

A dinuclear copper(II) complex based on bridging oxalate and single dicyanamide

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A discrete dinuclear species [Cu₂(dca)(ox)(tmen)₂](ClO₄) {*dca* = dicyanamide, *ox* = oxalate and *tmen* = N,N,N',N'-tetramethylethane-1,2-diamine} representing a rare example of a complex having bridging oxalate and single dicyanamide between two metal centres, has been synthesised and characterised by X-ray single crystal structure determination and low temperature magnetic measurements.

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The design and synthesis of polynuclear and dinuclear oxalato bridged metal complexes attracted much attention to coordination chemists during the last decade due to the strong magnetic coupling between the metal centres found in this kind of complexes^{1,2} for their potential application in the field of material chemistry³⁻⁵. Recently, a few groups have chosen dinuclear oxalato bridged metal(II) complexes as starting material^{5,6} to design multinuclear polymeric complexes using different bridging ligands. We have also applied the same strategy to design an alternating chain of oxalate and dicyanamide. However, our effort led to the discovery of an unexpected dinuclear Cu(II) complex [Cu₂(dca)(ox)(tmen)₂](ClO₄), with both oxalate and dicyanamide bridging. To the best of our knowledge, this complex represents a rare molecular complex having a single dicyanamide bridge between the two metal ions.

Experimental

IR (KBr disk) spectrum was recorded on a Perkin-Elmer 783 spectrometer. Elemental analysis was done on a Perkin-Elmer 2400 (series II) elemental analyser. Diffraction data were collected at *T* = 293(2) K on a Nonius DIP-1030H system equipped with Mo-K α radiation graphite monochromatized. Data reduction and cell refinement were carried out using the program Mosflm and Scala⁷. The structure was solved

by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on *F*² with all observed reflections⁸. The ethylene C atoms and perchlorate oxygens were found disordered over two sites with half occupancy. All the calculations were performed using the WinGX System, Ver 1.64.04⁹.

Crystal data: C₁₆H₃₂Cu₂N₇O₄ClO₄, *M* = 613.02, monoclinic, space group *P2/c*, *a* = 14.903(4), *b* = 6.510(2), *c* = 14.542(4) Å, β = 115.41(2)°, *V* = 1274.4(6) Å³, *Z* = 2, ρ_{calc} = 1.593 g/cm³, μ (Mo-K α) = 1.827 mm⁻¹, *F*(000) = 632. Final *R*1 = 0.0424, *wR*2 = 0.1084, *S* = 1.031 for 177 parameters and 5525 reflections, 2807 unique [*R*(int) = 0.0420], of which 2106 with *I* > 2 σ (*I*), max positive and negative peaks in ΔF map 0.729, -0.387 e Å⁻³.

To prepare the title complex, a methanolic solution (5 ml) of N,N,N',N'-tetramethylethane-1,2-diamine (*tmen*) was added dropwise to a methanolic solution (10 ml) of copper(II) perchlorate hexahydrate (1 mmol) with continuous stirring. To the resulting deep blue solution, a mixture (1:1, 0.5 mmol each) of disodium oxalate and sodium dicyanamide in water (10 ml) was added dropwise in stirring condition at room temperature separating a blue precipitate. The mixture was filtered and the filtrate was kept in a CaCl₂ desiccator. Blue single crystals suitable for X-ray analysis were obtained by slow evaporation of the filtrate. Anal. Calc. For C₁₆H₃₂Cu₂N₇O₄ClO₄: C, 31.32; H, 5.22; N, 15.98. Found: C, 31.16; H, 5.80, N, 15.85. IR: ν (-CO) 1640, ν (CN) 2150, ν (ClO₄) 1120-976 cm⁻¹.

Results and discussion

The single crystal consists of dinuclear copper(II) unit and perchlorate anion. The molecular structure of the dinuclear species located on a crystallographic two fold axis is depicted in Fig. 1. Each copper ion is in a distorted five-coordinate square-pyramidal environment. The oxygens of the bridging oxalate and the *tmen* N donors build the basal plane, whereas nitrogen N(4) of the *dca* anion occupies the apical site. The basal metal-ligand Cu-O and Cu-N distances are close comparable within their e.s.d.'s (1.991(2), 1.993(3) and 2.010(3), 2.012(3) Å, respectively), but significantly shorter than the apical Cu-N bond length of 2.375(3) Å, with the copper ions displaced by 0.20

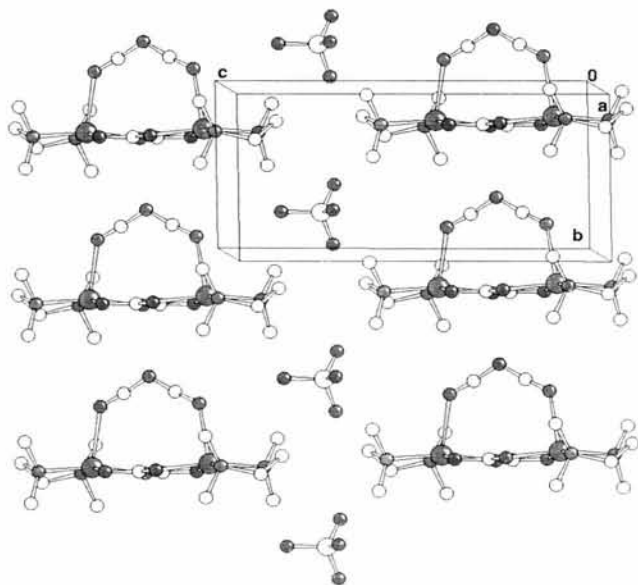


Fig. 1—Molecular structure of the dinuclear cation with atom labeling scheme of the asymmetric unit (ORTEP drawing, 40% thermal ellipsoids). Of the disordered ethylene C atoms, only one conformation is shown. Selected bond lengths and angles: Cu-O(1) 1.991(2); Cu-O(2) 1.993(3); Cu-N(1) 2.012(3); Cu-N(2) 2.010(3); Cu-N(4) 2.375(3) Å; O(2)-Cu-O(1) 83.86(9); N(2)-Cu-N(1) 87.81(12); O(1)-Cu-N(4) 89.41(9); O(2)-Cu-N(4) 89.55(10); N(1)-Cu-N(4) 101.49(11); N(2)-Cu-N(4) 101.37(10); C(7)-N(4)-Cu 124.6(3)°.

Å from the basal N_2O_2 plane towards the fifth coordination site.

In the oxalato complex chemistry, the adoption of the η^4 -chelation¹⁰, bridging the metal centres in an *anti-anti* fashion, is extensively predominant in the literature¹¹. In fact, the present relevant parameters are in good agreement with data reported previously for complexes of type $[Cu_2(ox)(N-N)_2X_2]^n$, where N-N = dinitrogen chelating ligand and X = H_2O ($n = +2$)¹², or coordinating anions ($n = 0$)¹³. In all of these centrosymmetric structures the two square-pyramids have opposite polarities, while in the present compound they are iso-oriented owing to the bridging *dca* anion. On the other hand, although *dca* anion has been widely used in the coordination chemistry, mainly with the aim to obtain polymeric compounds¹⁴, a single dicyanamide anion connecting two metal ions is rare. The *dca* is “confined” between the copper ions separated through the oxalate bridge by 5.167 Å, a feature that induces coordination Cu-N≡C bond angles of 124.6(3)°, and a distorted coordination geometry about the metal. In fact, the O-Cu-N(4) and N-Cu-N(4) bond mean angles are about 89.5° and 101.4° respectively. The crystal packing

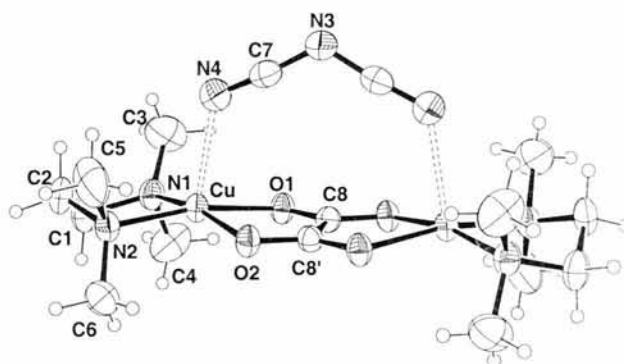


Fig. 2—Molecular packing of $[Cu_2(dca)(ox)(tmen)_2](ClO_4)$, showing the piled complex cations arranged about two fold axis.

(Fig. 2) evidences dinuclear cations piled along the crystallographic *b* axis, the shortest intermolecular Cu...Cu distance being 6.150 Å.

As a comparison, a search in the Cambridge Structural Database (CSD)¹¹ retrieved 203 M-N≡C-N-C≡N fragments (range 119.4–179.3°) with a mean value of 161.2° indicating a preference for *dca* nitrile nitrogen to be “linear” coordinated.

Magnetic study of the title complex was performed using variable temperature susceptibility measurements. Plot of $\chi_M T$ vs T shows that $\chi_M T$ value decreases continuously with decreasing temperature from 350 K ($\chi_M T = 0.4438 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) to 150 K ($\chi_M T = 0.10485 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) indicating the existence of strong antiferromagnetic interaction. The magnetic data are fitted using formula of susceptibility of a Cu(II) dimer model (Bleaney-Bowers equation). Least square fitting results $J = -353 \text{ cm}^{-1}$, $g = 2.08$ ($R = 8.5 \cdot 10^{-6}$). High J value indicates the presence of strong antiferromagnetic interaction within the molecule, which can be easily explained from the structure.

From X-ray diffraction analysis, the geometry around each Cu(II) results square pyramidal with a long axial Cu-N (dicyanamide) bond and four short equatorial bond lengths, e.g. two Cu-N (diamine) and two Cu-O (oxalate). From this structural pattern it is clear that the unpaired electron of Cu(II) centre occupies the $d_{x^2-y^2}$ orbital and an electron pair is contained in the d_z^2 . Thus, the magnetic orbital, responsible for paramagnetism of the title complex is lying along the equatorial base. The four oxygen atoms of the bridging oxalate connect the Cu(II) centres through their equatorial $d_{x^2-y^2}$ orbital which includes the spin unpaired electron. The outcome is a strong magnetic interaction, while the bridging

dicyanamide is not a good magnetic pathway since it binds the Cu(II) centres to their d_z^2 orbital containing spin paired electrons.

Supplementary data

The crystallographic data has been deposited to the Cambridge Crystallographic Data Center, reference number 197193.

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