Structure and Magnetic Properties of Novel 1,1-Azido-bridged and 1,1-Cyanato-bridged Binuclear Copper(II) Complexes

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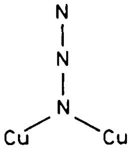
The crystal structures and the magnetic properties of two novel complexes, of formula $[Cu_2(C_{17}H_{27}N_4O)(C_2H_3O_2)L]PF_6$, L = N_3 or NCO, with a 1,1-azido or cyanato bridge in addition to phenolato and acetato bridges have been investigated and the relevance of the results to the fields of molecular magnetism and bioinorganic chemistry is discussed.

The investigation of azido-bridged copper(II) polymetallic complexes brings together two apparently widely separated areas of molecular magnetism and bioinorganic chemistry. In molecular magnetism, it has been established that when N_3^- bridges in an end-on fashion as in I, this favours the triplet ground state (ferromagnetic interaction) and when N_3^- bridges in an end-to-end fashion as in II, this favours the singlet ground state (antiferromagnetic interaction).[1] This versatility of the azido bridge has been attributed to a spin polarization effect.[2] There has been a great deal of synthetic effort from bioinorganic chemists in preparing binuclear copper(II) complexes with an exogenous azido bridge of



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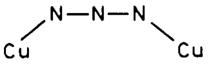

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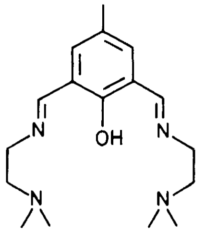

$C_{17}H_{27}N_4O$

(**1**)

type I or type II mimicking the azido derivatives of met-hemocyanine and met-tyrosinase.[3—6] Our report on the azido-bridged species is the first one containing magnetic analysis as well as structural data for an exogenous 1,1-azido bridging complex. In both molecular magnetism and bioinorganic chemistry, it seems particularly appropriate to compare the azido bridge with the isoelectronic cyanato bridge. Here, we report on the synthesis, the crystal structure, and the magnetic properties of two copper(II) binuclear complexes prepared from the same ligand (**1**); one contains an end-on azido bridge $[Cu_2(C_{17}H_{27}N_4O)(C_2H_3O_2)(N_3)][PF_6]$, (**2**), and the other one an end-on cyanato bridge $[Cu_2(C_{17}H_{27}N_4O)(C_2H_3O_2)(NCO)][PF_6]$, (**3**). Complex (**1**) was prepared by the action of 2×10^{-3} mol of 1,1-dimethylethylenediamine with 10^{-3} mol of 2,6-diformyl-4-methylphenol in a methanol–ethanol mixture. Compound (**2**) [or (**3**)] was synthesized by first adding 2×10^{-3} mol copper(II) acetate, then 10^{-3} mol NaN_3 (or NaNCO), and finally 2×10^{-3} mol $NaPF_6$. Single crystals were obtained by slow evaporation.

$[Cu_2(C_{17}H_{27}N_4O)(AcO)(N_3)][PF_6]$
(**2**)

$[Cu_2(C_{17}H_{27}N_4O)(AcO)(NCO)][PF_6]$
(**3**)

Crystal data: (**2**): triclinic, space group $P1$, $a = 13.973(2)$, $b = 11.289(1)$, $c = 9.224(2)$ Å, $\alpha = 74.97(2)$, $\beta = 74.22(2)$, $\gamma = 77.88(2)°$; $Z = 2$, $D_m = 1.66$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 18.1$ cm^{-1}, home made diffractometer, 3069 independent reflections, structure solved by automatic centrosymmetric, direct, and Fourier methods, and refined by full matrix least-squares, $R = 0.049$ for 2156 used reflections (Figure 1).

(**3**): Monoclinic, space group $P2_1/c$, $a = 10.352(9)$, $b = 26.44(1)$, $c = 10.459(1)$ Å, $\beta = 109.28(3)°$; $Z = 8$, $D_m = 1.68$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 17.9$ cm^{-1}, home made diffractometer, 3581 independent reflections, structure solved by Patterson and Fourier methods, and refined by full matrix least-squares $R = 0.038$ for 2922 used reflections.†

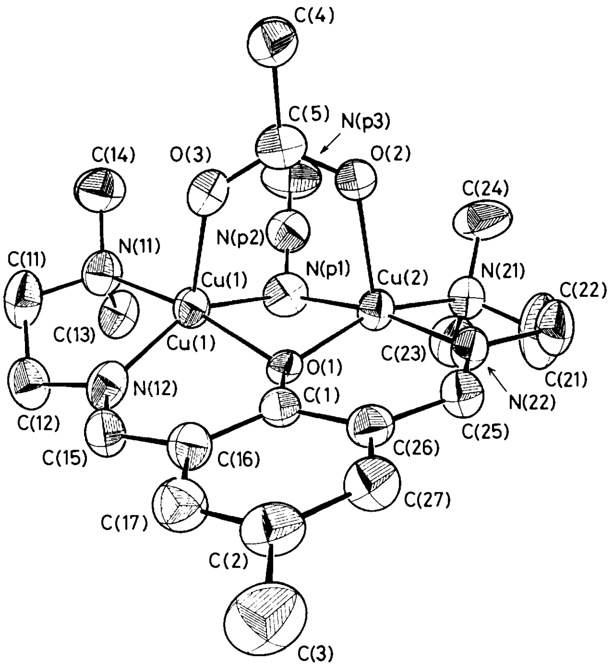

Figure 1. ORTEP view of the binuclear unit for compound (**2**).

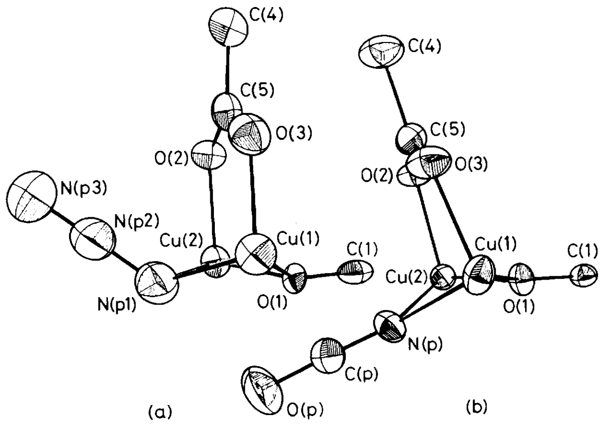

Figure 2. ORTEP view of the three bridges arrangement between copper atoms for the compounds (a) (**2**) and (b) (**3**). Important bond lengths, in Å; (**2**): Cu(1)–O(1) 1.980(6), Cu(1)–N(p1) 2.12(1), Cu(1)–O(3) 2.034(7), Cu(2)–O(1) 1.956(8), Cu(2)–N(p1) 2.049(8), Cu(2)–O(2) 2.200(6); Cu–Cu 2.978(2). (**3**): Cu(1)–O(1) 1.956(4), Cu(1)–N(p) 2.266(5), Cu(1)–O(3) 1.982(5), Cu(2)–O(1) 1.951(3), Cu(2)–N(p) 2.024(5), Cu(2)–O(2) 2.182(6), Cu–Cu 2.995(1).

The two structures are similar, with three different bridges between the copper atoms: the oxygen atom of a phenolato group, the nitrogen atom of N_3^- or NCO^-, and an acetato group. Compound (**3**) provides the first example of a structurally characterized end-on cyanato bridge. In both (**2**) and (**3**), the copper environments are dissimilar and highly distorted. The environment about Cu(2) is close to a square-based pyramid with an oxygen atom of the acetato bridge in an apical position. The other Cu environment is close to a bipyramid with N(11)–Cu(1)–O(1) as a trigonal axis in (**2**), and close to a square-based pyramid with the bridging nitrogen atom in an apical position in (**3**).

A striking difference between (**2**) and (**3**) is the geometry observed for the μ-N atoms of azido [in (**2**)] and cyanato [in (**3**)]. It is pyramidal for (**2**) and planar for (**3**); the sum of the

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

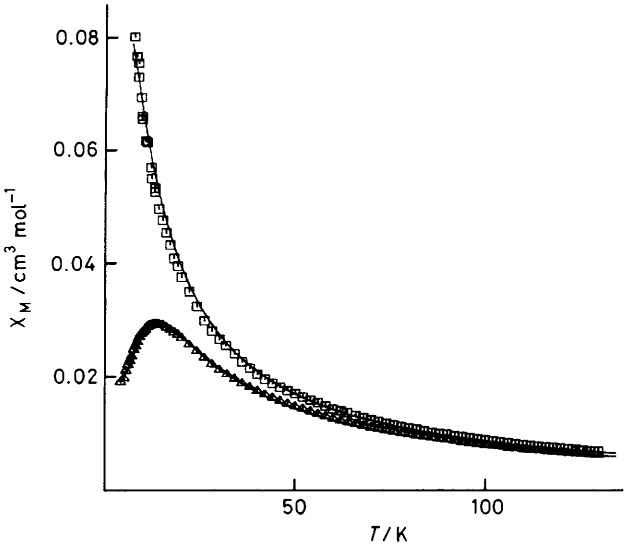

Figure 3. Experimental [△ for (**2**) and □ for (**3**)] and calculated (——) temperature dependences of the molar magnetic susceptibility for compounds (**2**) and (**3**). The equation of the calculated curves is $\chi_M = (2N\beta^2g^2/kT)[3 + \exp(-J/kT)]^{-1}(1 - \rho) + (N\beta^2g^2/2kT)\rho + 2N\alpha$. For (**2**), $J = -17.4$ cm^{-1}, $g = 2.10$, $\rho = 0.016$, $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}. For (**3**), $J = -6.3$ cm^{-1}, $g = 2.17$, $\rho = 0.041$, $N\alpha = 60 \times 10^{-5}$ cm^3 mol^{-1}.

angles around the bridging nitrogen arom is 321.5° and 357° respectively (Figure 2).

The nature and magnitude of the interaction between the metal centres were deduced from the magnetic properties studied down to 4.2 K (Figure 3). For both complexes, the ground state is the singlet state but the singlet–triplet energy gap J is weak: $J = -17.4$ cm^{-1} for (**2**) and -6.3 cm^{-1} for (**3**). The antiferromagnetic interaction in (**2**) and (**3**) is much weaker than in related complexes with chloride and hydroxide exogenous bridging ligands.[7] The contribution to the measured interaction from the phenolato bridge is expected to be antiferromagnetic[8] and that from the acetato bridge is expected to be very weak, whatever its sign may be. We therefore suggest that the azido and cyanato bridges exert a ferromagnetic stabilization strong enough to lower the magnitude of the antiferromagnetic interaction to the values that are observed.

To conclude, we want to emphasize the striking differences in the magnetic properties associated with the Cu(O)(N_3)Cu network due to N_3^- bridging in an end-to-end or an end-on fashion. In the former case, the compound is diamagnetic and without a detectable e.s.r. spectrum;[6] in the latter case, as shown by this work, it is weakly antiferromagnetically-coupled and exhibits a triplet state e.s.r. spectrum.

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