

## Epr study of some copper(II) mononuclear and copper(II)-copper(II)/ copper(II)-nickel(II) binuclear complexes

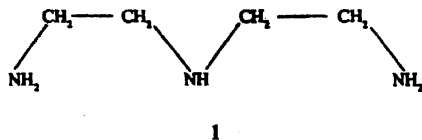
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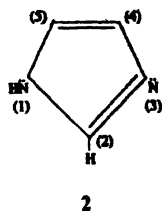
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X-Band epr spectra of polycrystalline samples of some copper(II) mononuclear and copper(II)-copper(II)/copper(II)-nickel(II) binuclear complexes using diethylenetriamine and imidazole have been reported.

Diethylenetriamine (1, dien) is a tridentate complexing nitrogen donor ligand with donor groups suitably placed for forming two five-member chelate rings. The ligand is known<sup>1</sup> to form imidazolate-bridged polynuclear complex of the type  $[\text{Cu}(\text{im})(\text{dien})]_n(\text{ClO}_4)_n$ , where im is an anion obtained by deprotonation of the imidazole (imH). In this complex the copper atoms are bridged by the imidazolate ring in two alternative orientations. The geometry around copper(II) is trigonal pyramidal, comprising the tridentate dien and two imidazolate ions. The copper atoms are bridged by imidazolate ring in two alternative orientations leading to two polynuclear units in each unit cell.



Imidazole (2; imH) is a monodentate ligand. Its ring contains two nitrogen atoms. The N-3 nitrogen is termed as pyridine nitrogen while N-1 as pyrrole nitrogen. Imidazole is a ligand of biological importance in active sites of metalloenzymes as a part of histidine moiety<sup>2</sup>. Imidazolate, the deprotonated form of imidazole, is involved in active site of bovine erythrocyte superoxide dismutase<sup>3</sup>. To explore



the properties of imidazolate-bridged binuclear complexes, model complexes, of the pairs copper-copper<sup>4,5</sup>, copper-cobalt<sup>6</sup> and copper-zinc<sup>7</sup>, have been synthesized. We report here, the synthesis and X-band epr spectra of some mononuclear copper(II) and bi-homo/heteronuclear

complexes with diethylenetriamine and imidazole.

### Results and Discussion

All the complexes gave satisfactory elemental analyses (Table 1). The complexes were found soluble in water, DMF, DMSO etc. we have recorded epr spectra at room temperature and at liquid nitrogen temperature. The representative epr spectra of some complexes are given in Figs. 1 and 2.

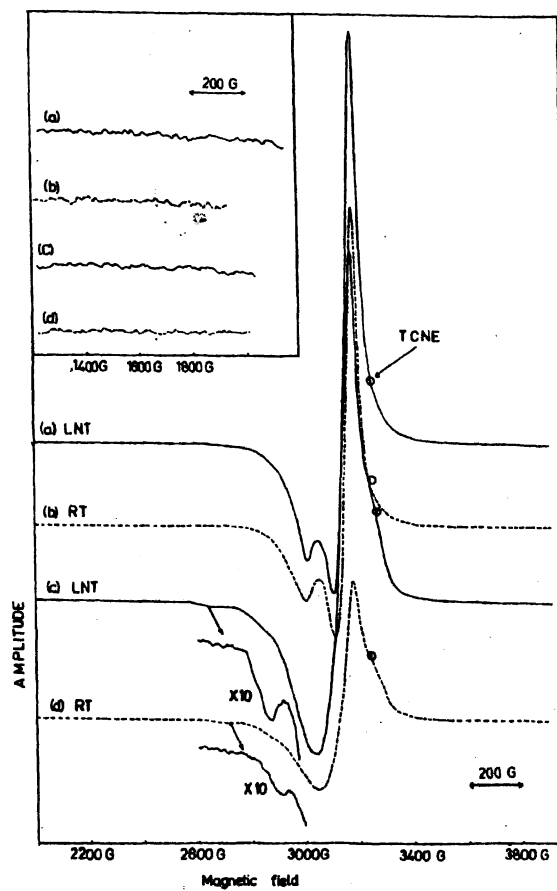


Fig. 1. X-Band epr spectra (polycrystalline) of (a) and (b)  $[\text{Cu}(\text{dien})\text{H}_2\text{O}](\text{ClO}_4)_2$ , (c) and (d)  $[\text{Cu}(\text{dien})\text{imH}](\text{ClO}_4)_2$ .

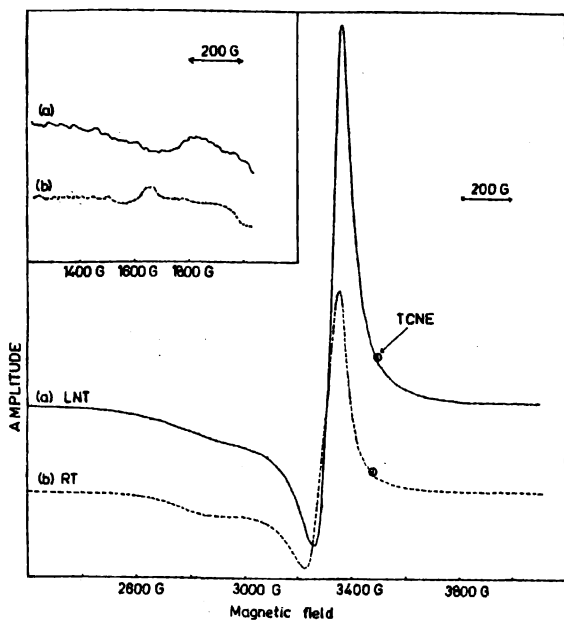


Fig. 2. X-Band epr spectra (polycrystalline) of  $[\text{dienCu}(\text{im})\text{Cu}(\text{dien})](\text{ClO}_4)_3$ .

Systems involving interaction between unpaired spins of two copper(II) centers (each  $S = 1/2$ ) give rise to singlet ( $S = 0$ ) and triplet ( $S = 1$ ) states. The spin Hamiltonian for the triplet state interacting with a magnetic field  $H$  is

$$\mathcal{H} = g\beta HS + DS_z^2 + E(S_x^2 - S_y^2) - (2/3)D$$

where  $D$  and  $E$  are zero field splitting parameters. Such a system should exhibit six epr transitions at the magnetic field defined below<sup>8</sup>:

$$\begin{aligned} H_{x1}^2 &= (g_e/g_x)^2 [(H_0 - D' + E')(H_0 + 2E')] \\ H_{y1}^2 &= (g_e/g_y)^2 [(H_0 - D' - E')(H_0 - 2E')] \\ H_{z1}^2 &= (g_e/g_z)^2 [(H_0 - D')^2 - (E')^2] \\ H_{x2}^2 &= (g_e/g_x)^2 [(H_0 + D' - E')(H_0 - 2E')] \\ H_{y2}^2 &= (g_e/g_y)^2 [(H_0 + D' + E')(H_0 + 2E')] \\ H_{z2}^2 &= (g_e/g_z)^2 [(H_0 + D')^2 - (E')^2] \end{aligned}$$

where  $H_0 = h\nu/g_e$ ,  $D' = D/g_e$ ,  $E' = E/g_e$  and  $H_{x1}$  and  $H_{x2}$  are for example the  $\Delta M = \pm 1$  resonance field, when the magnetic field is along the  $x$ -direction,  $g_e$  is the free electron  $g$ -value. In addition, a signal corresponding to  $\Delta M = \pm 2$  transition should also be observed when  $D < h\nu$ .

$[\text{Cu}(\text{dien})\text{H}_2\text{O}](\text{ClO}_4)_2$ : This complex shows an axial spectrum typical of monomeric copper(II). The half-field signals were not detected in room temperature as well as liquid nitrogen temperature hence the complex does not suggest spin-spin interaction. The spectra under discussion show lines as:  $H_1$ , 3115 G;  $H_{z1}$ , 3000 G;  $H_{z2}$ , 3185 G. From these resonance field the  $g$ -values are obtained as:  $g_{\perp} = 2.089$  and  $g_z (g_{\parallel}) = 2.104$ . The value of  $g$  is less than 2.3, thereby indicating a covalent nature<sup>9</sup> of the complex.

$[\text{Cu}(\text{dien})\text{imH}](\text{ClO}_4)_2$ : This complex exhibits epr characteristics commensurate with  $S = 1$  system, the signal for  $\Delta m_S \pm 2$  was absent in either temperature spectra. The epr spectra at room temperature as well as liquid nitrogen temperatures are shown in Fig. 1. The observed epr parameters are given in Table 1. The zero-field splitting parameters ( $D$  and  $E$ ) and copper-copper distance ( $R$ ) are also presented in

Table 1. Elemental analysis data and epr parameters for the  $\text{Cu}^{\text{II}}$  complexes\*

Sl. no.	Compd. (colour, yield%)	Analysis% : Found/(Calcd.)		Temp.**	$g_{\perp}$	$g_z (g_{\parallel})$	$D(\text{G}) (\text{cm}^{-1})$	$E(\text{G})$	$R (\text{Å})$	$G$
		Cu	Ni							
1.	$[\text{Cu}(\text{dien})\text{H}_2\text{O}](\text{ClO}_4)_2$ (Blue, 65)	16.58	-	RT	2.089	2.104	-	-	-	-
		(16.56)	-	LNT	2.092	2.099	-	-	-	-
2.	$[\text{Cu}(\text{dien})\text{imH}](\text{ClO}_4)_2$ (Blue, 70)	14.67	-	RT	2.134	2.188	311	23.93	4.75	1.40
		(14.65)	-	LNT	2.141	2.191	317	25.68	4.70	1.35
3.	$[(\text{dien})\text{Cu}(\text{im})\text{Cu}(\text{dien})](\text{ClO}_4)_3$ (Blue, 60)	18.19	-	RT	2.157	2.232	265	45.04	5.06	1.47
		(18.18)	-	LNT	2.147	2.232	262	49.99	5.12	1.57
4.	$[(\text{dien})\text{Cu}(\text{im})\text{Ni}(\text{dien})](\text{ClO}_4)_3$ (Blue, 60)	9.16	8.48	RT	2.048	-	-	-	-	-
		(9.15)	(8.46)	LNT	( $g_{\text{iso}}$ ) 2.053	-	-	-	-	-

\*All compounds gave satisfactory C, H and N analyses. \*\*RT = Room temperature, LNT = liquid nitrogen temperature.

Table 1. The values of the  $E$  and  $R$  are found to be less than that of imidazolate binuclear complex. The value of  $G^{10}$  for the present complex is less than 4 (Table 1), suggesting the presence of interaction in the solid complex.

$[(dien)Cu(im)Cu(dien)](ClO_4)_3$ : The epr spectra of this complex are presented in Fig. 2. There is no apparent difference in either the spectral features or the spectral parameters at the two temperatures (RT and LNT). In a binuclear complex of the type under discussion, one would look for the interaction between the unpaired spins on the two copper ions<sup>5</sup>. The spectra also  $\Delta M_s = \pm 2$  transition at  $\sim 1600$  G. The value  $g_{\perp}$  is calculated as 1.47. The presence of half-field and less value of  $G$  than 4 are evidently due to copper-copper interaction<sup>10</sup>. The values of zero-field parameters ( $D$  and  $E$ ) and copper-copper distance have also been evaluated (Table 1).

$[(dien)Cu(im)Ni(dien)](ClO_4)_3$ : The complex gives sharp epr spectral features at room temperature as well as liquid nitrogen temperature. In this binuclear complex there is no apparent difference in either the spectral features and parameters at the two temperatures. Also the spectra are isotropic ( $g_{ISO} = 2.048$ , Table 1).

We also recorded the epr spectrum of this complex in 100% DMSO at liquid nitrogen temperature and evaluated the epr parameters. Spectra could be fitted for  $g_{\parallel} > g_{\perp}$  from which it can be attributed that the ground state for copper(II) ion is  $d_{x^2-y^2}$ . Epr parameters and bonding coefficients are as follows:  $g_{\parallel}$ , 2.111;  $g_{\perp}$ , 2.037;  $A_{\parallel}$ , 190 G;  $\alpha^2$ , 0.75;  $\alpha^{-2}$ , 0.34;  $\beta^2$ , 0.81;  $\beta^{-2}$ , 0.53;  $a$ , 2.16;  $b$ , 0.36. The value of  $g_{\parallel}$  is less than 2.3, thereby indicating the covalent environment<sup>9</sup>. Also the value of out-of-plane  $\sigma$ -bonding ( $\alpha^2$ ) shows the covalent character of complex. The other bonding parameters extract the same covalent behaviour of the complex.

## Experimental

Diethylenetriamine, imidazole (both S.D. Finechem), copper perchlorate hexahydrate and nickel perchlorate hexahydrate (both Aldrich) were used as supplied. Other chemicals used were of reagent grade.

### Preparations of complexes:

$[Cu(dien)H_2O](ClO_4)_2$ : A mixture of  $Cu(ClO_4)_2 \cdot 6H_2O$  (2 mmol) and dien (2 mmol) in methanol-acetonitrile (5 : 1, 50 ml) medium was stirred well and left overnight. The resulting blue crystals of  $[Cu(dien)H_2O](ClO_4)_2$  were washed with ethanol and dried under reduced pressure at room temperature, yield 65%.

$[Cu(dien)imH](ClO_4)_2$ : A mixture of  $Cu(ClO_4)_2 \cdot 6H_2O$  (2 mmol), dien (2 mmol) and imH (2 mmol) in methanol-acetonitrile (5 : 1, 50 ml) medium was stirred well and left

overnight. The resulting blue crystals of  $[Cu(dien)imH](ClO_4)_2$  were washed with ethanol and dried under reduced pressure at room temperature, yield 70%.

$[(dien)Cu(im)Ni(dien)](ClO_4)_3$ : A mixture of  $Cu(ClO_4)_2 \cdot 6H_2O$  (2 mmol), dien (2 mmol) and imH (2 mmol) in methanol-acetonitrile (5 : 1, 50 ml) medium was stirred well (solution A). Similarly, a mixture of  $Ni(ClO_4)_2 \cdot 6H_2O$  (2 mmol) and dien (2 mmol) in methanol-acetonitrile medium was stirred well (solution B). Solutions A and B were then mixed together, stirred well, its pH was raised to 12.0 by adding 1 M NaOH solution and left overnight. The resulting blue crystals of  $[(dien)Cu(im)Ni(dien)](ClO_4)_3$  were washed with ethanol and dried under reduced pressure at room temperature, yield 60%.

The epr spectra were recorded with a Varian E-line Century Series spectrometer equipped with a dual cavity operating at X-band with 100 kHz modulation; TCNE ( $g = 2.00277$ ) was used as field marker. The frozen samples were placed in a Varian liquid nitrogen Dewar flask for measurement at 77 K. The  $g$  and  $A$  values were measured according to the standard procedure<sup>11</sup>. The epr spectra of frozen samples did not exhibit well-resolved  $g_{\perp}$ . The  $g$  values at the maximum absorption ( $g_m$ ), which is close to  $g_{\perp}$ <sup>12</sup> were measured instead. Bonding parameters were evaluated by the reported method<sup>12</sup>.

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## Note

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