Inorganica Chimica Acta, *182* (1991) 1–3

Inorganica Chimica Acta

LETTER

Peroxide (O_2^{2-}) as a bridging ligand for copper(II): strong exchange coupling in complexes derived from copper(I) and dioxygen

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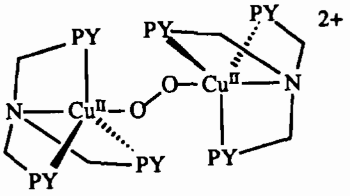
(Received January 17, 1991)

The effects of ligation and metal ion geometry upon the physical properties of bridged dinuclear copper(II) complexes continue to be of great interest [1–8]. Studies of the magnetic behavior of single-atom (e.g. halide, ^-OR) or multi-atom [3–8] (e.g. azide [3, 7], imidazolate [3, 6, 8]) bridged d^9 metal ion systems are important in elucidating fundamental information concerning the mechanisms and requirements for electronic and magnetic interactions between paramagnetic centers and for possible insights into electron-transfer pathways. In this report, we present magnetic susceptibility data demonstrating that a peroxide (O_2^{2-}) ligand bridging two Cu(II) ions can result in essentially diamagnetic behavior for the dinuclear complex. This *first* direct assessment of a magnetic interaction mediated by a bridging O_2^{2-} ligand has implications for the structures of both synthetic and biologically occurring peroxo–dicopper(II) species.



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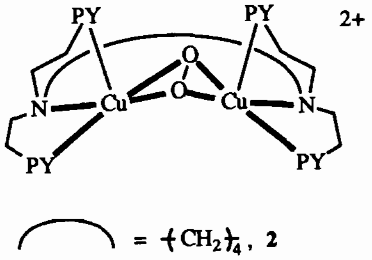

= $-(CH_2)_4-$, **2**
= $-CH_2CH(R)CH_2-$, **3**

As possible mimics for certain properties of the hemocyanin copper proteins (Hcs, O_2-carriers in molluscs and arthropods), some of us have recently characterized peroxo–dicopper(II) complexes species ($\{Cu_2–O_2\}^{2+}$, **1–3**), formed reversibly by the addition of O_2 to solutions of either mono- or dinuclear copper(I) complexes at −80 °C [9]. Complex $[(LCu)_2(O_2)]^{2+}$ (**1**, L = tris[(2-pyridyl)methyl]amine) has been characterized crystallographically and it features a single *trans*-μ-1,2-peroxo ligand [10]. We have also prepared O_2 adducts $[Cu_2(N4)(O_2)]^{2+}$ (**2**) and $[Cu_2(N3OR)(O_2)]^{2+}$ (**3**, R = $-C(O)-C_6H_4C_6H_5$) [11] and spectroscopic analyses lead to the suggestion that these contain a single bridging O_2^{2-} ligand having a bent μ-η^2:η^2 geometry [9, 11]. The occurrence of such a novel peroxo coordination mode has been confirmed in an X-ray structure reported by Kitajima and co-workers, with a planar μ-η^2:η^2 peroxo dicopper(II) moiety [12].

To determine the magnetic behavior of **1–3**, both solid- and solution-state susceptibility measurements have been performed. Using a SQUID magnetometer under a cold He atmosphere (4–190 K), reproducible magnetic susceptibility data were obtained using solid samples of the thermally unstable complex $[(LCu)_2(O_2)](ClO_4)_2$ (**1**)**. The μ versus T data suggest that **1** is essentially diamagnetic, with only impurity species contributing to the observed paramagnetism in this temperature range. A least-squares

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**The X-ray study was performed on $[(LCu)_2(O_2)](PF_6)_2 \cdot 5Et_2O$, but spectroscopic and chemical comparisons (e.g. UV–Vis, NMR, substrate reactivity) have shown that ClO_4^- and PF_6^- salts with solvate removed, e.g. $[(LCu)_2(O_2)]^{2+}$, behave identically.

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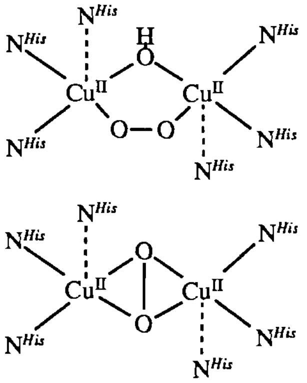
fitting of the susceptibility data using the Bleaney–Bowers equation is consistent with the presence of strong antiferromagnetic coupling between the Cu(II) ions, with a calculated singlet–triplet separation of 710 cm^{-1}, i.e. $-2J \sim 700$ cm^{-1} based on $H_{ex} = -2JS_1 \cdot S_2$. Frozen-solution magnetic susceptibility measurements (Faraday method, 80–160 K)* on **1** in EtCN and **2** in CH_2Cl_2 are also consistent with essentially diamagnetic behavior of both species. In these studies, the slopes of χ_{para} versus $1/T$ plots were not increased relative to those found for the solvent blank solutions. Thus, conservative lower limits can be assigned as $-2J \geqslant 600$ cm^{-1} for both **1** and **2****. These magnetic data suggest that both classes of peroxo-bridged Cu_2–O_2 complexes contain strongly coupled (essentially diamagnetic) copper(II) centers. Previous suggestions that **1**–**3** are diamagnetic were based only on indirect spectroscopic evidence [10, 11], while the present magnetic susceptibility data confirm this suspicion and for the first time quantitates the magnitude of a magnetic exchange interaction between Cu(II) ions through a O_2^{2-} bridging ligand.

In dinuclear copper(II) complexes, the magnitude and sign of the coupling constant (2*J*) is known to be sensitive to the overlap of appropriate metal and bridging ligand orbitals [1–8]. The strong antiferromagnetic coupling seen in the di-atom bridged complex **1** may not be unexpected [4, 5] since the axially coordinated bridging peroxo ligand (trigonal bipyramidal coordination geometry) [10] can couple the unpaired electrons in the Cu(II) d_{z^2} orbitals. The suggested bent μ-η^2:η^2 configuration in **2** and **3** might be expected to mediate strong magnetic coupling based on the connectivity through singly-occupied, in-plane $d_{x^2-y^2}$ orbitals in tetragonally coordinated Cu(II) ions. Kitajima's Hc model compound with planar μ-η^2:η^2-peroxo dicopper(II) group is apparently diamagnetic (NMR) evidence only). A nonplanar μ-η^2:η^2-structure (as proposed for **2**) would also not preclude strong magnetic coupling, based on the established magnetic behavior in doubly-bridged Cu(II) dimers†.

A *cis*-μ-1,2-peroxo unit has been proposed to occur in oxy-Hc, with an additional 'endogenous' bridging hydroxo ligand also suggested to be present to account for the strong magnetic coupling ($-2J > 625$ cm^{-1}, EPR silent) observed in this and spectroscopically similar peroxide displaced met [Cu(II)Cu(II)] forms of Hc [14]. The present results indicate that the diamagnetism of oxy-Hc could be due solely to magnetic coupling mediated by the O_2^{2-}-ligand itself, without necessitating an additional bridging moiety of any nature. Thus, a μ-η^2:η^2-peroxo structure would seem to be an attractive candidate for the oxy-forms of proteins having two copper ions in their active site. The spectral properties of **2** and **3** and Kitajima's complex resemble those of oxy-Hc [9, 11, 12], and the Cu...Cu distance in Kitajima's complex is close to the protein value [12]. Recent *Xα* calculations also suggest that the μ-η^2:η^2-peroxo coordination mode is a viable candidate for the oxy-Hc active site structure, including the expectations that it would mediate strong antiferromagnetic coupling between Cu(II) ions [15].



Structure proposals for oxy-hemocyanin

Acknowledgements

The authors thank the National Institutes of Health (KDK, GM28962; LJW, GM28451) and the Robert

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*Performed at Rice University. The instrumentation used was a modification of that described in ref. 13.

Plots of χ_{para} vs. $1/T$ were prepared for the oxygenated solvent blank and corresponding solvent plus oxygenated compound. These graphs were then compared; since in each case the blank possessed a higher observed paramagnetism (i.e. slope) than the blank plus oxygenated compound, it can be concluded that the compounds are essentially diamagnetic over the interval 80–160 K. This interpretation assumes the same amount of dissolved O_2 in both solvent blanks and sample solutions. The lower limit for $-2J$ was determined by fitting $H_{ex} = -2JS_1 \cdot S_2$ with increasing values of $-2J$ until the described line became linear, within experimental error, over the temperature range studied. Although both compounds exhibited a slope less than their respective blank, that for compound **2 is much closer to the blank, probably due to the presence of a greater (but small) amount of paramagnetic impurity.

†The Cu–O_{bridge}–Cu angle is an important parameter in the sign and extent of magnetic coupling seen in dibridged Cu–$(OR)_2$–Cu complexes; strong antiferromagnetic coupling is observed for angles greater than ~100° [4]. If one can apply such criteria to μ-η^2:η^2-O_2^{2-} structures, similar results may be expected. Thus assuming precedented Cu–O and O–O bond distances, the ∠Cu–O–Cu' in bent structures **2** and **3** should fall in the range of 120–127°, while this angle in Kitajima's planar complex [12] is 137°.

A. Welch Foundation (L.J.W.) for support of this research. We also acknowledge Graham Palmer for assistance in fitting the solution-state magnetic susceptibility data.

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