Asian Journal of Chemistry Vol. 5, No. 4 (1993), 826–830

Binuclear Metal Chelates of 1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene with Pd(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 Pd(II) and Cu(II) of the types $Pd_2L_2 \cdot 4H_2O$, Cu_2LX_4 (X = Cl or Br) have been prepared IR spectra suggest coordination of the ligand with the metal ions through azomethine nitrogen atoms in a bi-bidentate manner. The palladium complex is diamagnetic and is believed to be a dinuclear square planar complex. Its electronic spectra show the characteristic features of Pd(II) square planar complexes. Cu(II) complexes may have planar structures with two copper atoms bound in edge—on position to a single molecule of the ligand. Magnetic values show antiferromagnetic coupling between the metal centres.

INTRODUCTION

A series of bi-bidentato ligands have been studied during recent years[1–4]. We have reported earlier the inner type 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) and shown that the ligand acts in a bi-bidentate manner towards two metal ions[5]. In continuation of our earlier work, the present paper deals with isolation of inner type of Pd(II) complex and that the ligand is present in charged form coordinating in a bi-bidentate manner in dinuclear complex. It also deals with a new series of complexes with Cu(II), where the uncharged ligand acts in a tetrafunctional manner coordinating to two metal ions.

EXPERIMENTAL

α-Benzilmonoxime was prepared according to the procedure given in the literature[6,7]. The ligand α-benzil azine dioxime was prepared as reported earlier[5]. (M.pt. 191°C).

Preparation of (Tetrahydrate) bis-(1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene) dipalladium (II) $[Pd_2L_2 \cdot 4H_2O]$.

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 the 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 solution of palladium nitrate (0.004 mol) in distilled water was added dropwise to the above ligand solution with constant stirring. As each drop of the palladium salt came in contact with the ligand solution, a yellowish solid appeared, but it dissolved on shaking. After the addition was over, the solution was concentrated over a hot water bath where some solid was found to have settled down. It was filtered, washed with water followed by absolute alcohol and dried in vacuo. The compound was red in colour.

Preparation of (Tetrahalo) (1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene) dicopper(II) Cu_2LX_4 (X = Cl or Br).

α-Benzil azine dioxime (0.004 mol) was dissolved in minimum quantity of absolute alcohol. Ethanolic solution of $CuCl_2 \cdot 2H_2O$ or $CuBr_2 \cdot 2H_2O$ (0.008 mol) was added dropwise with constant stirring to the ligand solution. A bright green precepitate was readily formed which was filtered, washed with ethanol and dried in vacuo.

RESULTS AND DISCUSSIONS

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

TABLE 1
ANALYTICAL DATA OF THE COMPLEXES

Sl. No.	Compounds	Colour	Found (Calcd) %			Magnetic moment (B.M.)
			M	C	N	
1.	Benzil azine dioxime	White	—	75.12 (75.33)	12.32 (12.65)	—
2.	Pd_2L_2, $4H_2O$	Red	17.95 (18.19)	57.01 (57.27)	9.28 (9.54)	Diamagnetic
3.	Cu_2LCl_4	Green	17.54 (17.76)	46.85 (46.99)	7.62 (7.83)	1.65
4.	Cu_2LBr_4	Greenish brown	14.05 (14.22)	37.52 (37.62)	6.10 (6.27)	1.25

L-Benzil azine dioxime.

The infrared spectra of the ligand show 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[8]. The presence of multiple bands in the region 3300–2700 cm^{-1} show 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[9]. This band does not occur in metal complex of Pd(II) where the O–H bond has been broken in the formation of the metal complex. The band due to N–O–H deformation persists in the Cu(II) complexes and occur in the region 1700–1650 cm^{-1} showing the presence of O–H groups and the existence of the ligand in its unionized form. 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⩵N stretching vibration placed in two structural environments. The band found in high frequency region is ascribed to azine group and one that it observed in low frequency region to oxime group[3,4]. In Pd(II) complex a shift in band position is observed in low frequency side for azine group and positive frequency shift for oxime group. Both the νC=N bands due to the azine and oxime groups shift to higher frequency in the Cu(II) complexes indicating coordination through nitrogen atoms of these groups. The shift is due to metal to ligand π-electron interaction. The complexes, show a sharp band in the region 1010–1000 cm^{-1} which arise due to N–O stretching vibration. In free oxime this band is found near 970 cm^{-1} and the position of N–O band shifts on coordination. Besides these bands the spectra show 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 of Pd(II) complex 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 dinuclear complex (Fig. 1). On the other hand, the Cu(II) complexes have been assigned the structure (Fig. 2) in which a ligand molecule coordinates in a bi-bidentate manner in its unionized form to two Cu(II) ions, with four chloride or bromide ions completing the coordination spheres of the copper ions[10].

The palladium complex is diamagnetic and intensely coloured implying

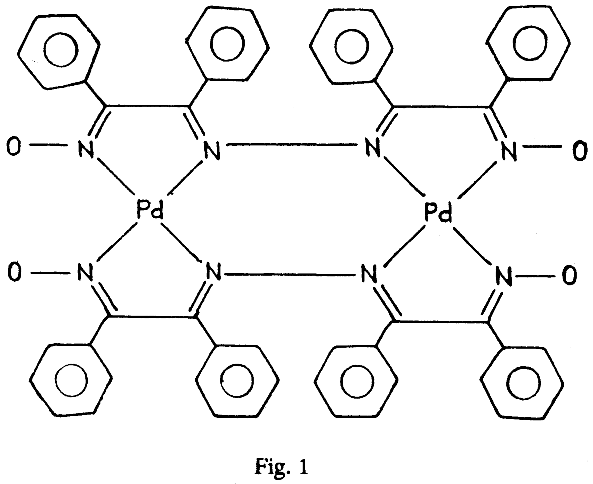
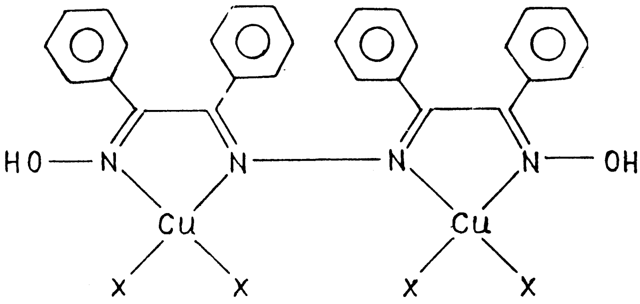


Fig. 1



X = Cl or Br

Fig. 2

a square planar coordination of the central ion by four nitrogen atoms which is further characterised by electronic spectra rich in absorption bands in the region 600–320μ. The spectra show a broad band at 18,500 cm^{-1} which is assigned to internal transition within the d-shell of the central metal ion[11]. Another band at 28,200 cm^{-1} arise from charge transfer and intraligand transition. The intraligand transition is observed at 28, 200 cm^{-1} and is believed to arise due to $\pi \rightarrow \pi^*$ transition.

The magnetic moment values for the Cu(II) complexes at room temperature are in the region 1.25–1.65 B.M. The low value of magnetic moment suggests that antiferromagnetic interaction takes place within a complex unit, the magnetic exchange interaction between copper atoms taking place through the intervening ligand atom. The Cu(II) complexes exhibit an asymmetric broad band at 19, 300 cm^{-1} and an intense charge transfer band at 23,500 cm^{-1} in their electronic spectra. The broad ligand field band represents two or three superimposed absorptions and leads to the belief that the Cu(II) complexes are essentially planar[12].

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(*Received*: 16 February 1992; *Accepted*: 15 January 1993) AJC–537.