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NOTE

Binuclear Metal Complexes of Cobalt (II) with the Ligand 1,2,5,6-Tetraphenyl-3,4-Diaza-1,6-Dihydroxyimino-2,4-Hexadiene

K. SAHU*, KAILASH MAHTO and SHIV CHANDRA YADAV
P.G. Department of Chemistry, B.R.B. College, Samastipur, India

Binuclear metal complexes of Co(II) with the ligand 1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene of the type $Co_2L_2X_4$ ($X = Cl^-$, Br^-, I^- or NO_3^-) have been prepared and characterized on the basis of analytical, IR, electronic and magnetic moment data. IR spectral data show coordination of the ligand with the metal ions through the azine and oxime nitrogens in a bi-bidentate manner. The complexes are suggested to possess a hydrogen bonded binuclear structure on the basis of IR data. Magnetic values and electronic spectra show a tetragonal crystal field around metal ions.

Binuclear metal complexes of azines and related ligands have generated considerable interest in recent years[1–6]. The present paper deals with the isolation of binuclear metal complexes of 1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene with Co(II) where the uncharged ligand acts in a tetra-functional manner coordinating to two metal ions.

α-Benzil monoxime was prepared according to the literature method.[7, 8]

The ligand α-benzil azine dioxime was prepared as reported earlier[9] (m.p. 191°C).

Preparation of tetrachloro bis-(1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene) dicobalt(II) $Co_2L_2Cl_4$

An ethanolic solution of cobalt(II) chloride hexahydrate (0.004 mol) was added to an ethanolic solution of α-benzil azine dioxime (0.004 mol) dropwise with constant stirring. It was then refluxed on hot water bath for 1 h. On cooling grey crystals separated out. It was filtered, washed with acetone and dried *in vacuo*. The dried product was analysed for its constituents. Bromo, iodo and nitrato complexes were prepared by a similar procedure.

The analytical data are reported in Table-1. The infrared spectra of the ligand show a band around 3370 cm^{-1} of medium strength that can be ascribed to O—H stretching vibration of N—O—H group. The presence of multiple bands in the region 3300–2700 cm^{-1} indicates inter and intramolecular hydrogen bonding in the free ligand.[10, 11] In the spectra of the Co(II) complexes the bands are broad in this region indicating the presence of hydrogen bonded structure of N—O—H groups of the uncharged ligand. A strong and sharp band at 1645 cm^{-1} has been assigned to scissoring mode of N—O—H group[10]. Band due to N—O—H deformation persists in the complexes and observed in the region 1660–1650 cm^{-1} exhibiting the presence of O—H groups and the existence of the ligand in its unionized form[12]. In metal complexes both the IR bands for C=N (azine) and C=N (oxime) groups shift to higher frequencies indicating co-ordination through —N atoms of these groups. This shift is due to metal to ligand π-electron interaction. The complexes show a sharp band in the region 1050–1000 cm^{-1} which is expected due to N—O stretching vibration. In free oxime this band is found near 970 cm^{-1} and the position N—O band is shifted on coordination. Besides these bands the spectra reveal three more bands in the region 1400–1200 cm^{-1} both in the ligand and the complexes which are chosen to represent phenyl ring vibrations.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Compounds	% Found (Calculated)				
	M	C	N	Halogen	$\mu_{eff.}$ (B.M.)
Benzil azine dioxime	–	75.20	12.32	–	–
		(75.33)	(12.55)	–	–
$Co_2L_2Cl_4$	10.12	58.17	9.35	12.05	2.15
	(10.23)	(58.33)	(9.72)	(12.32)	
$Co_2L_2Br_4$	8.47	50.21	8.16	23.85	2.00
	(8.86)	(50.54)	(8.42)	(24.04)	
$Co_2L_2I_4$	7.64	44.12	7.17	33.16	2.30
	(7.76)	(44.28)	(7.38)	(33.45)	
$Co_2L_2(NO_3)_4$	9.20	53.25	13.15	–	1.90
	(9.37)	(53.42)	(13.35)	–	

The magnetic moment values for Co(II) complexes have been found in the region 1.90 to 2.30 B.M. The low magnetic moment values favour that the Co(II) complexes are of low spin type having one unpaired electron. The slightly high value may be due to spin-orbit interaction of $^2A_{1g}$ state with $^2A_{2g}$ and other higher levels. The visible spectra show a pair of bands at 16,500 cm^{-1} and 20,400 cm^{-1}. The broad band lying in the vicinity of 20,400 cm^{-1} indicates some amount of tetragonal distortion in octahedral structure. The low frequency band appearing at 16,500 cm^{-1} is assigned to $^2A_{1g} \longrightarrow {}^2A_{2g}$ transition. The next band of greater intensity at 20,400 cm^{-1} is attributed to $^2A_{1g} \longrightarrow {}^2E_g$ transition. A highly intense band beyond 25,000 cm^{-1} may be due to metal ligands charge transfer M-L(π_g).

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