Isolation of a Spin-frustrated Imidazolate-bridged Trinuclear Copper(II) Complex Potentially Relevant to the Multicopper Oxidases

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The reaction of $Cu(MeCO_2)_2 \cdot H_2O$ with 1,4,7-trimethyl-1,4,7-triazacyclononane (L) and imidazole (ImH) in methanol affords, in the presence of a small amount of triethylamine and $NaClO_4$, the blue trinuclear complex $[L_3Cu_3(Im)_3](ClO_4)_3$ which has been characterized by X-ray crystallography, EPR and magnetic susceptibility measurements to be a spin-frustrated triangular imidazolate-bridged copper(II) complex without any μ_3-X ligand.

The impetus for the synthesis of trinuclear copper clusters and to study their physical and chemical properties is the recent realization that blue multicopper oxidases[1,2] (*e.g.* ascorbate oxidase and laccase) contain a triangular unit of copper atoms. These multicopper blue oxidases catalyse the $4e^-/4H^+$ reduction of O_2 to H_2O with concomitant one-electron oxidation of a variety of substrates such as ascorbate, polyphenols and aromatic polyamines. A recent X-ray structure determination[3] (resolution 2.5 Å) on oxidized ascorbate oxidase from courgettes unambiguously demonstrated the existence of a 3 + 1 arrangement of the copper atoms. Such a 3 + 1 structure has recently also been considered[2] as a possibility for the manganese cluster of the water oxidation centre, which catalyses the reverse reaction of ascorbate oxidase, in the photosystem II of plants. In addition, there is clear interest on trinuclear metal complexes[4,5] from the magnetochemists, because trinuclear complexes offer the opportunity to test magnetic exchange models on more complicated systems than the extensively studied binuclear systems.[6]

As a part of our efforts to prepare copper complexes with variable multiatom bridging ligands,[5] we have been studying copper complexes of the small tridentate cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane (L). The investigation of the reaction of $[L_2Cu_2(\mu\text{-}MeCO_2)_2]^{2+7}$ with imidazole (ImH) led to the isolation of the first example of a triangular trinuclear copper(II) complex without any μ_3-X ligand. While triangular Cu^{II} complexes with a μ_3-X ligand are available[8] for study, surprisingly similar compounds without a μ_3-X ligand with biomimetic ligands that might structurally model the trinuclear copper unit of ascorbate oxidase have not previously been reported. Here we report the synthesis and magnetic properties of the imidazolate-bridged trinuclear complex $[L_3Cu_3(Im)_3](ClO_4)_3$ whose X-ray structure is also included.

To a suspension of $Cu(OAC)_2 \cdot H_2O$ (0.2 g) in methanol (30 ml) were added solid imidazole (0.068 g) and triethylamine (0.5 ml). The solution was heated under reflux for 0.5 h after which time a solution (1 ml) of 1,4,7-trimethyl-1,4,7-triazacyclononane in methanol (1 mol dm⁻³) was added and the solution refluxed for further 0.5 h. To the now deep-blue solution sodium perchlorate (0.2 g) was added. After 2 days at 5 °C, blue crystals of $[L_3Cu_3(Im)_3](ClO_4)_3$† precipitated in 50% yield.

The structure of the trication has been established by a single crystal X-ray analysis‡ and is shown in Fig. 1. Each of the three LCu-units is coordinated *via* two imidazolate anions to two remaining LCu-units, yielding three distorted square pyramidal CuN_5-polyhedra. The three copper ions are arranged at the corners of an equilateral triangle with the Cu⋯Cu separation of 5.92 Å. The copper ion Cu(1) is coordinated to two nitrogen atoms, N(5) and N(6), of the cyclic amine, two nitrogen atoms N(1) and N(3), of the bridging imidazolate anions in the basal plane, and the third nitrogen atom, N(4), of the cyclic amine in the apical position.
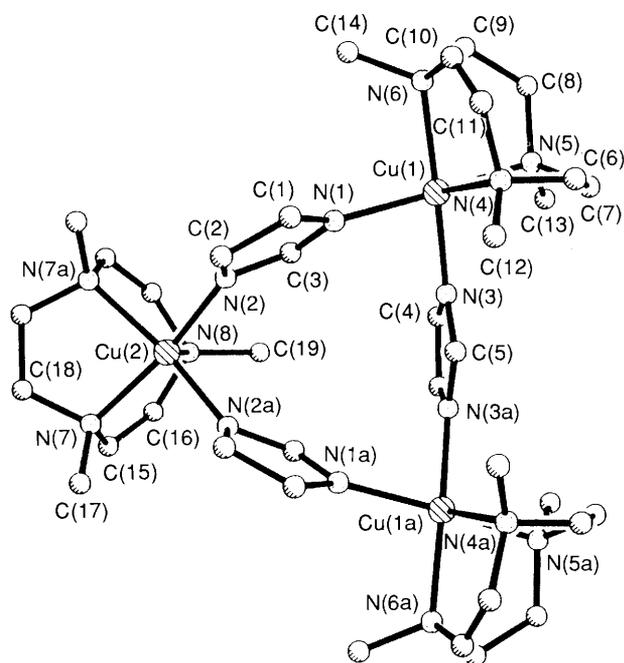

Fig. 1 Structure of the cation $[L_3Cu_3(Im)_3]^{3+}$. Selected bond lengths (Å) and angles (°): Cu⋯Cu 5.92, Cu(1)–N(1) 2.019(25), Cu(1)–N(3) 2.016(23), Cu(1)–N(4) 2.242(33), Cu(1)–N(5) 2.043(33), Cu(1)–N(6) 2.068(26), Cu(2)–N(2) 1.976(23), Cu(2)–N(7) 2.090(24), Cu(2)–N(8) 2.273(32); N(1)–Cu(1)–N(3) 85.4(10), N(1)–Cu(1)–N(4) 103.2(11), N(1)–Cu(1)–N(5) 173.0(11), N(1)–Cu(1)–N(6) 95.6(11), N(4)–Cu(1) –N(5) 83.6(11), N(4)–Cu(1)–N(6) 79.5(11), N(3)–Cu(1)–N(5) 94.2(10), N(3)–Cu(1)–N(6) 171.9(9), N(3)–Cu(1)–N(4) 108.1(11), N(5)–Cu(1)–N(6) 83.8(11), N(2)–Cu(2)–N(2a) 89.9(10), N(2)–Cu(2) –N(7) 166.6(10), N(2)–Cu(2)–N(7a) 91.6(10), N(2)–Cu(2)–N(8) 108.8(9), N(7)–Cu(2)–N(7a) 83.8(10), N(7)–Cu(2)–N(8) 83.3(9).

Fig. 2 Plot of χ_M and μ_{eff} vs T for solid $[L_3Cu_3(Im)_3](ClO_4)_3$. The solid lines represent the best least-squares fits of the experimental data to the theoretical equation.

A similar coordination is prevailing for Cu(2) which lies on a mirror plane that separates the molecule along Cu(2)–N(8)–C(19)–C(5). The average Cu–N (cyclic amine) and Cu–N (imidazolate) bond distances in the equatorial plane are 2.067 and 2.004 Å, respectively, and are considered as normal covalent bonds. The axial Cu–N (cyclic amine) bond is longer, 2.258 Å (av.), as is expected for square pyramidal complexes of copper(II) and as has been observed earlier.[5] The Cu–N (imidazolate) distance in this compound is slightly longer than published bridging Cu–N (Im) bond lengths,[9] which range from 1.919 to 1.974 Å.

The temperature dependences (2–295 K) of the molar magnetic susceptibility χ_M and of the effective magnetic moment μ_{eff} of the complex are shown in Fig. 2. The experimental magnetic moment decreases as the temperature is lowered until a plateau is reached at ca. 10 K with $\chi_M T$ = 0.415 cm^3 mol^{-1} K and μ_{eff} = 1.822 μ_B, which is nearly the theoretical value of μ_{eff} = 1.819 μ_B for an $S = 1/2$ ground state with $g = 2.1$. Thus the kind of magnetic interaction between Cu^{II} centres is antiferromagnetic. Below 10 K there is a decrease in μ_{eff}, reaching a value of 1.746 at 2 K. This deviation below 10 K from the theoretical value of 1.819 μ_B may be the result of saturation effect and of weak antiferromagnetic interactions between neighbouring trinuclear complexes. Variable temperature magnetic susceptibility data for crystalline $[L_3Cu_3(Im)_3](ClO_4)_3$ were fitted by means of least squares to the formula for the paramagnetic susceptibility which results from the spin Hamiltonian for isotropic magnetic exchange with $S_1 = S_2 = S_3 = 1/2$. The least-squares fits are of very good quality, (see Fig. 2) and result in the following values: exchange coupling constant $J = -75$ cm^{-1} and $g = 2.10$.

$$\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_1)$$

The X-band EPR spectrum at 4.2 K recorded on a powder sample yields a quasi-isotropic g value of 2.08. The spectrum does not show any half-field ($\Delta M_s = 2$) transition or fine structure and looks like a spectrum associated with isolated $S = 1/2$ spin systems possessing axial symmetry with the unpaired electron present in a $d_{x^2-y^2}$ orbital.

Spin frustration is a well-documented phenomenon in solid state physics[10] involved in exchange coupling interactions. In the equilateral triangle below if the exchange interaction between the copper ions Cu(1) and Cu(2) are antiferromagnetic in nature, then Cu(3) senses simultaneously spin parallel and antiparallel, thereby causing spin frustration. In other words, if all three metal ions in a triangle are equivalent and the pairwise exchange interaction is antiferromagnetic, then
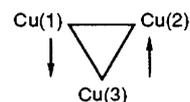
frustration develops.[11] In our complex $[L_3Cu_3(Im)_3]^{3+}$ the same type of frustration is present.

It must be noted that the Cu···Cu distance of 5.92 Å in the complex is larger than the Cu···Cu distances of 3.4, 3.9 and 4.0 Å observed in the trinuclear copper unit of ascorbate oxidase.[3] With this caveat in mind, this new structural class of trinuclear complexes can provide useful information toward our understanding of various properties of multicopper oxidases.

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