

## Copper(I) binds Carbon Monoxide in a Cubane-like Structure: Chemistry and X-Ray Crystal Structure of Tetrakis[(2-methylquinolin-8-olato)-carbonylcopper(I)]

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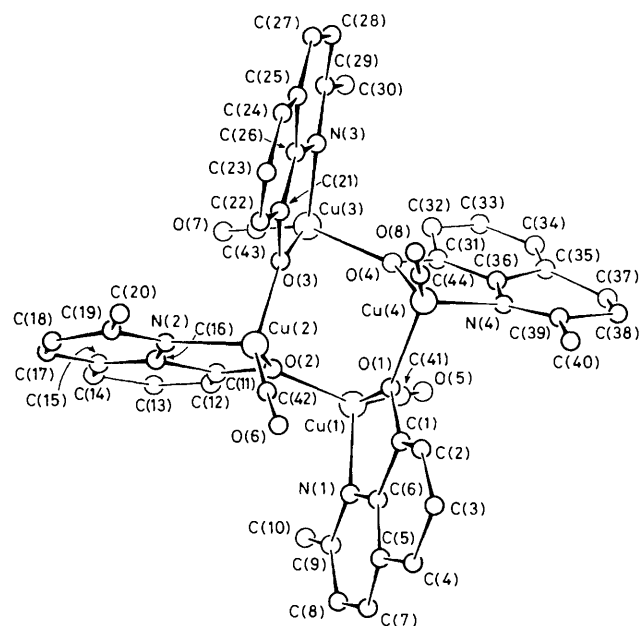
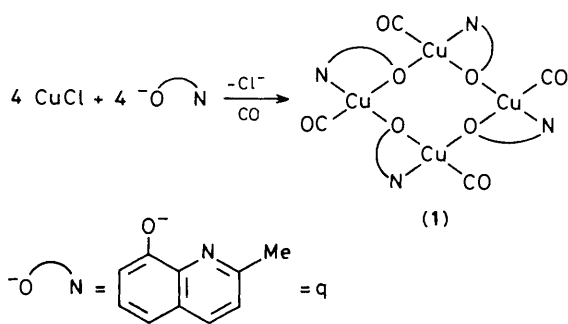
Copper(I) chloride reacts with a solution of sodium 2-methylquinolin-8-olate (qNa) in tetrahydrofuran under a pressure of 60 atm of CO at 65 °C to give a tetranuclear copper(I) carbonyl complex  $[\text{Cu}(\text{q})(\text{CO})]_4$ , (**1**),  $[\nu(\text{C}-\text{O}), 2050 \text{ cm}^{-1}]$ , having a cubane-like structure, with  $S_4$  symmetry, in which the copper atoms are bridged by the oxygen atom of the quinolinolato ligand.

Copper(I) aggregates exhibit an unusual tendency to bind small molecules, *e.g.* carbon monoxide and dioxygen. Copper(I) forms a wide range of polynuclear complexes, with two to eight copper atoms and a large variety of structural types.<sup>1,2</sup> However investigations into their chemistry have been limited to synthesis, while their reactivity, whether with one or more metal centre, has been largely unexplored.<sup>3</sup> A unique example of a dicopper(I) unit interacting with bridging carbon monoxide was recently reported.<sup>4</sup> The growth of copper(I)-carbon monoxide chemistry<sup>4,5</sup> can provide us with basic information concerning the synthesis and utilization of polynuclear copper(I) complexes in the activation of carbon monoxide and other small molecules.

We describe herein a tetranuclear copper(I) complex, whose metal atom framework may be suitable for the multicentre

activation of small molecules. It is found to bind carbon monoxide firmly and to have a cubane-like structure. A tetrahydrofuran (THF) suspension of sodium 2-methylquinolin-8-olate (qNa), was allowed to react with copper(I) chloride at 65 °C under a carbon monoxide pressure of 60 atm. A copper(I) carbonyl (**1**) was recovered in high yield as yellow crystals.† Complex (**1**) is thermally stable and insensitive to air in the solid state. The presence of terminal carbon monoxide is indicated by the i.r. spectrum which shows a single band at  $2070 \text{ cm}^{-1}$  (THF solution) and at  $2050 \text{ cm}^{-1}$  (Nujol mull). Complex (**1**) reacted with *p*-MeC<sub>6</sub>H<sub>4</sub>NC and

† Satisfactory analytical data have been obtained for all complexes reported.



**Figure 1.** View of complex (1) showing the atom numbering scheme.

$\text{PPh}_3$  to form  $[\text{Cu}(\text{q})(p\text{-MeC}_6\text{H}_4\text{NC})]_n$ ,<sup>†</sup> and  $[\text{Cu}(\text{q})(\text{PPh}_3)]_n$ ,<sup>†</sup> respectively. Unexpected characteristics in the structure of (1) have been revealed by X-ray analysis.<sup>‡</sup>

Figure 1 shows a view of the tetranuclear complex (1). The molecule has approximately  $S_4$  symmetry, with copper and oxygen atoms arranged in a cubane-like structure.<sup>3</sup> The four copper atoms are at the vertices of a tetrahedron. Each copper has a *pseudo*-tetrahedral co-ordination provided by the bidentate

<sup>‡</sup> *Crystal Data:*  $\text{C}_{44}\text{H}_{32}\text{O}_8\text{N}_4\text{Cu}_4$ ,  $M = 998.2$ , monoclinic,  $a = 15.591(3)$ ,  $b = 18.558(3)$ ,  $c = 15.850(3)$  Å,  $\beta = 90.08(2)^\circ$  (from least-squares fitting of setting angles of 25 reflections),  $Z = 4$ ;  $D_c = 1.445$  g cm<sup>-3</sup>, space group  $P2_1/n$  (from systematic extinctions). Intensity data were collected on a Philips PW 1100 automatic diffractometer using graphite monochromatized Mo- $K_\alpha$  radiation,  $\omega$ - $2\theta$  scans of width  $1.6^\circ$  in  $\omega$ , and a scan speed of  $0.04^\circ$  s<sup>-1</sup>. A total of 3456 independent reflections was measured in the range  $2^\circ < \theta < 20^\circ$ ; reflections having  $I < 3\sigma(I)$  were considered as unobserved (2042). The structure was solved by direct methods and refined by the full-matrix least-squares method. The final  $R$  value was 0.069 ( $R_w = 0.076$ ) for 1414 observed reflections and 214 parameters. 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.

quinolinolato anion, carbon monoxide, and the two bridging oxygens. Cu–O bond distances range from 2.01(2) to 2.08(2) Å [ $\text{Cu}-\text{O}_{\text{av}}$ , 2.04 Å] and Cu–N from 2.00(2) to 2.12(2) Å [ $\text{Cu}-\text{N}_{\text{av}}$ , 2.06 Å]. Copper . . . copper separations vary from 3.514(1) to 3.856(1) Å [ $\text{Cu} \dots \text{Cu}_{\text{av}}$ , 3.615 Å] and the average Cu . . . Cu . . . Cu angle is  $60.0^\circ$ . The Cu–C (mean value 1.76 Å) and C–O (carbon monoxide) (mean value 1.13 Å) bond distances compare very well with the values reported for other copper(I) carbonyls.<sup>4,5</sup> These structural parameters can be related to those of the analogous tetrameric structures of copper(I),  $[\text{Cu}-\text{OCMe}_3]_4$ <sup>6</sup> and  $[\text{Cu}(\text{mhp})]_4$  (mhp = 6-methyl-2-oxo-pyridine anion).<sup>7</sup>

Some characteristics of complex (1), which could be the prototype of a new class of copper(I) complexes, are worth mentioning: (i) the polynuclear structure is built up by a phenoxo group bridging two copper atoms.<sup>8</sup> A bridging oxygen atom has been invoked as the crucial ligand for the activity of the dicopper unit in binding dioxygen.<sup>3,9</sup> (ii) The Cu . . . Cu separation (3.615 Å) is suitable for the dinuclear activation of small molecules.<sup>5,10</sup> (iii) Each copper(I) has only one co-ordination site filled by a labile ligand, which can be easily replaced. (iv) The N and O donor atoms surrounding copper(I) are attached to an organic residue which has considerable electron flexibility, a property which is necessary for the metal to bind small molecules like dioxygen<sup>11</sup> and carbon monoxide. (v) The thermal stability is rather surprising because of the presence of a carbon monoxide molecule and of a Cu–OR bond which is believed to be unstable.<sup>8,12</sup>

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