
2.	[Co(HL) ₂]	3260s	1465b	1595s	1185m	610s
3.	[Co(HL) ₂ (NH ₃) ₂]	3265s	1470b	1590s	1180m	620s
4.	[Co(HL) ₂ (Py) ₂]	3270s	1460b	1585s	1175m	610s
5.	[Ni(HL) ₂]	3240s	1460b	1590s	1180m	605s
6.	[Ni(HL) ₂ (NH ₃) ₂]	3250s	1465b	1605s	1185m	615s
7.	[Ni(HL) ₂ (Py) ₂]	3245s	1470b	1610s	1180m	605s
8.	[Cu(HL) ₂]	3255s	1465b	1590s	1185m	610s
9.	[Cu(HL) ₂ (NH ₃) ₂]	3260s	1470b	1595s	1180m	615s
10.	[Cu(HL) ₂ (Py) ₂]	3265s	1465b	1585s	1175m	620s

Infrared spectra of the metal complexes show medium to strong bands in the range $3280\text{--}3200\text{ cm}^{-1}$ and assignable to $\nu(\text{O—H})$. The broad nature of the bands suggests presence of hydrogen bonding.

In the spectra of the complexes $\nu(\text{C=N})$ peak indicates a significant red shift whereas $\nu(\text{N—O})$ and $\nu(\text{O—H})$ remain almost unperturbed indicating coordination to take place through nitrogen atom of the azomethine group. Additional peak due to $\nu(\text{M—N})$ appears in the spectra of the complexes in the far infrared region.^{9–12}

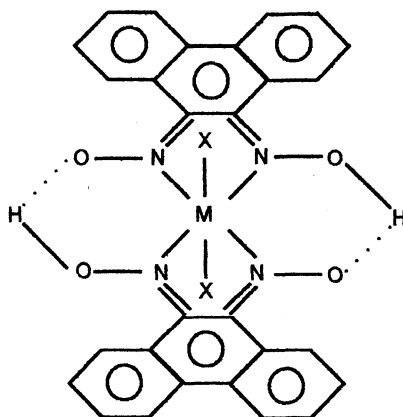
On the basis of above discussions complexes of the type $\text{M}(\text{HL})_2$ can be presumed to have the structure as shown in Fig. 1, whereas $[\text{M}(\text{HL})_2\text{X}_2]$ are assigned the structures as shown in Fig. 2.

The structures are strongly supported by the magnetic moment data, electronic spectra and conductivity measurements.



M = Co(II), Ni(II), Cu(II)

Fig-1



M as in Fig.-1, X = NH₃ or pyridine

Fig-2

Electronic Spectra and Magnetic Moment of the Complexes

Magnetic moment value for copper(II) complex of the type $[\text{Cu}(\text{HL})_2]$ is 1.81 B.M. and the electronic spectrum shows a broad band at about 19000 cm^{-1} . Complexes of the type $[\text{Cu}(\text{HL})_2\text{X}_2]$ have magnetic moment in the range 1.9 to 2.0 B.M. and electronic spectrum shows a sharp band at 15000 cm^{-1} . These features indicate complexes $\text{Cu}(\text{HL})_2$ to possess square planar geometry whereas complexes $[\text{Cu}(\text{HL})_2\text{X}_2]$ to be octahedral.

The magnetic moment values of 2.0 B.M. for $\text{Co}(\text{HL})_2$ complex indicate it to have square planar geometry whereas value in the range 4.8 to 5.0 B.M. for $[\text{Co}(\text{HL})_2\text{X}_2]$ is suggestive of the octahedral arrangement. The complexes $[\text{Co}(\text{HL})_2]$ show a sharp band at $21,000\text{ cm}^{-1}$ whereas complexes of the type $[\text{Co}(\text{HL})_2\text{X}_2]$ exhibit a sharp band in the range $16000\text{--}15000\text{ cm}^{-1}$ followed by a weak band at 21200 cm^{-1} . The above features support square planar arrangement for $[\text{Co}(\text{HL})_2]$ complexes whereas octahedral for the complexes $[\text{Co}(\text{HL})_2\text{X}_2]$.

The complex $\text{Ni}(\text{HL})_2$ is diamagnetic and is expected to be square planar. The complexes of the type $[\text{Ni}(\text{HL})_2\text{X}_2]$ have magnetic moment in the range 2.9 to

3.0 B.M. The electronic spectrum shows a group of three bands, one in the range $14000\text{--}13000\text{ cm}^{-1}$, next one in the vicinity of 20000 cm^{-1} and third one near 24000 cm^{-1} . These features suggest octahedral arrangement of the ligand atom around nicked(II) ion.

Conductivities of the complexes were measured in the solvent dimethyl sulphoxide and the complexes of the type $M(\text{HL})_2$ and $M(\text{HL})_2\text{X}_2$ have conductivity values in the range of $20\text{--}30\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ and indicate them to be non-electrolytic in nature.

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REFERENCES

1. R.B. King, *Progr. Inorg. Chem.*, **15**, 287 (1972).
2. H.C. Rai, J. Chakraborti and B. Sahoo, *Indian J. Chem.*, **18 A**, 242 (1979).
3. B.K. Mahapatra and B. Sahoo, *Indian J. Chem.*, **24A**, 653 (1985).
4. H.C. Rai, R. Kumar, S.N. Vidyarthi and B. Singh, *Indian J. Chem.*, **27A**, 886 (1988).
5. Marc Zimmer, Derck A. Tocher, Gautam K. Patra, Jnan P. Naskar and Dipankar Dutta, *Indian J. Chem.*, **38A**, 1087 (1999).
6. H.C. Rai, Ramesh Kumar, K.K. Sharma and B.K. Rai, *Asian J. Chem.*, **6**, 464 (1994).
7. H.C. Rai, Sushma Sinha and B.K. Rai, *Asian J. Chem.*, **12**, 922 (2000).
8. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longman, London (1968).
9. K. Nakamoto, *Infrared Spectra of Inorganic and Co-ordination Compounds*, 2nd Edn., John Wiley, New York (1963).
10. N. Nonayama, S. Tonntara and K. Yatrasi, *Inorg. Chim. Acta*, **12**, 33 (1975).
11. D.K. Rastogi, S.K. Dua and S.K. Sahni, *J. Inorg. Nucl. Chem.*, **42**, 423 (1980).
12. K. Dey, K. Chakrabarty, P.K. Bhattacharya, D. Bandyopadhyaya, S.K. Nag and R. Bhowmick, *Indian J. Chem.*, **38A**, 1139 (1999).

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