Inorganica Chimica Acta, 64 (1982) L189–L191

Imidazolate Bridged Binuclear Copper(II) Complexes of Macrocyclic Ligands: Electron Spin Resonance Spectra and Magnetic Susceptibility Studies

MICHAEL G. B. DREW

Department of Chemistry, The University, Reading RG6 2AD, U.K.

S. MARTIN NELSON

Department of Chemistry, Queen's University, Belfast BT9 5AG, U.K.

and JAN REEDIJK

Department of Chemistry, Gorlaeus Laboratories, State University, Leiden, The Netherlands

Received November 6, 1981

Introduction

It is recognized that the biological function of many metalloproteins is associated with the occurrence of the metal atoms in pairs. For example, X-ray crystallographic studies [1] have shown that in bovine erythrocyte superoxide dismutase pairs of Cu(II) and Zn(II) ions are bridged by an imidazole group. An antiferromagnetic super exchange coupling constant (J) of -26 cm^{-1}, where 2J is the singlet–triplet separation, has been estimated [2] for the derivative in which Zn(II) has been replaced by Cu(II). Both imidazolate [3] and hydroxo [4] bridges have been proposed for the more strongly coupled ($J > -200$ cm^{-1}) Fe(III)$\cdots$Cu(II) active site in cytochrome c oxidase. Antiferromagnetically coupled Cu(II) ions also occur in several other copper proteins including, for example, in oxyhaemocyanin [5] and tyrosinase. The investigation of synthetic binuclear complexes of known structure may contribute to the better understanding of the natural systems. Macrocyclic ligands having a cavity size large enough to accommodate two metal ions provide a convenient means whereby the interactions and structural relationships between the metal centres may be studied in the laboratory.

We have previously reported the X-ray structures of the imidazolate bridged bi-copper(II) complexes $Cu_2L^1(im)(ClO_4)_3 \cdot H_2O$ (*1*) [6] and $Cu_2L^2(im)(ClO_4)_3 \cdot H_2O$ (*2*) [7], where L^1 and L^2 are the 24- and 30-membered macrocyclic Schiff base ligands. The structures of the two complexes are very similar in that in each case each Cu(II) ion is strongly bonded in a square plane to three nitrogen atoms of the macrocycle and to one nitrogen atom of the bridging imidazolate group. In addition, in each case, the Cu(II) ions are weakly bonded to ClO_4^- or H_2O oxygen atoms in axial positions giving an overall tetragonal six-coordinate environment. The structures differ, however, in the dihedral angle between the plane of the imidazolate ring and the Cu(II) coordination square plane, being 88.6, 90.0° in (*1*) and 68.8, 79.1° in (*2*). We now report the results of magnetic susceptibility measurements in the temperature range 4–100 K, together with the X-band ESR spectra of frozen solutions measured at 77 K. Preliminary measurements [6] of the magnetic susceptibility of (*1*) in the limited temperature range 93–293 K led to a rough estimate of $J \sim -23$ cm^{-1}.

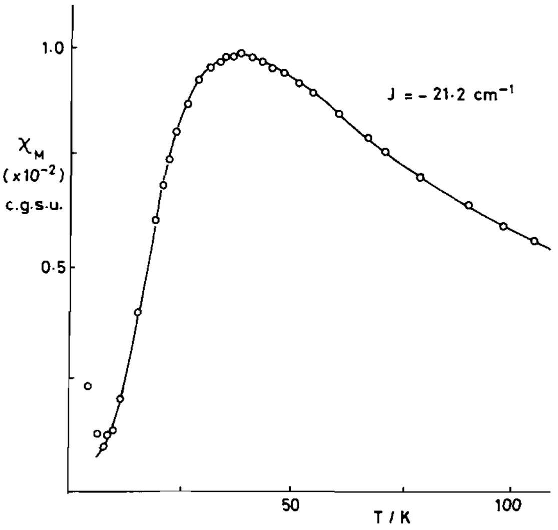
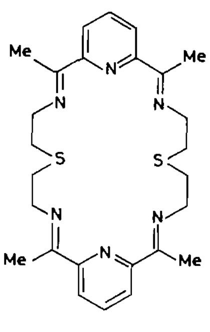
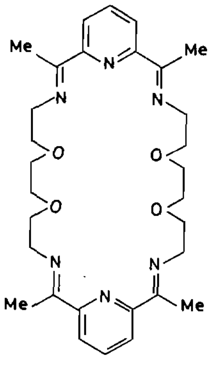


Fig. 1. The temperature dependence of the magnetic susceptibility of complex (*1*). The solid line represents the theoretical curve calculated from the Bleaney-Bowers equation (see text).



L^1



L^2

TABLE I. Comparison of Coupling Constant, J, with selected Structural Parameters for some Imidazole-Bridged Di-Copper(II) Complexes.

Complex		J/cm^{-1}	Cu–N(im)/Å	α	β	θ	γ^a	Ref.
					degrees			
(*1*)		−21.2	1.90, 1.93	128, 133	140	42	88.6, 90.0	6 and this work
(*2*)		−21.0	1.98, 1.92	131, 122	163	40	68.8, 79.1	7 and this work
(*3*) $Cu_2(TMDT)_2(im)(ClO_4)_2$	$ClO_4{}^b$	−25.8	1.944, 1.966	129	143	31.3	91.8, 90.0	10
(*4*) $Cu_2(bpim)(NO_3)(ClO_4)$	$ClO_4 \cdot H_2O^c$	−81.3	1.966, 1.961	143, 142	170	8.8	4.7, 13.4	13, 18

[a] For definitions of the angles α, β, θ, γ see text. [b] TMDT = 1,1,7,7-tetramethyldiethylenetriamine. [c] bpim = 4,5-bis[2-(2-pyridyl)ethylimino)methyl] imidazolate.

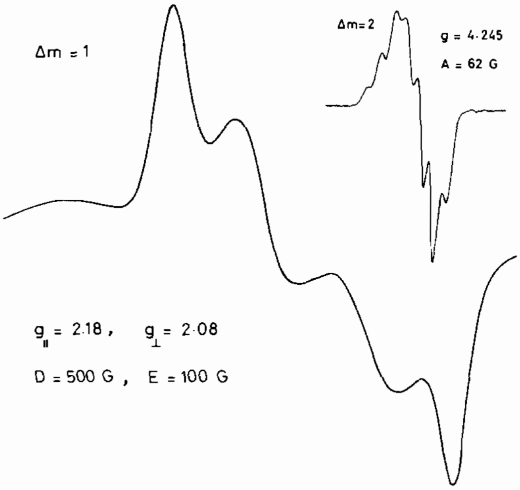


Fig. 2. The X-band ESR spectra of complex (*2*), in DMSO/MeOH glass at 77 K, in the g ~ 2 and g ~ 4 regions. the inset refers to the half-band (Δm = 2) spectrum at g ~ 4 (see text).

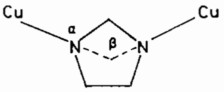
Results and Discussion

Figure 1 shows a plot of the magnetic susceptibility of (*1*) as a function of temperature, the maximum at *ca.* 38 K clearly indicating the occurrence of antiferromagnetic coupling. Application of the Bleaney-Bowers equation [8] for coupled pairs of Cu(II) ions gives J = −21.2(4) cm^{-1} for g = 2.110 (from the ESR spectra, *vide infra*) and the temperature independent paramagnetism N(α) = 60 × 10^{-6} c.g.s.u. An equally satisfactory fit of the experimental and calculated X_A/T curve was obtained for (*2*), for J = −21.0(4) cm^{-1}, g = 2.110, and N(α) = 60 × 10^{-6} c.g.s.u.

Powder X-band ESR spectra at room temperature showed only a broad band at g = 2.12 and a Δm = 2 transition at g = 4.25 for both compounds confirming the occurrence of a Cu···Cu magnetic exchange interaction. The absence of fine structure in the powder spectra points to a significant inter-dimer interaction, at least of the order of the zero field splitting. This is not unexpected especially in view of the fact that adjacent $[Cu_2L(im)]$ moieties are linked via the weakly coordinated axial ClO_4^- ions [6, 7]. However, well resolved spectra for isolated Cu_2 dimers were obtained in 3:1 DMSO:MeOH glasses [see Fig. 2 for complex (*2*)]. Analysis [9] of the spectra gives $g_{\parallel}$ = 2.18, $g_{\perp}$ = 2.08, D = 500 (±20) G and E = 100 (±20) G for both compounds. The seven-line spectra observed at g = 4.24 with A = 62 G confirm the retention of the imidazolate bridges in solution.

In recent years a number of im-bridged binuclear Cu(II) compounds have been synthesized as possible models for the naturally occurring systems [4b, 6, 7, 9–17]. Both ESR and magnetic studies have demonstrated the occurrence of antiferromagnetic superexchange between the Cu(II) centres with J values ranging between −10 and −90 cm^{-1}. It is of interest to try to correlate the magnitude of J with the structure of the binuclear complex. For example, it may be expected that J will depend on the stereochemistry of the Cu(II) coordination sphere (*e.g.* square pyramidal or trigonal bipyramidal) and on whether, for either geometry, the bridging im group occupies an axial or equatorial site. However, even for square based Cu(II) systems [($d_{x^2-y^2}$) ground state] in which the im group is sited equatorially a wide variation in J values has been observed. Table I compares the exchange coupling constant J with selected structural parameters for four square-based binuclear Cu(II) complexes for which data are available. The structural parameters considered include the Cu–N(im) bond length, the Cu–N–C bond angle (α), the angle (β) between the two Cu–N(im) vectors, the angle (θ) between the two 'CuN_4' coordination planes, and the dihedral angle (γ) between the plane of the imidazolate ring and the 'CuN_4' planes.

Inspection of Table I shows that no correlation between the Cu–N(im) bond distance and J exists.



At first sight a relationship between J and the dihedral angle (γ) and also the angle (θ) between the copper equatorial coordination planes, may be apparent, as suggested by Lippard and co-workers [10], in that the largest interaction occurs in complex (*4*) in which the imidazolate group and the two coordination planes are almost co-planar. However, a π-exchange pathway, as would be implied by such a correlation, is unlikely to be the major one. It might be expected that the interactions in (*1*) and (*2*) should differ, because the im plane and the coordination square planes are mutually perpendicular in (*1*) but not in (*2*). In fact, the coupling constants for the two compounds are, within experimental uncertainty, exactly the same. Moreover, Lippard *et al.* [18] have more recently reported a dependence of J on the pK_a values for a series of binuclear Cu(II) compounds containing substituted imidazolate bridges, an observation favouring a σ-exchange pathway.

A correlation between J and the angle (β) between the Cu–N(im) vectors has also been suggested [18]. However, this also appears unsatisfactory since the β value for complex (*2*) is out of line with the others (Table I). A better correlation can be seen when J is compared to the Cu–N–C bond angle (α)*, although the range of observed angles is small**. Haddad and Hendrickson [14] have previously proposed, for the case of some trigonal bipyramidal bi-Cu(II) complexes (d_{z^2} ground state) in which the bridging im group occupies an axial site, that improved overlap (and hence greater interaction) of the d_{z^2} orbital and the appropriate σ molecular orbital of the imidazolate bridge accompanies an increase in the angle (α). A similar dependence of J on α has also been proposed [17] for some distorted trigonal bipyramidal binuclear Cu(II) complexes containing imidazolate, benzimidazolate and benzotriazolate bridges. For a benzotriazolate complex, for which the X-ray structure has been determined, the Cu–N–N angle, corresponding to α in the im-bridged systems, is only 114° (most probably due to the steric effect of the benzene ring) while the exchange coupling constant J is -12 cm^{-1}. For the corresponding im-bridged compound, for which the angle (α) is unknown but likely to be larger than 114°, a larger interaction (J = -28 cm^{-1}) is observed [17].

Acknowledgements

We thank Dr. C. Cairns and Dr. M. McCann for preparations of the compounds.

References

1 J. S. Richardson, K. A. Thomas, B. H. Rubin and D. C. Richardson, *Proc. Natl. Acad. Sci. U.S.A., 72,* 1349 (1975).
2 J. A. Fee and R. G. Briggs, *Biochim. Biophys. Acta, 400,* 439 (1975).
3 M. F. Tweedle, L. J. Wilson, L. Garcia-Iniguez, G. T. Babcock and G. Palmer, *J. Biol. Chem., 253,* 8065 (1978).
4 (a) J. T. Landrum, C. A. Reed, K. Hatano and W. J. Scheidt, *J. Am. Chem. Soc., 100,* 3232 (1978);
(b) M. S. Haddad, E. N. Duesler and D. N. Hendrickson, *Inorg. Chem., 18,* 141 (1979).
5 D. M. Dooley, R. A. Scott, J. Ellinghaus, E. I. Solomon and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A., 75,* 3019 (1978).
6 M. G. B. Drew, C. Cairns, A. Lavery and S. M. Nelson, *J. Chem. Soc. Chem. Comm.,* 1122 (1980).
7 M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc. Dalton Trans.,* 1868 (1981).
8 B. Bleaney and K. D. Bowers, *Proc. Roy. Soc. Ser. A, 214,* 451 (1952).
9 J. Reedijk, D. Knetsch and B. Nieuwenhuijse, *Inorg. Chim. Acta, 5,* 568 (1971).
10 C-L. O'Young, J. C. Dewan, H. R. Lilienthal and S. J. Lippard, *J. Am. Chem. Soc., 100,* 7291 (1978).
11 P. K. Coughlin, S. J. Lippard, A. E. Martin and J. E. Bulkowski, *J. Am. Chem. Soc., 102,* 7617 (1980).
12 P. K. Coughlin, J. C. Dewan, S. J. Lippard, E.-I. Watanabe and J.-M. Lehn, *J. Am. Chem. Soc., 101,* 265 (1979).
13 G. Kolks and S. J. Lippard, *J. Am. Chem. Soc., 99,* 5804 (1977).
14 M. S. Haddad and D. N. Hendrickson, *Inorg. Chem., 17,* 2622 (1978).
15 W. Mori, A. Nakahara and Y. Nakao, *Inorg. Chim. Acta, 37,* L507 (1979).
16 H. M. J. Hendriko and J. Reedijk, *Inorg. Chim. Acta, 37,* L509 (1979).
17 H. M. J. Hendriks, P. J. M. W. L. Birker, G. C. Verschoor and J. Reedijk, *J. Chem. Soc. Dalton Trans.,* in press.
18 J. C. Dewan and S. J. Lippard, *Inorg. Chem., 19,* 2079 (1980).

---

*The angles α and β are, of course, related provided the copper atoms both lie in the plane of the imidazolate ring. In (*1*) the deviations (0.03, 0.04 Å) of the copper atoms from this plane are small. In (*2*) the copper atoms sit further out-of-plane (0.11, 0.13 Å), thus accounting for the fact that the differences between α and β in the two complexes are not the same.

***Note added in proof:* In a very recent paper (*J. Chem. Soc., Dalton Trans.,* 2045 (1981)) Matsumoto *et al.* describe the structure of the complex $Na[Cu_2(glyglyO)_2(im)]\cdot 6H_2O$, where gly-glyO is the glycylglycinate di-anion, for which a coupling constant J of -19 cm^{-1} has been observed. In this complex the angles α, β, θ and γ are respectively, 124°, 135°, 5.9° and 5.8°, 10.4°. These results confirm our own conclusions, namely, that J is determined mainly by the angle (α) and not the dihedral angle (γ).