J. Sci. I. R. Iran

Vol.9 No.2
Spring 1998

SYNTHESIS AND MAGNETIC CHARACTERIZATION OF THE COPPER(II) DIMER DI-μ-(SUBSTITUTED PHENOXO) BIS-[(2,2,6,6-TETRAMETHYL HEPTANE-3,5-DIONATO) COPPER(II)]

S. Amani[1]*, N. Foroughifar,[1] H. Hamidi[1] and L.J. Theriot[2]

[1] *Chemistry Department, Arak University, Arak 38156, Islamic Republic of Iran*
[2] *Chemistry Department, North Texas State University, Denton, Texas 76203, USA*

Abstract

A number of complexes in the series $(Cu\,LL')_2$, where L = $[(CH_3)_3C\text{-}CO\text{-}CH\text{-}CO\text{-}C(CH_3)_3]^{-1}$ and L'= 3-(Me) $C_6H_4O^-$, 2,6-(Di-Me)$C_6H_3O^-$, 4-(OH)$C_6H_4O^-$, 3- (F) $C_6H_4O^-$, 4-(Br)$C_6H_4O^-$, and 3,5-(Di-Me)$C_6H_3O^-$ have been prepared and their magnetic and optical properties determined. In chloroform, the complexes exhibit two bands in the visible and near UV regions. All complexes show room temperature magnetic moment order of 1.0 B.M. per copper atom. The X-band ESR spectrum of solution samples at room temperature shows typical Δm=1 transition. An electron release or withdrawing group on bridging ligand causes a great change in spin-spin interaction and is observable at Δm =2 transition at half-field, which is the characteristic of dimeric unit.

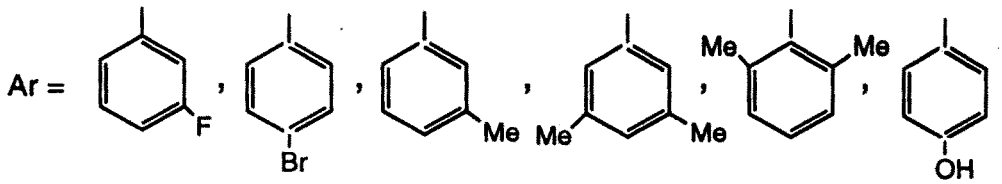
Introduction

The study of transition metal ion complexes by magnetic and optical techniques has furnished a considerable body of empirical data, much of which can be understood in terms of the phenomenological ligand field theory [1]. The major portion of this data is primarily concerned with complexes containing a single paramagnetic transition metal ion; relatively little information is available on dimeric or trimeric coordination complexes [2]. Compounds containing more than one metal atom with unpaired electrons can generally be categorized according to their magnetic behavior into three main groups, depending on the strength of the metal-metal interaction. In the strongly interacting type, formation of relatively strong metal-metal bonds occurs, and the molecule will display simple diamagnetic behavior. In the non-interacting type, the magnetic properties of the dimer (or polymer) are essentially unchanged from the paramagnetic monomer. In the weakly interacting type, there will be a weak coupling between the electrons of the two metal ions, leading to low-lying excited states of different spin which can be populated at thermal energies of about 1000 cm^{-1} [3-7]. The resulting magnetic behavior will be antiferromagnetic or ferromagnetic, depending on whether the low spin (spins paired) or high spin (spins parallel) state is in the ground state [8-13].

In the last forty years, there has been considerable interest in the development of binuclear copper(II) complexes [14-17]. It has been found that ligands (specially

Keywords: Binuclear copper(II) complexes

* Author to whom correspondence should be addressed



molecular orbitals (HOMO) accidentally degenerate into B_{1g}* and B_{2u}* orbitals [45], each of which is singly occupied. Hence, the study of copper(II) - copper(II) exchange interactions of substituted phenoxo-bridge binuclear copper(II) complexes has recently received extensive attention in our group. The complexes can be formulated as [(chelate) Cu $(OAr)_2$ Cu (chelate)] and their optical and magnetic properties are interesting. The mechanism of exchange interactions in polynuclear metal complexes has been the subject of much experimental and theoretical work. Such major interest arises because the subject occupies a frontier area between coordination chemistry and solid state physics [34-38].

In this paper, the synthesis and optical properties of six new binuclear copper(II) complexes bridged by substituted phenoxo ion, $(CuLL')_2$, where L is 2, 2, 6, 6-tetramethylheptanedionato and L' = 3-(Me)C_6H_4O-, 2, 6-(Di-Me)$C_6H_3O^-$, 4-(OH)$C_6H_4O^-$, 3-(F)$C_6H_4O^-$, 4-(Br)$C_6H_4O^-$, and 3,5-(Di-Me)$C_6H_3O^-$ are reported. The complexes have nearly identical ligand field spectra and therefore, undoubtedly, have close similar structures, [39,40]. The spectrum of the complexes in chloroform shows two absorption bands in the UV-visible region. The spectral data are presented in Table 1. The band with lower energy is due to d-d transition [41]. The second absorption band for these compounds is found in the higher energy region. This absorption band suggests that the complexes have oxo-bridged binuclear structure and the absorption is attributed to charge transfer from non-bonding orbitals of bridging oxygen atoms to the vacant copper d-orbitals [42, 43]. In all spectra which are measured in chloroform, this absorption is rather strong, while in the solid state, this absorption band is very weak or is seen only as a shoulder in the spectra. A similar behavior has been found in some other oxygen bridged copper(II) complexes [44]. The explanation as to why the complexes do not show a distinct absorption band in this region in the solid state spectra, is that the dimeric complexes are as tetramers or polymers in the solid state. In the tetramer case, the bridging oxygen has only one non-bonding orbital, and in the polymer case, there are no non-bonding orbitals. Thus, the charge transfer in the former case is weak and in the latter case non-existent. Hence, we conclude that the complexes are dimer in solution. As has been noted elsewhere [45, 46], the Cu_2O_2 bridging fragment has approximate D_{2h} symmetry. It is also found that the entire Cu_2O_6 system is approximately planar [47]. Thus, if one examines the σ-bonding framework of the bridge (under these conditions the ground state is the triplet and therefore J>0), any appreciable change in ϕ from this value raises the degeneracy of these two orbitals and eventually leads to a singlet ground state J<0.

Low resolution mass spectroscopic data provide initial support for the binuclear nature of most complexes which are collected in Table 3. The molar magnetic susceptibilities of complexes were measured in chloroform using the method described by Evan [48]. The shifts of the proton resonance lines of inert reference molecules in solution caused by paramagnetic substances are given by the following theoretical expression:

$$x_{(g)} = x_{(O)} + (3000\,\Delta f)/(2\pi f\, m)$$

Where $x_{(g)}$ is susceptibility of complex/gr., Δf is the frequency separation between the two lines in cycles /sec., m is the concentration of the solute in gr./L, f is the frequency at which the proton resonances are being studied

Table 1. UV//VIS and IR data for $(CuLL')_2$ complexes

Ligand L'	$\lambda_{(max)}$	ν (cm^{-1})	
		Cu-L	Cu-L'
L	532.5, 657.6	254, 270	-----
3- methylphenol	526, 642	256, 270	235, 303
2,6-dimethylphenol	532.5, 654.9	254, 283	237, -----
4-hydroxyphenol	537.7, 660.2	248, 270	283, -----
3-fluorophenol	529.9, 647.2	256, 270	248, 293
4-bromophenol	516.8, 579.2	256, 271	237, 302
3,5-dimethylphenol	524, 648	256, 271	-----

in cycles/sec., and $x_{(O)}$ is the mass susceptibility of the solvent. The chloroform solutions of complexes about 2% of *t*-butyl alcohol is as inert reference substance and the same concentration of *t*-butyl alcohol is also placed in a second NMR tube as the reference sample and their spectra obtained. The methyl proton signals for *t*-butyl alcohol in these two tubes were recorded. The presence of copper(II) dimer in the *t*-butyl alcohol solution makes the bulk susceptibility different from that of the reference. The separation of the two signals (Δf) was found and it is considered as paramagnetic shifts. By having the $x_{(M)}$, it is easy to calculate the effective magnetic moment ($\mu_{eff.}$) of all complexes with the following equation

$$\mu_{eff.} = 2.83\ (x_M T)^{1/2}$$

The effective magnetic moment of all complexes are calculated and presented in Table 2. The observed ESR parameters for the complexes are independent of the nature of the solvent. The X-band ESR spectra of the solution samples at room temperature except for Δm=2 transition, show typical triplet state features with Δm=1 transition. The spectroscopic splitting factor ($g_{av.}$) for all are presented in Table 3.

A much weaker Δm=2 transition for all complexes confirming the occurrence of a Cu..... Cu magnetic exchange interaction at half-field, which is the characteristic of the dimer unit [49-51].

The ESR spectra obtained at 130° K are similar to those observed for the room ition, but with higher resolutions. The suggestion that the complex is $(CuLL')_2$, is also supported by its infrared spectrum. A strong absorption at about 300-230 cm^{-1} region may be attributed to the symmetric infrared activity of Cu-O bond in D_{2h} symmetry and O-Cu-O deformation frequencies should be below 220 cm^{-1} [40]. The most important difference between the spectra of ligand L' and its copper(II) complex can be found in the region 3500-3300 cm^{-1}. When going from free L' ligand to the complex, the stretching vibration ν_{OH} disappears, showing that the OH group of the L' has been deprotonated on coordination to the copper(II) ion.

Acknowledgements

The authors would like to thank the Research Council of Arak University for its financial support and North Texas State University for the chemicals and physical measurements.

References

1. Kokoszoka, G.E. and Duerset, R. W. *Coord. Chem. Rev.*, **5**, 209, (1970).
2. Hoffmann, R., Hay, P.J. and Thibeault, J. C. *J. Am. Chem. Soc.*, **97**, 4884, (1975).
3. Estes, E.D. and Hodgson, D.J. *Inorg. Chem.*, **14**, 334, (1975).
4. Hatfield, W.E. ACS Symp. Ser. No. 5, Chapter 10, (1974).
5. Estes, E.D., Hatfield, W. E. and Hodgson, D. J. *Inorg. Chem.*,

Table 2. Elemental analysis of copper and magnetic moment effect of complexes

Ligand L'	Cu % (cal.)	Cu % (found)	$\mu_{eff.}$ (30°C)
L	14.78	14.67	1.84
3-methylphenol	17.95	17.87	1.43
2,6-dimethylphenol	17.27	17.19	1.47
4-hydroxyphenol	17.85	17.78	1.37
3-fluorophenol	17.76	17.52	1.41
4-bromophenol	15.28	15.09	1.61
3,5-dimethylphenol	17.27	17.12	1.60

Table 3. ESR, MS and m. p. data for $(CuLL')_2$

Ligand L'	Δm = 1 $g_{av.}$	Δm = 2 $g_{av.}$ at half-field	M/z	m.p. (°C)
L	2.0682	-------	430	203-205
3-methylphenol	2.0674	4.2849	708	128-130
2,6- dimethylphenol	2.0561	4.1690	735	190-193
4-hydroxyphenol	2.0836	4.3314	713	122-125
3-fluorophenol	2.0623	-------	715	131-133
4-bromophenol	2.0685	4.4240	829	135-137
3,5-dimethylphenol	2.0775	4.2343	735	148-150

13, 1654, (1974).
6. Bertrand, J.A., Kelly, J.A. and Breece, J. L. *Inorg. Chim. Acta*, **4**, 247, (1970).
7. Bertrand, J. A. and Kelly, J. A. *Ibid.*, **4**, 203, (1970).
8. Martin, R.L. In *New pathways in inorganic chemistry*, Chapter 9. Cambridge, University Press, (1968).
9. Ball, P. W. *Coord. Chem. Rev.*, **4**, 361, (1969).
10. Sinn, E. *Ibid.*, **5**, 313, (1970).
11. Ginsberg, A. P. *Inorg. Chim. Acta Rev.*, **5**, 45, (1971).
12. Gray, H. B. *Adv. Chem. Ser.*, **100**, 365, (1971).
13 Kato, M., Jonassen, H. B. and Fanning, J. C. *Chem. Rev.*, **64**, 99, (1964).
14. Figgis, B. N. and Martin, R. L. *J. Chem. Soc.*, 3837, (1956).
15. Reeves, R. E. and Bragg, R. *J. Am. Chem. Soc.*, **84**, 2491, (1962).
16. Bennett, M. C. and Schmidt, N. O. *Trans. Farad. Soc.*, **51**, 1412, (1955).
17. Bjerrum, J., Ballhausen C. J. and Jorgensen, C. K. *Acta Chem. Scand.*, **8**, 1275, (1954).
18. Martin, R. L. and Waterman, H. *J. Chem. Soc.*, 2960, (1959).
19. Barraclough, C. G. and Ng, C.F. *Trans. Farad. Soc.*, **60**, 836, (1964).
20. Hall, G. R., Duggan, D. M. and Hendrickson, D. N. *Inorg. Chem.*, **14**, 1957, (1975).
21. Sinn, E. *Ibid.*, **15**, 366, (1976).
22. Hasty, E. F., Wilson, L. J. and Hendrickson, D. N. *Ibid.*, **17**, 1834, (1978).
23. Girerd, J. J., Jeanin, S., Jeanin, Y. and Kahn, O. *Ibid.*, **17**, 3034, (1979).
24. Crowford, V. H., Richardson, H. W., Wasson, J. R., Hodgson, D. J. and Hatfield, W. E. *Ibid.*, **15**, 2107, (1976).
25. Theriot, L. J., LeNay, H. E., Pruetianghura, P. and Hodgson, D. J. *J. Chem. Soc. Dalton*, 781, (1979).
26. Theriot, L. J. and Pauley, C. R. *Inorg. Chem.*, **13**, 2033, (1974).
27. Theriot, L. J. *J. Inorg. Nucl. Chem.*, **38**, 695, (1976).
28. Theriot, L. J. and Gupta, S. *J. Coord. Chem.*, **5**, 153, (1976).
29. Theriot, L. J. and Gupta, S. *Inorg. Chim. Acta*, **25**, L131, (1977).
30. Theriot, L. J., Jones, W. J., Gupta, S., Helm, F. T. and Baker, W. A. *Inorg. Chem.*, **17**, 87, (1976).
31. Theriot, L. J. and Syamal, A. *J. Coord. Chem.*, **2**, 276, (1972).
32. Theriot, L. J., Carlisle, G. O., Syamal, A. and Ganguli, K. K. *J. Inorg. Nucl. Chem.*, **34**, 2761, (1972).
33. Amani, S., Zolgharnien, J. and Theriot, L. J. *Iran. J. Chem. & Chem. Eng.* In press.
34. Mandal, P. K. and Manoharan, P. T. *Inorg. Chem.*, **34**, 270, (1995).
35. Ramasesha, S. and Rao, C. N. R. *Phys. Rev.*, **B44**, 7046, (1991).
36. Mandal, P. K., Sinha, B., Manoharan, P. T. and Ramasesha, S. *Chem. Phys. Lett.*, **191**, 448, (1992).
37. Mandal, P. K. and Manoharan, P. T. *Chem. Phys. Lett.*, **210**, 463, (1993).
38. Yamamoto, Y., Nanai, N. and Chuyo, R. *Bull. Chem. Soc. Japan*, **64**, 3199, (1991).
39. Nelson, S. M., Esho, F. and Lavery, A. *J. Am. Chem. Soc.*, **105**, 5693, (1983).
40. Robichaud, P. and Thompson, L. K. *Inorg. Chim. Acta*, **85**, 137, (1984).
41. Lindgren, T., Sillanpa, R., Nortia, T. and Pihaja, K. *Inorg. Chim. Acta*, **73**, 153, (1983).
42. Mikuriya, M., Okawa, H. and Kida, S. *Bull. Chem. Soc. Japan*, **53**, 3717, (1980).
43. Nishida, Y. and Kida, S. *J. Inorg. Nucl. Chem.*, **38**, 451, (1976).
44. Ishimura, Y., Nonaka, Y., Nishida, Y. and Kida, S. *Bull. Chem. Soc. Japan*, **46**, 3728, (1973).
45. Hodgson, D. J. *Prog. Inorg. Chem.*, **19**, 173, (1975).
46. Bertrand, J.A. and Kirkwood, C. E. *Inorg. Chim. Acta*, **6**, 248, (1972).
47. Hoskins, B. F. and Whillans, F. D. *J. Chem. Soc. Dalton Trans.*, 1267, (1975).
48. Evan, D. F. *J. Chem. Soc.*, 2003, (1959).
49. Bleaney, B. and Bowers, K. D. *Proc. R. Soc. London Ser.*, **A 214**, 451, (1952).
50. Drew, M. G. B., Cairns, C., Lavery A. and Nelson, S. M. *J. Chem. Soc. Chem. Comm.*, 1122, (1980).
51. Drew, M. G. B., McCan, M. and Nelson, S.M. *J. Chem. Soc. Dalton Trans.*, 1868, (1981).