Asian Journal of Chemistry Vol. 20, No. 6 (2008), 4397-4404

Synthesis and Spectroscopic Studies of Dichloromono-(1-*n*-butylamidino-O-methylurea)copper(II), Dichloromono(1-*i*-butylamidino-O-methylurea)copper(II) and Dichloromono-(1-*i*-butylamidino-O-ethylurea)copper(II) Complexes

O. IBOPISHAK SINGH†, A. BIMOLA DEVI‡,
R.K. HEMAKUMAR SINGH* and R.M. KADAM§
Department of Chemistry, Manipur University, Imphal-795 003, India
Fax: (91)(385)2435145; E-mail: rkhemakumar@rediffmail.com

Electron paramagnetic resonance studies of dichloro(1-*n*-butylamidino-O-methylurea)copper(II) (**1**), dichloro(1-*i*-butylamidino-O-methylurea)copper(II) (**2**) and dichloro(1-*i*-butylamidino-O-ethylurea)copper(II) (**3**) complexes were carried out in the temperature range 300-77 K. In complexes **1** and **2** apart from a strong signal at g ~ 2.0711 a weak half field signals ($\Delta M_s = \pm 2$) were also observed suggesting the formation of dimeric complexes. The photo acoustic spectra of the complexes had shown a band around 25000 cm^{-1} suggesting weak metal-metal interactions. The EPR spectral features of complex **3** are characteristic of axial symmetry and the hyperfine structure on parallel components of Cu^{2+} species is resolved. The EPR spectra at 77 K in pyridine has shown axial ligation of solvent molecules. The high magnetic moment values of complexes **1** and **2** had given evidence for the formation of ferromagnetically coupled Cu^{2+} dimers.

Key Words: EPR, Photo acoustic spectra, Dimer, *n*-Butyldicyandiamide, *i*-Butyldicyandiamide.

INTRODUCTION

Metal-metal interaction in organometallic complexes particularly those of *d*-electron systems have been the subject of many investigations for a long time[1-5]. The main interest of such investigations is to elucidate metal-metal interaction among *d*-electron systems and also to get insight into the structural aspects by electron paramagnetic resonance (EPR), with special reference to investigate the nature of coupling in dimeric complexes. Whenever, the symmetry at all the paramagnetic ions is identical and exchange

---

†Department of Chemistry, Modern College, Imphal-795 001, India.
‡Department of Chemistry, Churachandpur College, Churachandpur-795 128, India.
§Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai-400 085, India.

interaction mediated through a shared ligand, there is a greater possibility of formation of antiferromagnetically coupled dimers. On the other hand, if neighbouring ions have different site symmetries, the formation of dimers with ferromagnetic interaction is favoured. Some aspects of special interest in these investigations are to unravel the nature of interactions that coupled magnetic ions forming a dimer *viz.*, to distinguish between exchanged coupled dimers and dipole coupled dimers In our earlier paper[6], the EPR studies of dichloromono (1-phenylamidino-O-alkylurea)copper(II) complexes (alkyl = Me, Et, Pr, Bu and Pe) have shown that the comlexes exist as monomers having square planar structure at the copper site and clear evidence for the magnetic field induced molecular alignment in field cooled samples (R = Et) having degree of alignment estimated to be around 20 %. As a part of our investigations on the alcoholysis of nitrile group ligands in the presence of metal ions[7-9] we have synthesized and discussed spectroscopic and magnetic susceptibility studies on the dichloro(1-*n*-butylamidino-O-methylurea)copper(II), dichloro(1-*i*-butylamidino-O-methylurea) copper(II) and dichloro(1-*i*-butylamidino-O-ethylurea)copper(II) complexes.

EXPERIMENTAL

All chemicals used were of analytical grade. *n*-Butyldicyandiamide and *i*-butyldicyandiamide were prepared according to the literature method[10].

IR spectra (KBr disks) were recorded on a Shimadzu FT-IR-8400S and solution absorption spectrum was recorded on a Lamda 35UV-Visible spectrophotometer. Photoacoustic spectra on solid samples were recorded using home made spectometer in 350-800 nm range using Tungsten halogen lamp as a source. EPR spectra of the complexes in solid and solution (Py) at 300 K and 77 K were recorded using Bruker ESP-300 spectrometer at the X-band frequency (9.5 GHz). The molar conductivity was determined by Systronics conductivity meter 306. Magnetic susceptibility was measured on a vibrating sample magnetometer (VSM) at room temperature.

Preparation of complexes

Dichloromono(1-*n*-butylamidino-O-methylurea)copper(II): *n*-Butyldicandiamide (1 mol) and copper(II) chloride dihydrate (1 mol) were dissolved in 50 mL of dry MeOH and refluxed on a steam bath for 24 h and kept in a refrigerator overnight. A green complex that crystallized out was washed by MeOH, acetone and dried in air. (yield 80 %) decomposition temperature 200 ºC.

Dichloromono(1-*i*-butylamidino-O-methylurea)copper(II): *i*-Butyldicyandiamide (1 mol) and copper(II) chloride dihydrate (1 mol) were dissolved in 50 mL MeOH and refluxed on a steam bath for 20 h. It was kept in a refrigerator. A green complex has collected, washed with MeOH, finally by acetone and dried in air (yield 90 %) m.p. 180 ºC.

Dichloromono(1-*i*-butylamidino-O-ethylurea)copper(II): 1-*i*-Butyldicyandiamide (1 mol) and copper(II) chloride dihydrate (1 mol) were dissolved in 50 mL EtOH and refluxed on a steam bath for 12 h. It was kept in a refrigerator. A green complex was collected, washed with EtOH, finally by acetone and dried in air (yield 88 %) m.p. 165 ºC.

RESULTS AND DISCUSSION

The complexes obtained are microcrystalline coloured compounds, whose melting points are higher than that of the free ligands. They are stable at room temperature and insoluble in common solvents except the complex **3** which is soluble in pyridine only. The molar conductivity in pyridine is 4.98 Ω^{-1} cm^2 mol^{-1} showing non-electrolytic nature[11].

Pure *n*-butyl and *i*-butyldicyandiamides show a strong (C≡N) band[12-14] at 2176 and 2154 cm^{-1} and a band at *ca.* 1615 cm^{-1} for the azomethine (C=N) group. When complexed with copper(II) in the presence of ROH, the free nitrile was completely absent and hence the possibility of the guanylurea structure[15-17] was ruled out. The decrease in ν(C=N) on complexation indicates coordination of the butylamidine C=N group, lowering the ν(C=N) band at *ca.* 1578 cm^{-1} which is supported by lowering the ν(C–N) band[13]. The increased value of ν(C=N) to *ca.* 1673 cm^{-1} in all the complexes, is presumably due to the change in the C=N bond order, on coordination through the nitrogen atom, facilitated by transfer of electron density from the C-O-C moiety. The electron density on the N=C-O-C fragment of the ligand is more delocalized in complexes and the =C-O-bond order is raised[7,9]. The complexes show a ν_s(C-O-C) stretch at *ca.* 1200 cm^{-1} and ν_a(C-O-C) at *ca.* 960 cm^{-1} indicating that alcohol addition reaction has taken place. The stretching band at 280-265 cm^{-1} suggests the presence of Cu-Cl bonding which supports the formation of dichloro-mono (ligand) copper(II) complexes.

For complexes **1** and **2** room temperature magnetic moments are 2.73 and 2.83 BM, respectively. The higher values of magnetic moment suggest that the two copper ions are ferromagnetically coupled. The photo acoustic spectra of the complexes **1** and **2** (Fig. 1b and 1c) exhibit a broad band at *ca.* 16000 and 16393 cm^{-1} due to *d-d* transition and weak absorption band around 26000 cm^{-1} indicating the possibility of metal-metal bonding[7]. The photo acoustic spectrum of antiferromagnetic coupled copper acetate (S=O ground state) exhibited an absorption around 26500 cm^{-1} typical of metal-metal bonding (Fig. 1a) in addition to a broad *d-d* band around 16400 cm^{-1}. The optical absorption spectrum of complex **3** in pyridine shows *d-d* transition around 13655 cm^{-1} suggesting distorted octahedral structure[6].

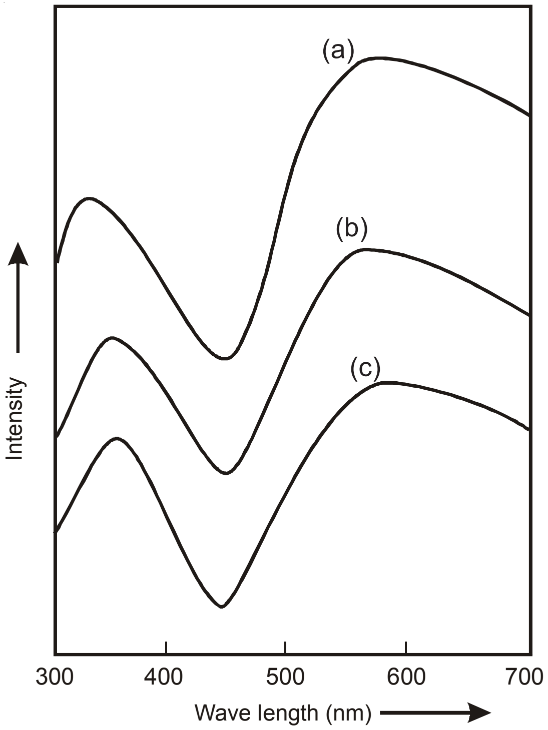


Fig. 1. Absorption spectrum of (a) copper acetate (b) dichloro-(1-*n*-butylamidion-O-methylurea)copper(II) and (c) dichloro-(1-*i*-butylamidino-O-ethylurea) copper(II) complexes using PAS

TABLE-1
CHARACTERIZATION DATA OF DICHLOROMONO (LIGAND) COPPER(II) COMPLEXES

Compound / (colour)	Elemental analysis %: Found (Calcd.)				μ_{eff} (BM)
	C	H	N	Cu	
Complex **1** (Light green)	25.90 (25.80)	5.55 (5.54)	17.20 (17.26)	19.60 (19.58)	2.73
Complex **2** (Light green)	25.87 (25.88)	5.60 (5.54)	17.70 (17.26)	19.61 (19.58)	2.83
Complex **3** (Green)	28.36 (28.35)	5.96 (5.90)	16.50 (16.54)	18.80 (18.76)	1.98

The EPR spectra of the Cu(II) complexes were recorded at X-band in the solid state at room temperature (300 K) and liquid nitrogen temperature (77 K). The g-values are given in Table-2. At room temperature the EPR

TABLE-2
EPR PARAMETERS OF THE DICHLOROMONO (LIGAND) COPPER(II) COMPLEXES IN THE SOLID STATE AT 300 K

Compound	$g_{\parallel}$	$g_{\perp}$	g_{av}
Complex **1**	2.4336	2.0798	2.1652
Complex **2**	2.4209	2.0711	2.1877
Complex **3**	2.1794	2.0615	2.1008

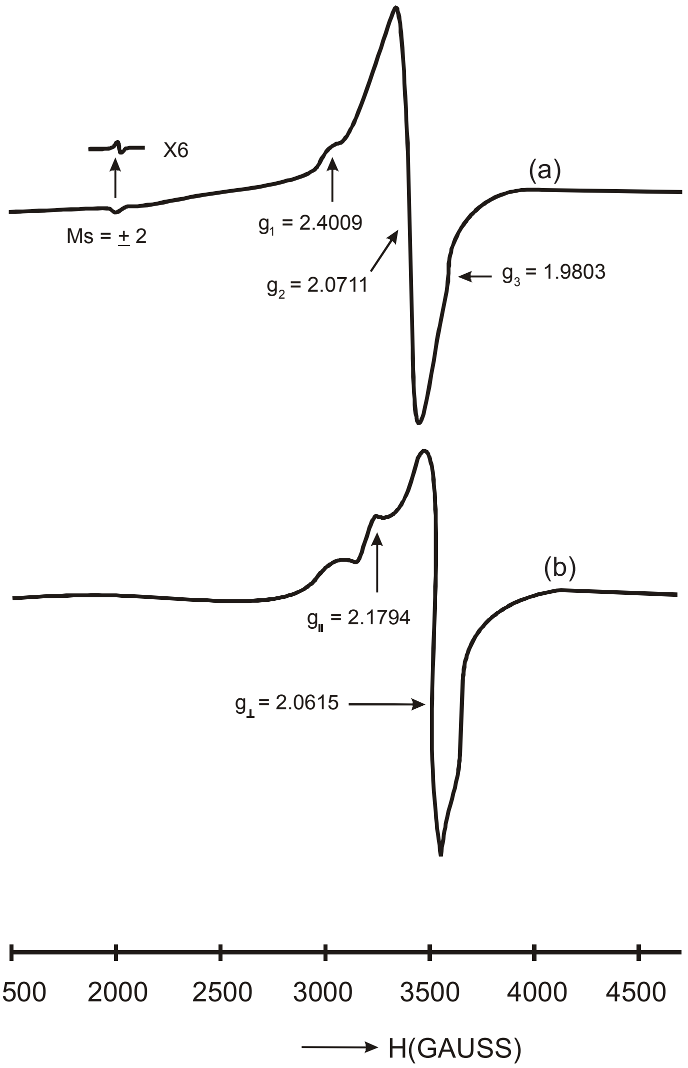


Fig. 2. EPR spectrum of (a) dichloro-(1-*i*-butylamidino-O-methylurea)copper(II) and (b) dichloro-(1-*i*-butylamidino-O-ethylurea)copper(II) complexes at 300 K

spectra of the complexes **1** and **2** consisted of a single asymmetric derivative centred around $g_{\perp} = 2.0711$ with a wide parallel component around $g_{||} = 2.4209$. A shoulder (g = 1.9803) on the high field side of signal is also observed. In addition relatively very weak signal $\Delta M_s = \pm 2$ observed at 1600G (g~ 4.23) indicating formation of exchange coupled dimers. Since the $g_{||} > g_{\perp} > \pm 2$ in all the Cu complexes the unpaired electron in copper has predominantly $d_{x^2-y^2}$ character. EPR spectra of the complexes **1** and **2** at 77 K showed no change in the g-values but an increase in their intensities which suggest the ferromagnetic interaction.

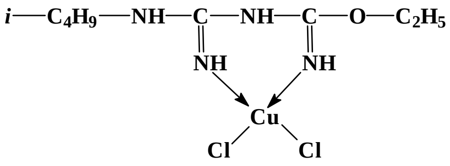
Since the complexes **1** and **2** are insoluble in organic solvents, its solution spectra could not be investigated. It is pertinent to mention here that the EPR studies on the solid copper(II) binuclear complexes of 1-phenylamidino-O-alkylurea (alkyl = *n*-propyl, *n*- and *i*-butyl) with 1,3-diaminopropane or ethylenediamine at room temperature consisted of fine-structure transitions ($\Delta M_s = 1$) with zero field splitting of 0.0500 cm and a half-field signal ($\Delta M_s = 2$) at *ca.* 1600 G, suggesting the formation of binuclear complexes (S = 1). The formation of ferromagnetically coupled copper binuclear complexes was further confirmed from the high magnetic moment values at room temperature. The present report on the dichloro-(1-*n*-butylamidino-O-methylurea)copper(II) and dichloro (1-*i*-butylamidino-O-ethylurea)-copper(II) complexes) indicates the limited spectroscopic evidence for the formation of binuclear complexes of these series. The EPR spectrum of cmplex **3** was recorded in the pyridine solution at 300 K and 77 K. The spectrum at 300 K is not fully resolved into superhyperfine structure. This slight increase in the g_{iso} or $g_{||}$ values (Table-2) indicating a weak interaction with the solvent[18,19]. The complex shows a well defined hyperfine structure of four lines due to coupling of the electron with the nuclear spin (I = 3/2) of the copper atom.

$g_{||}$, $g_{\perp}$, $A_{||}$ (Cu) and $A_{\perp}$(Cu) values were measured accurately from the 77 K EPR spectra (Table-3). The observation shows that the unpaired electron is in the $d_{x^2-y^2}$ orbital of the copper(II) ion and line spectral features are characteristics of the axial symmetry. Since there is no half-field signal at 1600 G due to the $\Delta M_s = \pm 2$ transition characteristic of magnetic interaction, thus, it rules out the possibility of dimeric nature. Since the value of $g_{||}$ is 2.3164, it is covalency nature. The value of α^2 (0.8200) together with $K_{||} < K_{\perp}$, suggests the presence of significant covalent of the in-plane π-bonding[20]. Further, the value of G (3.9682) suggests the covalency of the complex. The value of Fermi contact hyperfine interaction term, K(0.3454) which is a measure of the contribution of s electron to the hyperfine interaction, agrees with values estimated by Assour[21]. Thus, based on the magnetic moment and spectral evidence, the complex **3** has a square planar stereochemistry (**I**).

TABLE-3
EPR SPECTRAL DATA AND BONDING PARAMETERS OF COMPLEX **3** IN PYRIDINE SOLUTION

Temperature 77 K			
$A_{\parallel}$	151.6600	α^2	0.7654
$A_{\perp}$	33.3300	β^2	0.9823
A_{av}	72.7700	Y^2	0.9847
$g_{\parallel}$	2.2766	K	0.3454
$g_{\perp}$	2.0712	$K_{\parallel}$	0.7519
g_{av}	2.1396	$K_{\perp}$	0.7537
A_o^N(G)	20.0000	G	3.9682

At temperature 300 K, A_{iso} = 53.88, g_{iso} = 2.3643



(**I**)

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Dr. V.K. Manchanda, Head, Radiochemistry Division, BARC for his keen interest in this work. The authors thank Prof. P. Banerjee, IACS for VSM results and Dr. A.R. Dhobale of RCD, BARC, Mumbai for photoacoustic results, One of the authors (O.I.S) is grateful to University Grants Commission NER, Gauhati for the Minor Research Project.

REFERENCES

1. T.D. Smith and J.R. Pilbrow, *Coord. Chem. Rev.*, **13**, 173 (1974).
2. G.F. Koloszka and R.W. Duerst, *Coord. Chem. Rev.*, **5**, 209 (1970).
3. S.K. Mandal, L.K. Thompson, M.J. Newlands, E.J. Gabe and F.L. Lec, *Inorg. Chem.*, **29**, 3556 (1990).
4. M. Valko, M. Melnik, H. Morris, R.F. Bilton and P. Pilikan, *Chem. Phys. Lett.*, **5**, 372 (1991).
5. J.P. Costes, F. Dahan and J.P. Laurent, *Inorg. Chem.*, **31**, 284 (1992).
6. L.A. Sharma, O.I. Singh, A.M. Singh, R.K.H. Singh, R.M. Kadam, M.K. Bhide and M.D. Sastry, *Transition Met. Chem.*, **26**, 532 (2001).
7. A.A. Sharma, O.I. Singh, A.M. Singh, R.K.H. Singh, R.M. Kadam, M.K. Bhide, A.R. Dhobale and M.D. Sastry, *Spectrochem. Acta A*, **60**, 1593 (2004).
8. O.I. Singh, M.D. Devi, N.R. Singh, R.K.H. Singh, M. Mohapatra and R.M. Kadam, *Polyhedron*, **24**, 909 (2005).

9. S.P. Devi, R.K.H. Singh and R.M. Kadam, *Inorg. Chem.*, **45**, 2193 (2006).
10. F.H. Curd and F.L. Rose, *J. Chem. Soc.*, 729 (1946).
11. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
12. R.A. Penneman and L.H. Jones, *J. Chem. Phys.*, **24**, 293 (1956).
13. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compound, John Wiley and Sons, New York, edn. 2, p. 80 (1970).
14. J.R. Dyer, Application of Absorption Spectroscopy of Organic Compounds, Prentice Hall, Inc., p. 37 (1987).
15. A.D. Cross, Practical Infrared Spectroscopy, Butterworth and Co., edn. 2, p. 67 (1964).
16. R.L. Dutta and A. Syamal, *J. Indian Chem. Soc.*, **44**, 571 (1967).
17. R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley and Sons, Inc., New York, edn, 4, p. 117 (1981).
18. K.K. Narang and P.V. Singh, *Transition Met. Chem.*, **21**, 507 (1996).
19. P. Thomas, D. Rchorak and H. Spindler, *Z. Anorg. Hlleg. Chem.*, **397**, 138 (1973).
20. J.R. Wasson and C. Trapp, *J. Phys. Chem.*, **73**, 3763 (1969).
21. M. Assour, *J. Chem. Phys.*, **43**, 2477 (1965).

(*Received*: 31 May 2007; *Accepted*: 6 March 2008) AJC-6400