The First Dinuclear Copper(II) Complex bridged by a Single Thiolate-sulphur Atom: Synthesis, Properties, and Structure

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A novel compound, $[Cu_2(cyclops)_2(SC_6H_4Me\text{-}p)][ClO_4]$,† bridged by a thiolate-sulphur atom, has been isolated for the first time and structurally characterised.

Copper(II) complexes ligated by a thiolate-sulphur atom are of interest in relation to the active site of blue (type 1) copper proteins.[1] To date, however, only a few mononuclear copper(II)–thiolate complexes have been isolated and structurally characterised,[2—5] because of the thermodynamic instability of such complexes, which readily undergo redox reactions (equation 1). Thus, the synthesis of a copper(II)–thiolate complex is of interest. In this communication we describe the preparation, properties, and molecular geometry of a copper(II) complex, $[Cu_2(cyclops)_2(SC_6H_4Me\text{-}p)][ClO_4]$.† This is the first example of a dinuclear copper(II) complex bridged by a thiolate ligand.

$$Cu^{II} + RS^- \text{ (or } Cu^{II}SR) \rightarrow Cu^{I} + \tfrac{1}{2}RSSR \qquad (1)$$

To a cold methanol (10 cm^3) solution of $[Cu(cyclops)][ClO_4]\cdot H_2O$[6] (1) (0.46 mmol), $NaSC_6H_4Me\text{-}p$ (0.23 mmol) in MeOH (10 cm^3) was added dropwise under a nitrogen atmosphere. The resulting dark green solution was refrigerated at −15 °C for 15 h to give dark green crystals of $[Cu_2(cyclops)_2(SC_6H_4Me\text{-}p)][ClO_4]$ (2), which were collected by filtration, washed with a small amount of diethyl ether, and dried *in vacuo* (yield 47%).‡

$[Cu(cyclops)][ClO_4]\cdot H_2O$
(1)

$[Cu_2(cyclops)_2(SC_6H_4Me\text{-}p)][ClO_4]$
(2)

The structure of the cation of (2), determined by an *X*-ray crystallographic analysis,§ together with the atom labelling

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† Cyclops = 1,1-difluoro-4,5,11,12-tetramethyl-3,6,10,13-tetra-aza-1-bora-2,14-dioxacyclotetradeca-3,5,10,12-tetraenate.

‡ Satisfactory elemental analysis was obtained.

§ *Crystal data:* $[Cu_2(C_{11}H_{18}N_4O_2BF_2)_2(SC_6H_4Me\text{-}p)][ClO_4]$, triclinic, space group, $P\bar{1}$, $a = 12.329(6)$, $b = 15.447(6)$, $c = 11.018(7)$ Å, $\alpha = 94.45(5)$, $\beta = 92.22(5)$, $\gamma = 96.13(4)°$, $U = 2078(2)$ Å^3, $Z = 2$, $D_c = 1.447(2)$ g cm^{-3}. The structure analysis is based on 2167 independent reflections $|F_o| > 3\sigma(F)$ (Mo-K_α) and R is 0.089. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

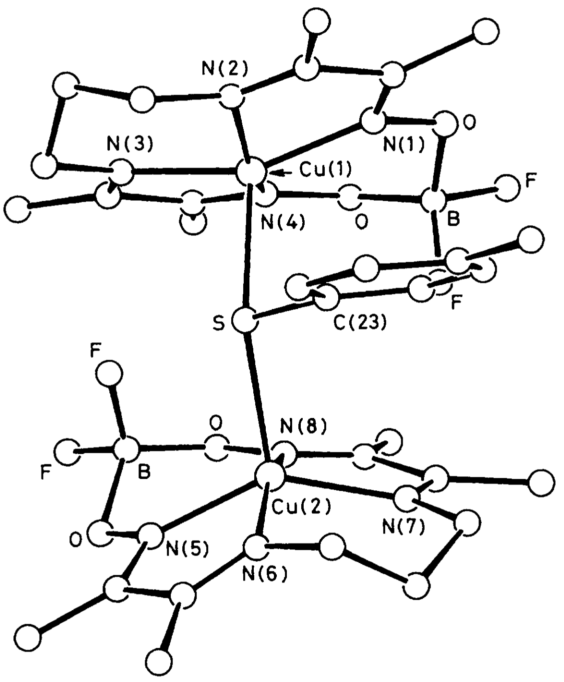

Figure 1. ORTEP view of the [$\mathrm{Cu_2(cyclops)_2(SC_6H_4Me}$-*p*)]$^+$ cation with the atom labelling scheme. Important bond lengths (Å) and angles (°): Cu(1)–S 2.506(7), Cu(2)–S 2.436(7), Cu(1)–N(1) 1.924(15), Cu(1)–N(2) 1.996(19), Cu(1)–N(3) 1.994(16), Cu(1)–N(4) 1.931(18), Cu(2)–N(5) 1.986(17), Cu(2)–N(6) 1.955(19), Cu(2)–N(7) 2.008(17), Cu(2)–N(8) 1.924(19); Cu(1)–S–Cu(2) 128.6(3), Cu(1)–S–C(23) 99.8(8), Cu(2)–S–C(23) 107.8(7), N(1)–Cu(1)–N(3) 154.0(7), N(2)–Cu(1)–N(4) 154.0(7), N(5)–Cu(2)–N(7) 141.2(7), N(6)–Cu(2)–N(8) 157.3(8).

scheme is depicted in Figure 1. The two copper atoms are bridged by a thiolate group, and there exist two distinct copper(II)–thiolate linkages. The Cu(1)–Cu(2) distance is 4.453(5) Å. Each copper atom is co-ordinated by the four nitrogen atoms of the cyclops ligand and by a sulphur atom of the thiolate ligand forming a square pyramidal geometry. The Cu(1)–S [2.507(7) Å] and Cu(2)–S [2.463(7) Å] bond distances differ significantly from each other. The displacement of the Cu atoms out of the basal plane formed by the four macrocyclic nitrogen atoms are 0.43 [Cu(1)] and 0.52 Å [Cu(2)]. The displacements are larger than those in Cu(cyclops)–X (1 : 1) complexes; 0.38, 0.40, and 0.32 Å for X = $\mathrm{I^-}$,[7] pyridine,[8] and H_2O,[9] respectively. This is indicative of the Cu–S linkages in (**2**) being much stronger than in the Cu(cyclops)X complexes.[6]

A CH_2Cl_2 solution of (**2**) at room temperature exhibits a strong absorption maximum at 415 nm (ε 6480 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$) with a shoulder band around 360 nm, as shown in Figure 2. These bands may be attributed to the sulphur-to-copper charge transfer transitions in the dimer unit of (**2**), since (**1**) exhibits no strong bands in that region. Moreover, (**2**) in CH_2Cl_2 is extremely stable even at room temperature, and the dinuclear structure is firmly retained without fission of the Cu–S–Cu linkage even in very dilute solution (*ca.* 10^{-5} mol $\mathrm{dm^{-3}}$), as confirmed from the electronic absorption spectrum. Complex (**2**) in dimethylformamide, DMF, however, exhibits

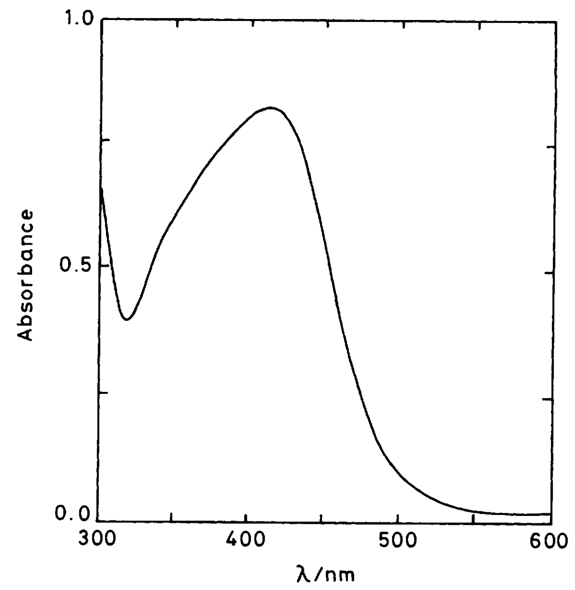

Figure 2. Electronic absorption spectrum of (**2**) (1.0×10^{-4} mol $\mathrm{dm^{-3}}$) in CH_2Cl_2 at room temperature.

a strong absorption maximum at 432 nm, differing significantly from the spectrum in CH_2Cl_2, whose position is very close to that of the absorption maximum observed in mononuclear [$\mathrm{Cu(cyclops)(SC_6H_4Me}$-*p*)] in DMF,[5] indicating that (**2**) dissociates into a mononuclear species in DMF. The cyclic voltammetry of (**2**) in CH_2Cl_2 containing 0.1 mol $\mathrm{dm^{-3}}$ [$\mathrm{NBu^n_4}$][$\mathrm{BF_4}$] as a supporting electrolyte gave two quasi-reversible redox waves at $E_{\frac{1}{2}} = -0.416$ and -0.679 V *vs.* normal hydrogen electrode with ΔE = 110 and 90 mV, respectively, which may be assigned to two successive one electron processes (equation 2) as confirmed from the e.s.r. spectra under controlled potential electrolysis conditions at room temperature.

$$\mathrm{Cu^{II}SCu^{II}} \underset{-e^-}{\xrightarrow{+e^-}} \mathrm{Cu^{I}SCu^{II}} \underset{-e^-}{\xrightarrow{+e^-}} \mathrm{Cu^{I}SCu^{I}} \qquad (2)$$

Thus, the Cu–S–Cu linkage of (**2**) is still retained in the two reduced forms.

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