A Novel Octanuclear Copper(I) Complex with a Compressed Square Antiprismatic Cu_8 Core

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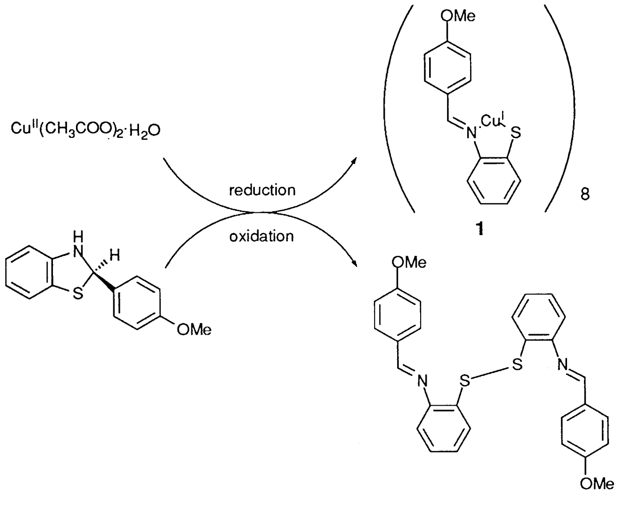
A novel octanuclear copper(I) complex, which has a compressed square antiprismatic core of copper atoms (Cu···Cu = av. 2.651(9) Å), was prepared by the reaction of copper(II) acetate with 2-(4-methoxyphenyl)benzothiazoline.

There is much interest in polynuclear complexes of transition metals with sulfur-containing ligands, since these complexes display a wide variety in composition and in structure. Indeed, some octanuclear copper(I) complexes have been isolated with the cubic Cu_8 core.[1] However, few reports emerge on octanuclear complexes with a square antiprismatic Cu_8 core.[2] We report here the synthesis and structure of the novel octanuclear copper(I) complex **1** with a hexadeca Cu_8S_8 core.[3]

Reaction of copper(II) acetate with 2 equiv. of 2-(4-methoxyphenyl)benzothiazoline[4] in benzene led to a reddish brown powder of **1**.[5] This reaction product **1** was diamagnetic as indicated by sharp resonances in the ^1H NMR spectrum and the elemental analysis presents unambiguous evidence that a 1:1 (Cu:ligand) complex was formed. Thus the gross structure of **1** was presumed to be distinct from those of the nickel(II) and palladium(II) complexes with similar ligands being a 1:2 (metal:ligand).[6] In addition, from the ^1H NMR study of reaction mixture after removal of **1**, the formation of 2,2'-di(4-methoxyphenylmethyleneaminophenyl)disulfide as a main product was confirmed in comparison with an authentic sample.[7] These facts show that the formation of **1** results from copper reduction, Cu(II) → Cu(I), accompanied by the oxidation of 2-(4-methoxyphenyl)benzothiazoline.



In order to determine the molecular structure of **1** an X-ray crystal structure analysis was carried out[8] and the results revealed an octanuclear copper complex of formula $[Cu_8\{S(C_6H_4)NCH(C_6H_4)OCH_3\}_8]$. The molecular structure is shown in Figure 1.

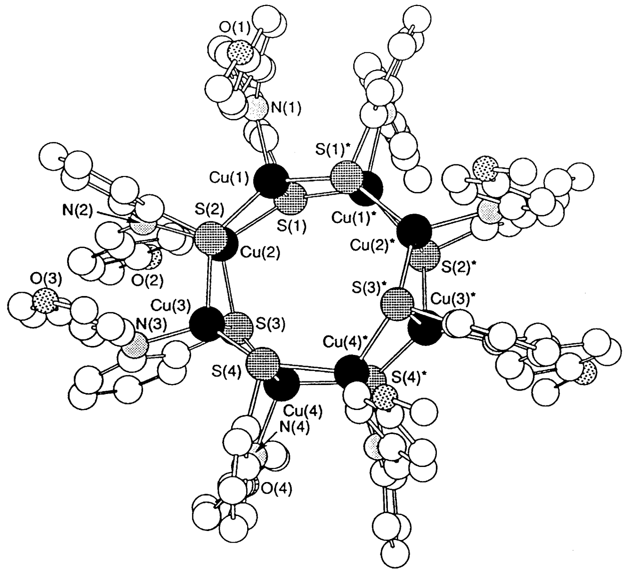


Figure 1. The molecular structure of **1**. (Hydrogen atoms and CH_2ClCH_2Cl molecules have been omitted for clarity.) Selected bond lengths (Å) and angles (°): Cu(1)-S(1) 2.439(15), Cu(1)-S(1)* 2.337(14), Cu(1)-S(2) 2.355(13), Cu(2)-S(1) 2.320(14), Cu(2)-S(2) 2.446(14), Cu(2)-S(3) 2.344(13), Cu(3)-S(2) 2.382(13), Cu(3)-S(3) 2.418(15), Cu(3)-S(4) 2.306(13), Cu(4)-S(3) 2.349(14), Cu(4)-S(4) 2.431(15), Cu(4)-S(4)* 2.348(14), Cu(1)-N(1) 2.06(4), Cu(2)-N(2) 2.07(4), Cu(3)-N(3) 2.03(4), Cu(4)-N(4) 2.07(4), Cu(1)···Cu(1)* 2.695(9), Cu(1)···Cu(2) 2.588(9), Cu(2)···Cu(3) 2.692(9), Cu(3)···Cu(4) 2.605(9), Cu(4)···Cu(4)* 2.673(9), S(1)-Cu(1)-S(1)* 111.2(5), S(1)-Cu(1)-S(2) 113.1(5), S(2)-Cu(2)-S(3) 110.5(5), S(1)*-Cu(1)-S(2) 111.6(5), S(2)-Cu(3)-S(3) 110.1(5), S(2)-Cu(3)-S(4) 100.9(5), S(1)-Cu(2)-S(2) 114.1(5), S(1)-Cu(2)-S(3) 104.8(5), S(3)-Cu(3)-S(4) 113.3(5), S(3)-Cu(4)-S(4) 111.3(5), S(3)-Cu(4)-S(4)* 111.3(5), S(4)-Cu(4)-S(4)* 111.6(5), Cu(1)-S(1)-Cu(1)* 68.7(4), Cu(1)-S(1)-Cu(2) 65.8(4), Cu(1)*-S(1)-Cu(2) 120.9(6), Cu(1)-S(2)-Cu(2) 65.2(4), Cu(1)-S(2)-Cu(3) 120.1(6), Cu(2)-S(2)-Cu(3) 67.8(4), Cu(2)-S(3)-Cu(3) 68.8(4), Cu(2)-S(3)-Cu(4) 119.4(6), Cu(3)-S(3)-Cu(4) 66.2(4), Cu(3)-S(4)-Cu(4) 66.7(4), Cu(3)-S(4)-Cu(4)* 123.0(6), Cu(4)-S(4)-Cu(4)* 68.0(4).

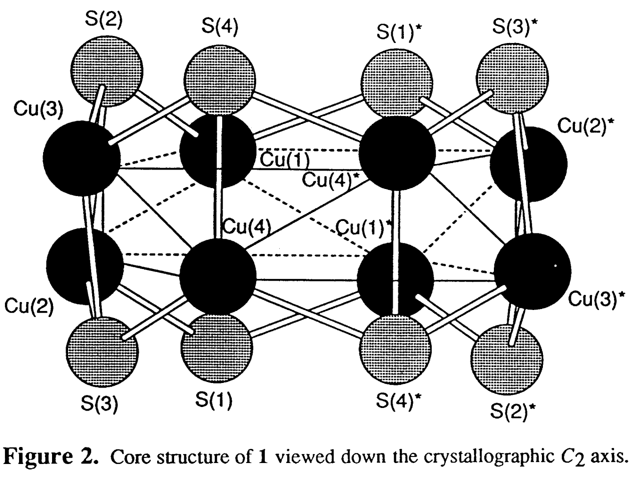


Figure 2. Core structure of **1** viewed down the crystallographic C_2 axis.

The molecule has a crystallographic C_2 axis. The cyclic ladder structure of **1** consists of two Cu_4S_4 heterocyclic rings. The Cu_4S_4 units are crown-shaped rather than planar (Figure 2). Each copper(I) ion is bonded to N,S atoms of one ligand and two μ_3-S atoms of the neighboring ligand to give a tetrahedral configuration. The average Cu-S and Cu-N distances of 2.373(14) and 2.06(4) Å respectively are within the range normally found for tetra-coordinate Cu(I)-sulfur compounds[9] and tetra-coordinate Cu(I)-imino nitrogen ones.[10] However, it is noteworthy that all Cu(I)-bridging S distances are shorter than the terminal ones. The average Cu···Cu distance is only 2.651(9) Å, rather short compared to corresponding distances in the other copper-sulfur complexes.[9] Furthermore the Cu-S-Cu angles in the four-membered ring defined by Cu(1)-S(1)-Cu(2)-S(2), Cu(2)-S(2)-Cu(3)-S(3) and so on are remarkably acute. These short distances and the accompanying acute bridge angles suggest an electron-deficient three-center two-electron (3c-2e) bond.[9,11]

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References and Notes

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3. Very recently, the similar N-bridge cyclic ladder structure was observed in the lithium primary amide molecule. N. D. R. Barnett, W. Clegg, L. Horsburgh, D. M. Lindsay, Q. -Y. Liu, F. M. Mackenzie, R. E. Mulvey, and P. G. Williard, *J. Chem. Soc., Chem. Commun.*, **1996**, 2321.
4. All compounds were prepared under argon. 2-(4-Methoxyphenyl)benzothiazoline: 2-Aminothiophenol (2.22 g, 17.7 mmol) was added to a solution of 4-methoxybenzaldehyde (2.42 g, 17.7 mmol) in ethanol (20 mL). The mixture was heated under reflux for 45 min and then cooled to room temp. The light yellow precipitate was dried *in vacuo*. Yield: 3.72 g (86%). IR (Nujol mull): ν(N-H) at 3345 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz, 298 K): δ 3.81(s, 3H), 4.31(s, 1H), 6.37(s, 1H), 6.64(d, 1H), 6.75(dt, 1H), 6.88(d, 2H), 6.94(dt, 1H), 7.04(d, 1H) and 7.48(d, 2H). Anal. Found: C, 68.95; H, 5.38; N, 5.71%. Calcd for $C_{14}H_{13}NOS$: C, 69.10; H, 5.39; N, 5.76%.
5. Complex **1**: To a solution of 2-(4-methoxyphenyl)benzothiazoline (0.78 g, 3.2 mmol) in benzene (30 mL) was added copper(II) acetate monohydrate (0.31 g, 1.6 mmol). The reaction solution was heated under reflux for 2 h. The resulting solution was cooled at *ca.* -20 °C overnight to obtain reddish brown crystals. Yield: 0.47 g (96% based on Cu). X-ray-suitable crystals were obtained by slow diffusion of ether into a concentrated solution of **1** in CH_2ClCH_2Cl. IR (Nujol mull): ν(C=N) at 1604 and 1592 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz, 223 K): δ 3.76(s, 24H), 6.43(d, 16H), 6.8 - 7.0(m, 24H), 7.37(d, 16H), 7.60(d, 8H) and 8.26(s, 8H). Anal. Found: C, 56.13; H, 4.20; N, 4.44%. Calcd for $(C_{14}H_{12}CuNOS)_8\cdot C_6H_6$: C, 56.13; H, 4.07; N, 4.44%. When copper(II) acetate monohydrate was allowed to react with 1 equiv. of 2-(4-methoxyphenyl)benzothiazoline, significant quantities of unreactive copper(II) acetate were left on the glassware.
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7. An authentic sample of 2,2'-di(4-methoxyphenylmethyleneaminophenyl)disulfide was independently prepared. 2,2'-Di(4-methoxyphenyl-methyleneaminophenyl)disulfide: 2,2'-Di(aminophenyl)disulfide (0.42 g, 1.7 mmol) was added to a solution of 4-methoxybenzaldehyde (0.46 g, 3.4 mmol) in ethanol (20 mL). The mixture was heated under reflux for 45 min and then cooled to room temp. The light yellow precipitate was isolated by filtration and dried *in vacuo*. Yield: 0.75 g (92%). IR (Nujol mull): ν(C=N) at 1620 and 1592 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz, 298 K): δ 3.89(s, 6H), 7.00(d, 4H), 7.03(dd, 2H), 7.12(dt, 2H), 7.19(dt, 2H), 7.64(dd, 2H), 7.93(d, 4H) and 8.42(s, 2H). Anal. Found: C, 69.10; H, 5.08; N, 5.76%. Calcd for $C_{28}H_{24}N_2O_2S_2$: C, 69.39; H, 4.99; N, 5.78%.
8. Crystal data for complex **1**: $C_{112}H_{96}Cu_8N_8O_8S_8\cdot 3CH_2ClCH_2Cl$, $M = 2743.78$, monoclinic, space group $C2/c$, $a = 16.598(7)$ Å, $b = 23.602(10)$ Å, $c = 29.810(15)$ Å, $\beta = 96.12(4)°$, $U = 11612(9)$ Å^3, $Z = 4$, crystal size 0.20 × 0.20 × 0.15 mm, $D_c = 1.57$ g/cm^3, μ(Mo-Kα) = 1.78 mm^{-1}. Data were measured on a Mac Science MXC3 diffractometer using graphite-monochromated Mo-Kα radiation in the range $3 \le 2\theta \le 50$ °; 2892 with $I > 3\sigma(I)$ were used in the refinement. The structure was solved by direct methods (SIR92) and refined by full-matrix least squares. The refinement converged at $R = 0.064$, $R_w = 0.067$.
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