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# A Tetragonal Bisphenoidal Tetracopper(I) Arrangement Supported by a Potentially Tridentate Ligand Containing Thiolate, Secondary Amine, and 2-Pyridine Functions: Hydrogen-Bonded Instead of Cu(I)-Coordinated Pyridine Rings in an $S_4$-Symmetric Compound

**Andreas F. Stange, Karl Wilhelm Klinkhammer, and Wolfgang Kaim***

Institut für Anorganische Chemie der Universität,
Pfaffenwaldring 55, D-70550 Stuttgart, Germany

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The self-assembly of oligonuclear coordination compounds, starting from simple metal precursors and specially chosen chelate ligands, has been particularly successful with copper(I) as structurally and electronically flexible coordination centers.[1−3] An additional incentive[3−5] to use particularly mixed thiolate/N-donor ligands has recently come from the structural elucidation of dinuclear $Cu_A$ sites in cytochrome *c*-oxidase and other enzymes.[4a,6]

We have therefore applied the anodic oxidation of copper[4b,7] in the presence of chelating N- and bridging S-ligands to investigate the possibility of self-assembly processes. Combining one terminal, potentially bridging thiolate center with two nitrogen donor functions in an arrangement allowing for five-membered chelate ring formation, we used the electrogenerated anion $MEPA^-$ of *N*-(2-mercaptoethyl)picolylamine (MEPAH)[8] as a ligand for copper(I). Recently reported mono-, di-, and trinuclear zinc(II) complexes of $MEPA^-$ showed the participation of all three kinds of donor centers, thiolate, secondary aliphatic amine and 2-pyridine, in coordination by the metal.[8]

## Experimental Section

**Synthesis.** A solution containing 1.0 mL of *N*-(2-mercaptoethyl)-picolylamine[8] and 20 mg of tetrabutylammonium perchlorate in 30 mL of acetonitrile was electrolyzed using a copper anode and a platinum cathode for 2.5 h (17 V, 20 mA). The initially colorless solution turned yellow during electrolysis, and a yellow oil separated at the bottom of the vessel. After electrolysis, the acetonitrile phase was decanted and the remaining oil dissolved in 30 mL of hot toluene. Yellow crystals, some suitable for X-ray diffraction, began to separate from this solution after a few days standing at ambient temperature. Yield: 148 mg of $Cu_4(MEPA)_4$ (43% based on consumed Cu metal), with good solubility only in protic media. Anal. Calcd for $C_{32}H_{44}Cu_4N_8S_4$: C, 41.63; H, 4.80; N, 12.14%. Found: C, 42.30; H, 4.70; N, 11.70%. $^1$H-NMR ($CD_3OD$): $\delta$ 2.59 (s, br, 8H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{S}$), 2.68 (s, br, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2S}$), 3.94 (s, br, 8H, $\mathrm{PyC}\mathit{H}_2\mathrm{NH}$), 7.27 (t, 4H, $^3J = 6.4$ Hz, 5-*H*), 7.37 (d, 4H,$^3J = 7.9$ Hz, 3-*H*), 7.74 (t, 4H, $^3J = 7.7$ Hz, 4-*H*), 8.58 (d, br, 4H, $^3J = 3.6$ Hz, 6-*H*); N−H not observed due to H/D exchange.

**Instrumentation**. EPR studies were performed in the X band on a Bruker System ESP 300. $^1$H-NMR spectra were taken on a Bruker AC 250 spectrometer, infrared spectra were obtained using a Perkin Elmer FT-IR 1000 PC instrument. UV/vis/near-IR absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out in *N,N*-dimethylacetamide/0.1 M $Bu_4NPF_6$ using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference electrode) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as external reference.

**Crystallography.** Crystals of $Cu_4(MEPA)_4$ were immersed into degassed nujol. One well-shaped crystal of dimensions 0.3 × 0.3 × 0.2 mm was transferred into a capillary and immediately mounted on a Siemens P4 diffractometer equipped with a low temperature device. Unit cell parameters were determined by least-squares analysis of 65 automatically centered reflections in the range $25° < 2\theta < 30°$. The data were collected at 173 K, using monochromatized Mo K$\alpha$ radiation (0.710 69 Å) and the $\omega$-scan technique. An empirical absorption correction ($\psi$ scan, minimum 0.62/maximum 0.96, XEMP[9a]) was applied.

Although the data conform to tetragonal Laue class 4/*mmm* ($R_{\mathrm{int}} = 0.07$), a reasonable solution (SHELXTL-PLUS)[9a] of the phase problem was only achieved in space group $I\bar{4}$ belonging to Laue class 4/*m* ($R_{\mathrm{int}} = 0.05$). This face and the observed distribution of *E*-values ($E^2 - 1 = 0.522$) strongly suggest twinning about (1$\bar{1}$0). Refinement of the proposed Cu and S atom sites with full-matrix least-squares techniques based on $F_o^2$ values (SHELXL-93) [9b] and subsequent analyses of difference-Fourier syntheses revealed the positions of all non-hydrogen atoms. At this point, refinement remained at $R_1 = 0.14$. Moreover, the anisotropic displacement parameters refined to meaningless values. Application of a twinning model assuming merohedral twinning about the mirror plane (1$\bar{1}$0) led to significantly improved *R* values as well as meaningful displacement parameters. Additional maxima in subsequent difference-Fourier syntheses could then be assigned to the hydrogen atoms. Their positions were refined without geometrical constraints, adjusting their isotropic displacement parameters to 1.2 times the value for the bound carbon and nitrogen atoms. Although these positions seem to be meaningful, they should be taken with care corresponding to the low contribution of hydrogen to the total diffracted intensity, especially in the presence of heavy atoms such as copper. The final Flack absolute parameter[9c,d] indicates additional racemic twinning. Thus, batch scale factors were refined leading to the following fractional contributions from the four components (corresponding transformations of the reciprocal lattice in brackets): 0.30 (*hkl*), 0.36 (*khl*), 0.08 ($\bar{h}\bar{k}\bar{l}$) and 0.26 ($\bar{k}\bar{h}\bar{l}$). Additional details of the data collection and refinement are listed in Table 1.

## Results and Discussion

The product of the anodic oxidation of copper in acetonitrile/2 mM $Bu_4NClO_4$ and in the presence of MEPAH is a yellow tetrameric compound $Cu_4(MEPA)_4$ which could be crystallized and structurally characterized in space group $I\bar{4}$ despite crystal-

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**Table 1.** Crystallographic Data for $Cu_4(MEPA)_4$

formula: $C_{32}H_{44}Cu_4N_8S_4$
cryst system: tetragonal
$a = 12.556(2)$ Å
$c = 11.826(2)$ Å
$V = 1864.4(5)$ Å$^3$
$Z = 2$
$\theta$ range: 2.3−28°
no. of reflns collcd: 4347
no. of unique reflns ($R_{int}$): 2169 (0.088)
fw: 923.15
space group: $I\bar{4}$ (No. 82)
$T = -100$ °C
$\lambda = 0.71069$ Å
$d$(calc) = 1.644 g cm$^{-3}$
abs coeff = 25.10 cm$^{-1}$
$R_1$,[a] $wR_2$:[b] 0.037, 0.096
GOF:[c] 1.014
largest peak in final diff map (e Å$^{-3}$): 0.42

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ (based on 2090 reflections with $F_o > 4\sigma(F_o)$). [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ with $w = 1/[\sigma^2(F_o^2) + (0.0556P)^2]$; $P = [\max(F_o^2,0) + 2F_c^2]/3$ (all data). [c] $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]]^{1/2}$ ($n$ = no. of reflections, $p$ = no. of parameters).

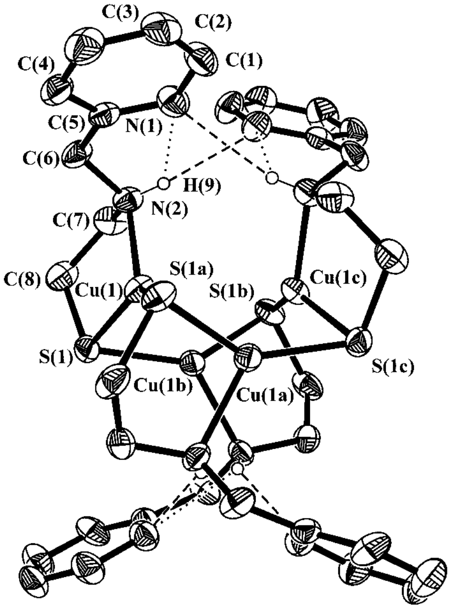


**Figure 1.** Structural representation of $Cu_4(MEPA)_4$, including the hydrogen-bonding interactions (50% ellipsoid probability level).

**Table 2.** Selected Distances (Å) and Angles (deg) for $Cu_4(MEPA)_4$[a]

| | | | |
|---|---|---|---|
| Cu(1)−N(2) | 2.106(5) | Cu(1)−S(1a) | 2.191(2) |
| Cu(1)−S(1) | 2.267(2) | Cu(1)··Cu(1a) | 2.6957(11) |
| Cu(1)··Cu(1c) | 3.270(1) | N(2)−H(9) | 0.78(7) |
| N(1)··H(9) | 2.32(7) | N(1)··H(9c) | 2.56(7) |
| N(1)··N(2) | 2.728(7) | N(1)··N(2c) | 3.263(8) |

| | | | |
|---|---|---|---|
| N(2)−Cu(1)−S(1a) | 126.54(13) | N(2)−Cu(1)−S(1) | 91.48(13) |
| S(1a)−Cu(1)−S(1) | 137.49(3) | N(2)−Cu(1)··Cu(1a) | 135.5(2) |
| S(1a)−Cu(1)··Cu(1a) | 54.08(4) | S(1)−Cu(1)··Cu(1a) | 113.88(5) |
| N(2)−Cu(1)··Cu(1a) | 97.54(14) | S(1a)−Cu(1)··Cu(1b) | 127.24(4) |
| S(1)−Cu(1)··Cu(1b) | 51.53(4) | Cu(1a)··Cu(1)··Cu(1b) | 74.68(3) |
| Cu(1a)··Cu(1)··Cu(1c) | 52.66(1) | N(2)−H(9)··N(1c) | 145(7) |
| N(2)−H(9)··N(1) | 114(6) | | |

[a] Symmetry transformations used to generate equivalent atoms: (a) $y + 1, -x + 1, -z + 1$; (b) $-y + 1, x - 1, -z + 1$; (c) $-x + 2, -y, z$.

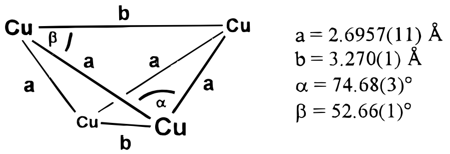
lographic twinning.

$$4Cu + 4MEPAH \xrightarrow{\text{electrolysis}} Cu_4(MEPA)_4 + 2H_2$$

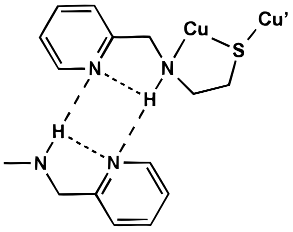
Figure 1 shows the molecular structure, Tables 1 and 2 provide the crystallographic data and selected structural parameters.

At first glance, the metal backbone of $Cu_4(MEPA)_4$ adopts a butterfly arrangement as observed previously for some tetracopper(I) compounds with mixed N,S-ligands.[2,10] However, a closer inspection of the metal arrangement exhibits $D_{2d}$ symmetry (Chart 1),[10b] i.e. a higher symmetry than in general butterfly structures ($C_{2v}$). An ideal tetragonal bisphenoid ($D_{2d}$; Chart 1) has two different distances and angles und thus lies between the butterfly structure (three distances and three angles) and the tetrahedron (one distance and one angle of 60°). Chart 1 reveals the present bisphenoid as flattened tetrahedron as was previously found in an example with a non-chelating N,S-ligand;[10b] with 2.6957(11) Å, the shorter metal−metal distances are in the range established for related copper(I) structures.[2,10] The molecule $Cu_4(MEPA)_4$ itself has $S_4$ symmetry. Not unexpectedly, the thiolate sulfur atoms act as bridging centers ($\mu_2$) toward the $(Cu^I)_4$ backbone, however, the nitrogen atoms participating in the chelation and coordinating in a nonbridging fashion are those of the "hard" secondary amine function and not those of the "softer" pyridine group. The coordination at the individual copper(I) centers is not planar[2,10] but slightly pyramidal with distances of 0.252(2) Å between the metal centers and corresponding NSS′ planes.

**Chart 1**



While one reason for this unusual nitrogen coordination preference of copper(I) lies in the favorable five-membered chelate ring formation $(\mu\text{-})\overline{\mathrm{SCH_2CH_2N(HR)Cu}}$, there is another type of cooperative interaction which stabilizes this remarkable structure:



All pendant 2-pyridyl groups participate in a hydrogen-bonding network with the metal-bound and thus activated $R_2N-H$ functions of the same and of other ligands within one cluster molecule. The NH- -N distances between centers of *different* ligands are 3.263(8) Å which would indicate relatively weak hydrogen bonds ($\nu_{NH}$ 3231 cm$^{-1}$).[11] The N(1)- -N(2) distance between centers at the *same* ligand is smaller and suggests a further, secondary hydrogen-bond interaction, although the angle N(1)··H−N(2) of 114(6)° at the crystallographically found $\mu_3$-proton is rather small. Under a different viewpoint, the free pyridine bases do not directly bind to metal centers but activate the normally not very efficient secondary amine donor sites for metal coordination via multiple hydrogen bond formation. Modulation of the metal-binding capacity via hydrogen-bonding interactions is a concept that has been developed particularly for metalloproteins such as Cu,Zn-superoxide dismutase.[12]

Attempts to further oxidize electrochemically obtained $Cu_4(MEPA)_4$ in *N,N*-dimethylacetamide (DMA)/0.1 M $Bu_4NPF_6$

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resulted in an irreversible cyclovoltammetric wave (200 mV/s) with an anodic peak potential at $-0.47$ V vs $FeCp_2^{+/0}$. At slow scan rates (20 mV/s), this first irreversible wave is followed by a quasireversible wave ($\Delta E_{pp}$ 180 mV) at $E_{1/2} = -0.36$ V. The oxidized solution did not show an EPR signal at 110 K (frozen solution), suggesting antiferromagnetic coupling in a rearranged cluster product which could not yet be crystallized. Similarly as other copper(I)/thiolate clusters,[13] the yellow $Cu_4(MEPA)_4$ with a long-wavelength absorption shoulder at about 320 nm in methanol exhibits yellow-orange luminescence in the solid.

In summary, we have shown that anodic oxidation of copper in the presence of MEPAH yields the tetranuclear copper(I) compound $Cu_4(MEPA)_4$ where the ligands support a bisphenoidal ($D_{2d}$) arrangement of the metal centers. The $MEPA^-$ ligands use $\mu$-thiolate and secondary amine nitrogen centers for coordination,[14] while the 2-pyridyl groups are not involved in Cu(I) coordination but in an intramolecular hydrogen-bonding network with the metal-bound and thus activated secondary amine functions (cooperativity).

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**Supporting Information Available:** Two stereoviews (2 pages). One X-ray crystallographic file in CIF format is available. Access and/or ordering information is given on any current masthead page.

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