

ESR Studies on the Copper(II) Complexes of Phenothiazines

JAYARAMA* & M VIOLET D'SOUZA

Department of Chemistry, University of Mysore,
Manasagangotri, Mysore 570 006

Received 18 June 1985; revised and accepted 22 August 1985

Copper(II) forms six coordinated paramagnetic complexes with phenothiazines. ESR spectra of the complexes have been studied with a view to assigning their stereochemistries. Various ESR parameters have been calculated. The g , A , G and P values for all the complexes are consistent with a distorted octahedral stereochemistry in all the Cu(II) complexes of phenothiazines.

In our earlier studies, we have reported the complexes of Cu(II)¹⁻², Pd(II)³, Hg(II)⁴ and Pt(II)⁵ with phenothiazines and analogous compounds. In continuation of our work, we report here the ESR spectral data on the paramagnetic copper(II) complexes of phenothiazine (PZ), chlorphenothiazine (CZ), diethazine (DZ), promethazine (PRZ), fluphenazine (FPZ), chlorpromazine (CPZ), mepazine (MZ) and promazine (PMZ).

Copper(II) complexes of phenothiazines were prepared by the method reported earlier¹. The ESR spectra of the complexes at room temperature (RT) and liquid nitrogen temperature (LNT) were recorded at the Sophisticated Instrumentation Centre, IIT, Madras using an X-band Varian E-4 spectrometer with 100 kHz modulation.

Copper(II) forms six coordinated paramagnetic 1:2 complexes with monodentate PZ and CZ and 1:1 complexes with other phenothiazines. PZ and CZ use their heterocyclic nitrogen while other phenothiazines use both heterocyclic and tertiary amino nitrogens as the binding sites in their reaction with CuCl₂. All the

complexes contain two molecules of coordinated water.

The ESR spectra of polycrystalline powder samples of PZ, CZ, DZ and CPZ complexes of copper (undiluted) exhibited similar spectral feature (Fig. 1). All the complexes show ESR spectra with $g_{\parallel} > g_{\perp}$ characteristic of a tetragonally distorted octahedral geometry with $d_{x^2-y^2}$ orbital lowest in energy. Various parameters have been calculated by the method of approximation suggested by Kneuhl⁶ and Garmen⁷ and the values are given in Tables 1 and 2. The g_{\parallel} and g_{\perp} values obtained in these complexes suggest that the principal axes of the octahedra are parallel to each other and all the sites are equivalent in every orientation in the static magnetic field. The powder ESR and the acetone solution ESR spectra at RT gave nearly the same g_{av} values showing that the equilibrium symmetry around Cu(II) for these complexes in solution is the same as in the solid state. In all the complexes, the g_{\parallel} values are less than 2.3 which show that the complexes are largely covalent. Further, the values are consistent with the mixed Cu-N and Cu-O bonded copper complexes. Since $G [(g_{\parallel} - 2)/(g_{\perp} - 2)]$

Table 1—ESR Data of Copper(II) Complexes of Phenothiazines in Polycrystalline State at RT

Sl No.	Complex	g_{\perp}	g_{\parallel}	g_{av}	G
(1)	(PZ) ₂ CuCl ₂ ·2H ₂ O	2.044	2.244	2.187	>4
(2)	(CZ) ₂ CuCl ₂ ·2H ₂ O	2.044	2.248	2.219	>4
(3)	(DZ)CuCl ₂ ·2H ₂ O	2.046	2.247	2.189	>4
(4)	(PRZ)CuCl ₂ ·2H ₂ O	2.045	2.288	—	>4
(5)	(FPZ)CuCl ₂ ·2H ₂ O	2.088	2.298	2.069	<4
(6)	(CPZ)CuCl ₂ ·2H ₂ O	2.043	2.249	2.185	>4
(7)	(MZ)CuCl ₂ ·2H ₂ O	2.047	2.155	2.083	<4
(8)	(PMZ)CuCl ₂ ·2H ₂ O	2.023	2.249	—	>4

Table 2—ESR Data at RT and LNT in Acetone Solution

Complex*	g_{\perp}	g_{\parallel}	g_{av}	A_{\perp} $\times 10^{-4}$ (cm ⁻¹)	A_{\parallel} $\times 10^{-4}$ (cm ⁻¹)	A_{av}	α^2	P (cm ⁻¹)
1	2.040	2.234	2.104	26	190	80.6	0.82	0.025
2	2.039	2.232	2.103	17	187	73.6	0.79	0.026
3	2.041	2.240	2.107	18	183	73.0	0.82	0.026
4	2.038	2.257	2.111	24	167	71.6	0.83	0.023
5	2.065	2.289	2.139	15	150	60.0	0.80	0.023
6	2.042	2.235	2.106	32	158	74.0	0.80	0.020
7	2.041	2.152	2.078	14	162	63.3	0.79	0.021
8	2.035	2.228	2.096	17	170	68.0	0.81	0.024

*Numbers as given in Table 1.

$g_{av} = 1/3 [2g_{\perp} + g_{\parallel}]$, $A_{av} = 1/3 [2A_{\perp} + A_{\parallel}]$.

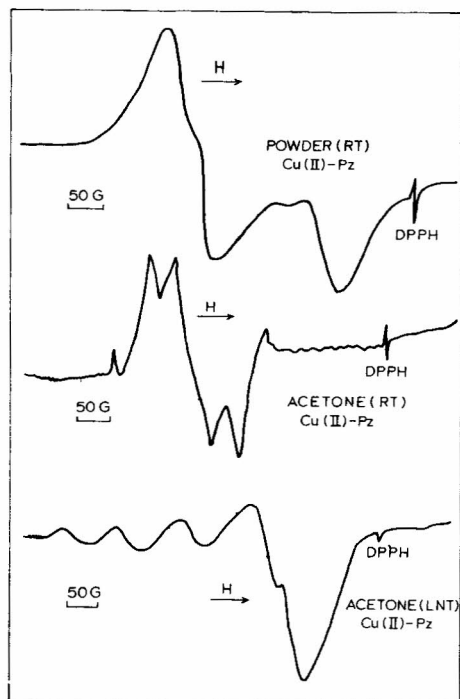


Fig. 1—ESR spectra of Cu(II)-Pz complex

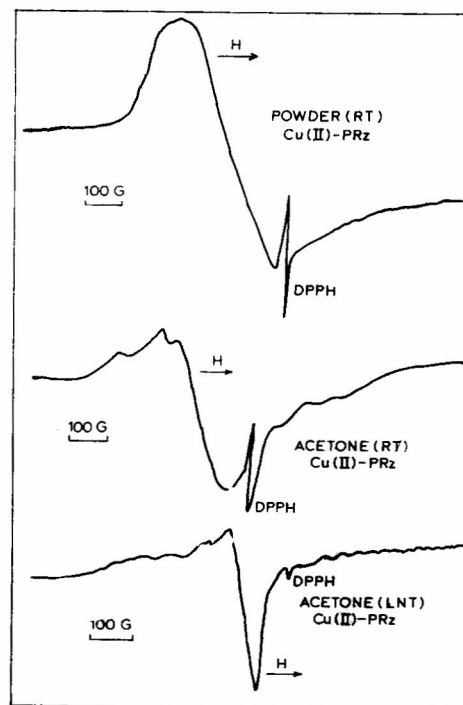


Fig. 2—ESR spectra of Cu(II)-PRz complex

–2)] value is higher than 4 in all the cases, exchange interactions are considered to be absent. Extra-fine structure was absent in the parallel and perpendicular components in the acetone frozen ESR spectra taken at LNT which indicates that the donor atoms involved in the complexes do not provide effectively the same field strength around Cu(II) ion at LNT.

On the other hand PRz and PMz complexes exhibited a pseudoisotropic spectra with only two g values. Acetone solution spectra at RT and at LNT were very poorly resolved. The poor resolution may be due to the low crystallinity of the complexes. However, acetone solutions of the complexes containing a little dilute HCl gave well resolved spectra (pure acetone solution spectra at RT and LNT are shown in Fig. 2). In these two complexes, the lowest g value is more than 2.03 and G is greater than 4; these facts are consistent with the presence of an unpaired electron in the $d_{x^2-y^2}$ ground state in an elongated axial symmetry^{8,9}.

FPz and Mz complexes of copper(II) exhibited normal orthorhombic ESR spectra (Fig. 3). In acetone solution, fine structure is observed in the perpendicular component while no hyperfine lines are observed in the parallel component. Exact reason for the appearance of this fine structure is not clear. However, it can be argued that one of the M–N bonds in these complexes (probably in the perazine ring) is longer than the other one resulting in the resolution of only the perpendicular component. Interestingly, in these complexes G is less than 4 suggesting the presence of an

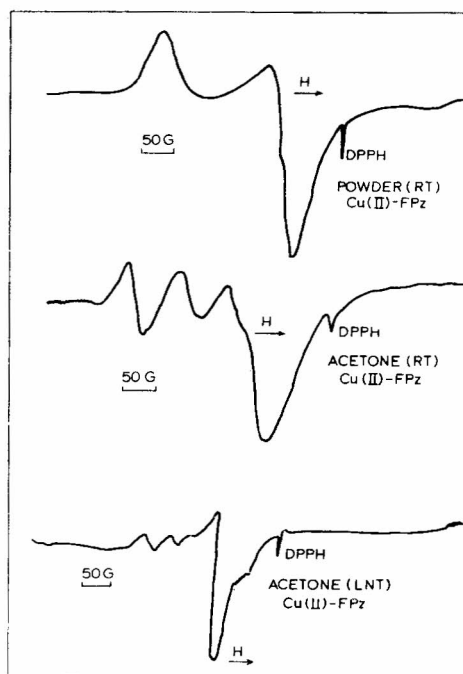


Fig. 3—ESR spectra of Cu(II)-FPz complex

exchange coupling and misalignment of the local tetragonal axes.

In all the complexes under study, the calculated α^2 values show that the bonds are largely covalent in nature. The dipolar term P , calculated for the present

complexes using the standard equation, is found to be between 0.022 and 0.026, in agreement with the bonding of copper(II) to two N atoms and two O atoms. In conclusion, it may be stated that the differences in ESR line shapes and behaviour of copper(II) complexes of phenothiazines might be due to the specific structural differences in the phenothiazine moiety.

The authors thank Prof. G. Aravamudan, IIT, Madras and Prof. C.C. Patel, IISc, Bangalore for their help and useful suggestions.

References

- 1 Sankegowda H & Jayarama, *J inorg nucl Chem*, **43** (1981) 2329.
- 2 Sankegowda H & Jayarama, *Curr Sci*, **50** (1981) 569.
- 3 Sankegowda H & Jayarama, *J less-common Metals*, **72** (1980) 37.
- 4 Jayarama, Thimmaiah K N & Violet D'Souza M, *J Indian chem Soc*, (in press).
- 5 Jayarama, *Structural studies on the complexes of copper, palladium and platinum with phenothiazines*, Ph.D. Thesis, Mysore University, 1979.
- 6 Knebuhl F K, *J chem Phys*, **33** (1960) 1074.
- 7 Garmen H R & Swallen J D, *J chem Phys*, **56** (1962) 3221.
- 8 Hathaway B J & Billing D E, *Coord Chem Rev*, **5** (1970) 143.
- 9 Hathaway B J & Tomlison A A G, *Coord Chem Rev*, **5** (1970) 1.