Asian Journal of Chemistry Vol. 3, No. 4 (1991), 408-415

Electron Spin Resonance Spectral Studies of Some Copper-Oximates

K. RAJAKRISHNA, K. G. MALLIKARJUN AND R. SESHADRI NAIDU*

Chemistry Department, S. V. University,
Tirupati—517 502, India

Cu(II) chelates of *o*-hydroxyacetophenoneoxime, resacetophenoneoxime, peonoloxime and 2-hydroxy-1-naphthaldoxime have been prepared. Analysis shewed 1:2 metal to ligand stoichiometry and chelation occurs by the replacement of the hydrogen of the phenolic OH and coordination through the nitrogen of the oxime group. ESR spectral studies have been made on dimethyl formamide solutions of these chelates at room as well as liquid nitrogen temperatures. At low temperature the interaction between the unpaired electron and each copper isotope (Cu^{63}, Cu^{65}) was detected. Cu-2-hydroxy-1-naphthaldoxime chelate showed only a single broad line at room temperature but a well resolved spectrum was observed at LNT. Electronic spectra of the chelates taken in nujol mull and in DMF indicates interaction of the solvent in the axial plane.

INTRODUCTION

Electron Spin resonance has been widely used to investigate the covalent character of metal-ligand bonding in Cu(II) complexes with organic ligands containing oxygen and nitrogen donor atoms[1-4]. Physiological studies[5] carried out on several *o*-phenolic oximes and their Cu(II) chelates in our laboratories on germination of mungbeen seedlings indicated that the ligands as well as their copper chelates caused inhibition of the seedling growth due to enzymatic activity. They were also found to inhibit the bio-synthesis of water soluble vitamines, pyridoxine and vitamin-C. The above investigations prompted to study the ESR spectra of some copper chelates of *o*-phenolic oximes having (CuO_2N_2) chromophore. These copper chelates were studied to serve as model compounds for the investigation of nature of Cu(II) binding in more complicated biological systems such as those of copper amino acid and copper protein molecules.

EXPERIMENTAL

Cu(II) chelates of 2-hydroxyacetophenoneoxime, resacetophenoneoxime, peonoloxime, and 2-hydroxy-1-naphaldoxime were prepared according to the procedures described in our earlier communication[6,7]. The purity of these was determined by elemental analyses and metal content determination. A Shimadzu Uv-180. Spectrophotometer was used to record electronic spectra in nujol mull and dimethylformamide at room temperature. ESR spectra of the chelates in polycrystalline form and in solution were recorded using varian E 4x-band spectrometer which was operated at a frequency of 9.09 G Hz. The spectra were recorded at room temperature as well as liquid nitrogen temperature (77°K) in dimethyl formamide solvent. DPPH was used as the g marker.

RESULTS AND DISCUSSION

The electronic spectra of the present chelates in DMF exhibit a single broad and weak absorption band around 18.18 to 19.04 kK which may be assigned to d-d transitions of copper(II) in a tetragonal field.[8] The maximum was observed at higher region in nujol mull spectra of the polycrystalline samples. The shift d–d transition towards lower region in DMF solution can be attributed to the weak interaction of the solvent with the chelate along the *Z*-axis.[9]

The ESR spectra of complexes in polycrystalline form at room temperature exhibit only one line (Fig. 1). Whereas the room temperature ESR spectra of copper oxime chelates in DMF (Fig. 2) exhibit several interesting features. Except for Cu-2-hydroxy-1-naphthaldoxime, spectra of all the other three chelates consist of four apparently equally spaced absorption lines. These four lines in the multiplet correspond to the (2I + 1 = 4) Spin orientations of the copper nuclei with I = 3/2. The hyperfine structure in the solution is resolvable even at room temperature is of some interest since Bagguely and Griffiths[10] found it impossible to resolve the hyperfine structure in dilue copper Tutton salts at room temperature due

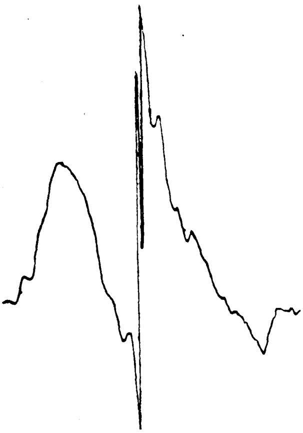

Fig. 1 ESR spectrum of Cu-2-hydroxy-acetophenoneoxime in powder

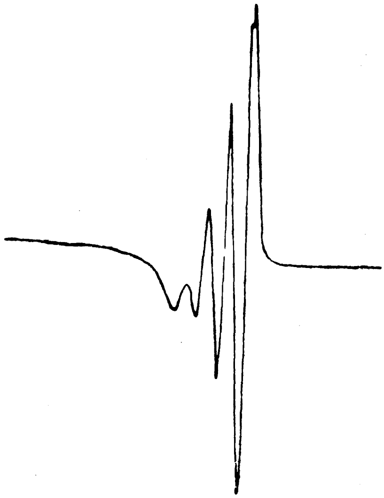

Fig 2 ESR spectrum of Cu-2-hydroxyacetophenoneoxime in DMF at RT

to a short spin-lattice relaxation time. Measurement on the resonance of $[Cu(NH_3)_4]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ ions in water solutions have also shown no hyperfine structure.[11] Apparently the spin-lattice relaxation times in the present copper oxime chelates are greater than in the ionic Tutton salts. This may be caused by much stronger bonds between the copper and its neighbours with the result that the oscillational frequencies are much higher giving a smaller Fourier component in the region of the resonance frequency. Cu-2-hydroxy-1-naphthaldoxime chelate did not give a four line spectrum at room temperature in DMF but showed only one line. However, a normal spectrum was obtained when the chelate was diluted with a diamagnetic zinc complex of this oxime. It would, therefore, appear that the anisotropic molecular reorientation of the chelate in solution is responsible for this. Unusual spectra of this type have been noted earlier for complexes bearing large organic ligand substituents[12,13]. At room temperature the expected nuclear interaction between the unpaired electron and each copper isotope (Cu^{63} and Cu^{65}) is not detected whereas at liquid nitrogen temperature the shoulders on the high field peaks were observed from the hyperfine interaction due to Cu^{65} nucleus.

The low temperature esr spectra of all the four chelates in DMF (Fig. 3–6) showed highly resolved hyperfine lines due to Cu(II). The low field part of the spectrum consisted of three of the four expected hyperfine lines and the fourth line overlapping with the high field line. These spectra are characteristic of axial symmetry. The spectrum is

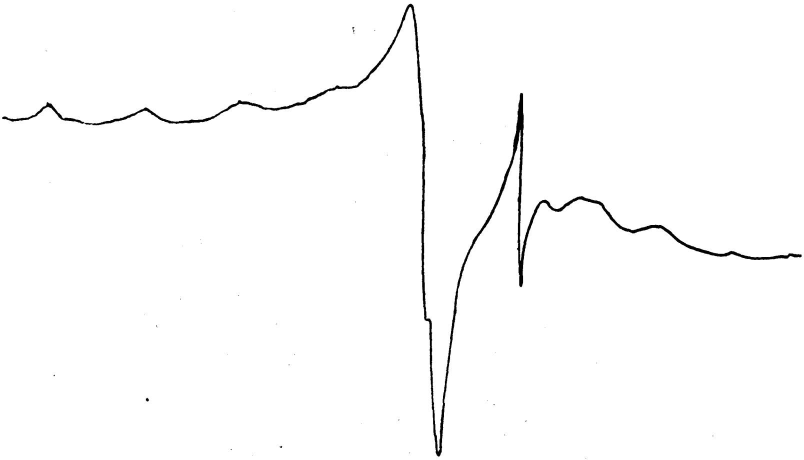

Fig. 3 ESR spectrum of Cu-2-hydroayacetophenoneoxime in DMF at LNT

Fig. 4 ESR spectrum of Cu-resacetophenoneoxime in DMF at LNT

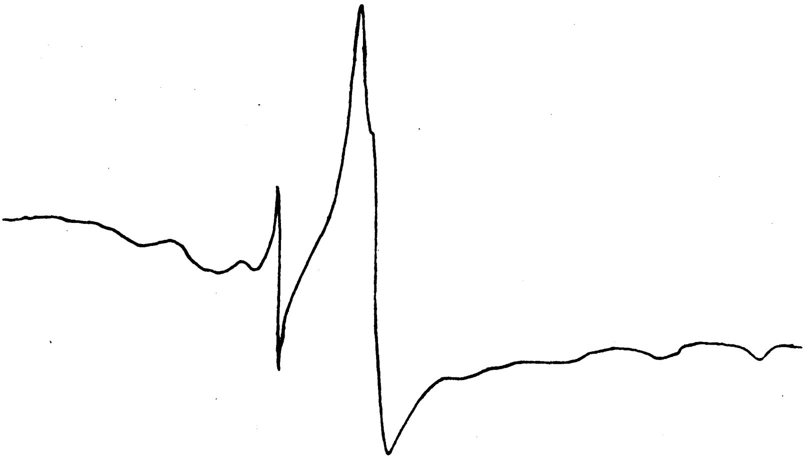

Fig. 5 ESR spectrum of Cu-phenoloxime in DMF at LNT

composed of two parts, the O = O (g_{11}) part and the $\theta = 90°$ (g_{1}) part where θ is the angle between H and the axis perpendicular to the coordination plane formed by the two oxygens and two nitrogens of the oxime molecule. Therefore the copper hyperfine line of the $m_I = -(3/2)$ of the g_{11} absorption overlapped with the g_1 part. No hyperfine structure due to the coordinating nitrogens could be resolved at room temperature or at LNT. Further there is variation in the widths of the low field absorption peaks at room and low temperatures. This suggests the contribution of spin-lattice relaxation to the line widths.

The esr data are presented in Table 1. The isotropic data were taken from the room temperature spectra and anisotropic data from frozen

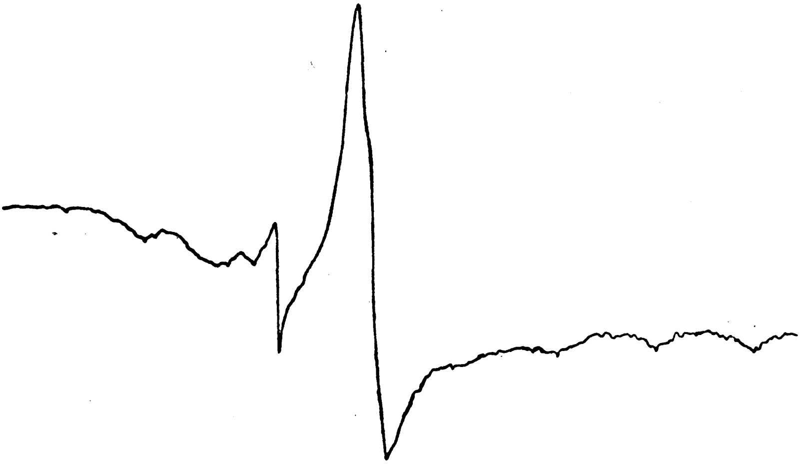

Fig. 6 ESR spectrum of Cu-2-hydroxy-1-naphthaldoxime in DMF at LNT

TABLE 1
ESR AND ELECTRONIC SPECTRAL DATA
OF COPPER-OXIMATE CHELATES

Chelates	g_0	g_{11}	g_1	$A_0(cm^{-1})$ $x10^{-4}$	$A_{11}(cm^{-1})$ $x10^{-4}$	$A_1(cm^{-1})$ $x10^{-4}$	max in DMF (kK)
$Cu(C_8H_8O_2N)_8$	2.123	2.248	2.061	56.17	150.91	8.80	18.18
$Cu(C_8H_8O_3N)_2$	2.124	2.249	2.061	54.84	148.74	7.90	19.04
$Cu(C_9H_{10}O_3N)_2$	2.145	2.254	2.060	51.98	141.62	7.17	18.18
$Cu(C_{11}H_8O_2N)_2$	2.146	2.292	2.073	50.44	135.23	8.06	18.52

solution spectra. Values of g_1 and A_1 were than calculated from the following equations

$$g_0 = 1/3\, g_{11} + 2/3\, g_1$$
$$A_0 = 1/3\, A_{11} + 2/3\, A_1$$

Kivelson and Neiman[14] have shown that g_{11} is a moderately sensitive function for indicating covalency. Normally g_{11} is 2.3 or more for ionic environment and it is less than 2.3 for more covalent environment. The present ESR results show that the bond between Cu(II) and the oxime moiety is more covalent in nature. Massacesi *et al*[15] reported that g_{11} is 2.3 — 2.4 for copper-oxygen bonds, 2.2 — 2.3 for copper-nitrogen bonds and mixed copper-nitrogen and oxygen systems and 2.1 — 2.2 for copper sulfur bonds. For the present copper-oxime complexes $g_{11} = 2.29 - 2.24$, in conformity with the presence of mixed copper-nitrogen and oxygen bonds in these chelates.

The parameter G defined as $(g_{11} - 2)/(g_1 - 2)$ is in the range 4.00 – 4.28 for the present chelates and is an evidence for the presence of $d_{x^2-y^2}$ ground state. This is also supported[16] by the low g values since for d_{z^2} ground state the low g value should be $\angle 2.04$. The esr parameters g_{11}, g_1,

TABLE 2

BONDING AND MAGNETIC PARAMETERS OF COPPER-OXIMATES

Complexα^2	α^2	α'^2	$\beta_1{}^2$	G	P (cm^{-1})	K	λ (cm^{-1})	μ (B.M.)
$Cu(C_8H_8O_2N)_2$	0.74	0.36	0.92	4.06	0.023	0.318	564	1.84
$Cu(C_8H_8O_3N)_2$	0.73	0.37	0.91	4.08	0.023	0.314	593	1.84
$Cu(C_9H_{10}O_3N)_2$	0.71	0.36	0.88	4.23	0.022	0.305	577	1.85
$Cu(C_{11}H_8O_2N)_2$	0.73	0.38	0.94	4.00	0.022	0.313	675	1.85

A_{11}, A_1 and absorption maxima from electronic spectra are used to evaluate the bonding parameters α^2, α'^2 β_2^1, P and the Fermi contact hyperfine interaction term K, α^2 measures the covalency of the in-plane σ bonds, β_1^2, of the in-plane π bonds. These parameters are close to 1.0 for ionic bonds and become smaller with increasing covalent bonding. α^2 can be calculated using the formula[14].

$$\alpha^2 = \frac{A_{11}}{p} + (g_{11} - 2.0023) + \frac{3}{7}(g_1 - 2.0023) + 0.004$$

Where $P = 0.036$ cm^{-1} for Cu^{2+} (free ion) and A_{11} is expressed in cm^{-1}. The α^2 values for the present complexes fall in the range 0.71 – 0.74, indicating appreciable in plane covalency. The α^2 values also indicate that the 4S contribution to the orbital bearing the unpaired electron is not considerable. The α^2 values are almost equal to those of copper chelates of salicylaldoxime ($\alpha^2 = 0.76$) and chalconeoximes ($\alpha^2 = 0.75$). This can be attributed to the presence of same amount of σ bond covalency probably due to hydrogen bonding of the oxime function in these systems. The value of α'^2 derived from α^2 using the expression.

$$\alpha^2 + \alpha'^2 - \alpha 2 \alpha' S = 1$$

Where S is the overlap integral between the metal and the normalised ligand orbitals. We have assumed the overlap integral value calculated by Assour[18]. $S = 0.093$ and the values of α'^2 are calculated.

The π bonding parameter β_1^2 may be obtained from the expression[17]

$$\beta_1^2 = -\frac{(A_0)}{PK} + (g_0 - 2.0023)/K$$

Where P = 0.036 cm^{-1}, K is the fermi contact term. The β_1^2 parameter is a measure of covalency of in plane π bonding. β_1^2 values of the present complexes suggest less covalent nature of in-plane π bonding.[18]

The parameter P has been used as a variable to absorb the effect of electron delocalization by use of the expression.[19]

$$P = \frac{A_{11} - A_1}{(g_{11}{}^{-2}) - \frac{5}{14}(g_1 - 2)} - \frac{6}{7}$$

The identification of the bonding groups may be obtained from the values of P i.e. for bonding to four sulphor atoms P lies in the range 0.026 – 0.016 cm^{-1} and for bonding to two nitrogen and two oxygen atoms the values of P obtained for the copper-oxime complexes are found to be 0.022 – 0.029 cm^{-1} and are consistent with bonding of Cu(II) to two nitrogens and two oxygens (CuO_2N_2 chromophere). Fermi contact interaction term K is obtained from the expression[20]

$$K = \frac{A_0}{\rho\beta_1^2} + \frac{g_0 - 2.0023}{\beta_1^2}$$

Where the free ion diploar term $P = g_e g_N B_e B_N (r^{-3}) = 0.036$. β_1^2 is assumed as one. K is a dimensionless quantity which is a measure of the contribution of 'S' electrons to the hyperfine interaction and is generally found to have a value of about 0.3. The magnetic moment (μ) of the chelates has been evaluated using ESR parameters and the calculated values are in good agreement with the experimental ones. The spin-orbit coupling constant for the complexes is found to be less than that of the free metal ion ($\lambda_0 = -828$ cm^{-1}) indicating considerable mixing of ground and excited terms.

ACKNOWLEDGEMENTS

The authors thank the Head, RSIC, IIT, Madras for recording ESR spectra and Prof. R. Raghava Naidu for valuable suggestions.

REFERENCES

1. B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).
2. L. A. Zyzyck, H. Frummer and J. F. Villa, *J. Inorg. Nucl. Chem.*, **37**, 1653 (1975).
3. D. W. Smith, *J. Chem. Soc.*, A, 3108 (1970).
4. C. Natarajan and M. Palaniondavar, *Transition Met. Chem.*, **8**, 229 (1983).
5. C. Vinayasree, M. Phil. thesis, S. V. University, Tirupati (1984).
6. R. Seshadsi Naidu, A. Ramesh and R. Raghava Naidu, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **89**, 417 (1980).
7. V. Suresh Babu, A. Ramesh, P. Raghuram and R. Raghava Naidu, *Polyhedron*, **1**, 607 (1982).

8. B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
9. R. L. Belford, M. Calvin and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).
10. D. M. S. Bagguley and J. H. E. Griffiths, *Proc. Phys. Soc. London*, **A65**, 594 (1952).
11. A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, **68**, 2316 (1964).
12. J. J. Stoklosa, H. L. Huffman and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **37**, 1397 (1975).
13. D. K. Johnson, H. J. Stoklosa, J. R. Wasson and G. L. Seebach, *J. Inorg. Nucl. Chem.*, **37**, 1397 (1975).
14. D. Kivelson and R. Neiman, *J. Chem. Phys.*, **29**, 35 (1958).
15. M. Massacesi and G. Ponticelli, V. Buddha and V. G. Krishnan, *J. Mol. Struct.*, **41**, 55 (1978).
16. J. M. Assour, *J. Chem. Phys.*, **43**, 2477 (1965).
17. J. I. Zink and R. S. Drago, *J. Am. Chem. Soc.*, **94**, 4550 (1972).
18. V. C. Swett and E. P. Dudek, *J. Phys. Chem.*, **72**, 4 (1968).
19. G. Giordana and R. D. Bereman, *J. Am. Chem. Soc.*, **96**, 1019 (1974).
20. S. H. Laurie, T. Lund and J. B. Raynor, *J. Chem. Soc.*, 1398 (1975).

[*Received*: 22 January 1990; *Accepted*: 10 July 1990] AJC–206