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Binuclear Metal Chelates of 1,2,5,6-tetraphenyl-3,4-diaza-1,6 Dihydroxyimino-2,4-hexadiene with Ni(II), Co(II), Mn(II) and Cu(II)

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Binuclear metal chelates of 1,2,5,6-tetraphenyl-3;4-diaza-1,6-dihydroxyimino-2,4-hexadiene with Ni(II), Co(II), Mn(II) and Cu(II) of the type $M_2L_2\cdot XH_2O$ have been synthesised. IR spectra show coordination of the ligand with the metal ions through azomethine nitrogen atoms in a bi-bidentate manner. Electronic spectra and magnetic moment suggest dinuclear square planar structure about the metal ion.

INTRODUCTION

A series of bi-bidentato ligands have been studied during recent years[1-4]. The present paper deals with isolation and structural elucidation of Ni(II), Co(II), Cu(II) and Mn(II) complexes with the ligand 1,2,5,6-tetraphenyl-3,4 diaza-1,6-dihydroxyimino-2,4-hexadiene.

EXPERIMENTAL

α-Benzil monoxime was prepared according to the procedure given in the literature[5,6]. A new ligand α-benzil azine dioxime was synthesised by the help of the literature[7]. α-benzilmonoxime (0.04 mol) was taken to a 10 ml. of absolute alcohol. Hydrazine hydrate (0.02 mol) and few drops of glacial acetic acid was also added to the above solution. The entire mixture was then heated to boiling for few minutes. After cooling the mixture to room temperature water was added slowly in portions which produced first emulsion and finally crystals. Then a large proportion of water was added after which the mixture was cooled in ice. The crude product was filtered and recrystallised from absolute alcohol. By the addition of water and cooling in ice crystals separated out. The crystals were filtered, washed with alcohol, dried in air and finally in vacuum (or P_2O_5), M.pt–191°C.

Isolation of the Complexes

$NiL_2\cdot 4H_2O$. A warm solution of Ni(I) acetate tetrahydrate (0.004 mol) was taken in *ca.* 100 ml. of distilled water. Then a solution of α-benzil azine dioxime (0.004 mol) in *ca.* 60 ml. of dimethyl formamide was added dropwise to the above solution with constant stirring. A reddish solid was formed immediately. After nearly 15 minutes of stirring it was cooled in ice. Crystals were filtered, washed thoroughly with water and

finally with demethyl formamide. Crystals were dried in vaccum. A reddish brown solid was obtained. Co(II) complex was prepared in a similar manner.

$Cu_2L_2 \cdot 2H_2O$. α-Benzil azine dioxime (0.004 mol) was dissolved in minimum quantity of acetone. A warm acetonic solution of cupric nitrate hexahydrate (0.004 mol) was added dropwise to the above solution with constant stirring. A green solution was obtained. The whole solution was refluxed on a hot water bath for 1 hr. After cooling the solution in ice overnight crystals separated out. It was filtered, washed with acetone and dried.

$Mn_2L_2 \cdot 4H_2O$. α-Benzil azine dioxime (0.004 mol) was dissolved in minimum quantity of dilute NaOH solution and a clear pale yellow solution was obtained. A very dilute solution of acetic acid was added dropwise to the above solution to neutralise slight excess of alkali present, with constant stirring. The addition of acid was continued till a faint permanent turbidity was obtained. After filtration a clear filtrate was collected. A warm solution of manganese nitrate (0.004 ml) in distilled water was added dropwise to the above ligand solution with constant stirring. A brown solid separated out. It was filtered after 15 minutes, washed thoroughly with water and finally by rectified spirit.

RESULTS AND DISCUSSION

The analytical and physical data of the compounds are presented in Table 1.

TABLE 1

ANALYTICAL DATA OF THE COMPLEXES

Compounds	Colour	Found (Calc.) %			μ_{eff} (B.M.)
		M	C	N	
Benzil azine dioxime	White	—	75.12 (75.33)	12.32 (12.65)	—
$Ni_2L_2 \cdot 4H_2O$	Reddish brown	11.05 (11.20)	64.20 (64.31)	10.56 (10.72)	2.62
$Co_2L_2 \cdot 4H_2O$	Violet brown	11.12 (11.28)	64.10 (64.24)	10.59 (10.71)	2.64
$Cu_2L_2 \cdot 2H_2O$	Green	10.25 (10.32)	54.20 (54.59)	13.62 (13.65)	1.18
$Mn_2L_2 \cdot 4H_2O$	Brown	8.85 (9.06)	55.15 (55.35)	13.70 (13.84)	4 33

L = Benzil azine dioxime.

The infrared spectrum of the ligand shows a band around 3370 cm^{-1} of medium intensity that can be assigned to O—H stretching vibration of N—O—H group. The —OH stretching vibrations of several oximes involving intramolecular or intermolecular hydrogen bonding are found to occur in 3250–2350 cm^{-1} region[9]. The presence of multiple bands in the region 3300–2700 cm^{-1} indicates inter- and intramolecular hydrogen bonding in the free ligand. A strong and sharp band at 1645 cm^{-1} has been assigned to scissoring mode of N—O—H group[10]. The band assignment gets its support from its dissappearance in the metal complexes due to elimination of oxime protons. In addition to these bands the IR spectrum of the ligand shows a pair of bands of medium intensity occurring at 1595 and 1442 cm^{-1} which are believed to have arisen from $C \overset{\cdots}{—} N$ stretching vibration placed in two structural environments. The band found in high frequency region is ascribed to azine group and one that is observed in low frequency region to oxime groups[3,4]. These bands show an opposite trend in metal complexes. A shift in band position upto 25 cm^{-1} is observed in low frequency side for azine group and the other set of IR data is reported for oxime group showing positive frequency shift 20 cm^{-1}. The complexes show a sharp band in the region 1010–1000 cm^{-1} which arises due to N—O stretching vibration. In free oxime this band is found near 970 cm^{-1} and the position of 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 complexes which can be assigned as phenyl ring vibrations. The IR data support the attachment of metal to the ligand by N atoms and that the ligand is present in charged form coordinating in a bi-bidentate manner in all dinuclear complexes.

The magnetic moment value for the Mn(II) complex at room temperature is 4.33 B.M., closely corresponds to three unpaired electrons. The magnetic data of the complex implies the structure of the complex to be square planar as is in the case of manganese phthalocyanine[11]. The lower value of magnetic moment is attributed to antiferromagnetic interaction. The electronic spectra show a band at 27,000 cm^{-1}. This band is believed to arise due to intraligand transition ($\pi \rightarrow \pi^*$). The magnetic moment value of Co(II) is found to be 2.64 B.M. per metal ion. The magnetic moment value corresponds to the square planar structure[3]. The complex shows a broad band in the region 19,000–28,000 cm^{-1}. This band is not well resolved and the broadness of band indicates the overlapping of a series of bands associated with d-d transition and charge transfer transitions arising from $\pi \rightarrow \pi^*$ transition of the ligand[12]. The magnetic moment value of Ni(II) is found to be 2.62 B.M. per metal ion possessing a high spin system with the presence of some metal-metal interaction. The complex is believed to be square planar. The spectrum shows five absorption bands at 11,200, 17,200, 19,500, 22,700 and 30,700 cm^{-1} respectively which possibly have arisen from orbital triplet $^3A_{2g}$ ground state. The presence of both π and π^* orbitals of the ligand gives rise to a series of charge transfer bands rendering the band assignment almost impossible. The magnetic moment value of green Cu(II) complex is found to be 1.18 B.M. per metal ion with square planar structure. The low value of magnetic moment is attributed to the presence of antiferromagnetic exchange interaction. The complex shows a single band around 16,500 cm^{-1} that can be assigned to d-d transition favouring square planar arrangement about each copper atom in the complex.

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