N(2)—Co(2)—N(8)	122.1 (1)	Co(4)—N(6)—N(5)	116.4 (2)
N(2)—Co(2)—N(11)	117.2 (1)	N(6)—Co(4)—N(7)	118.4 (1)
N(8)—Co(2)—N(11)	114.1 (1)	N(6)—Co(4)—N(9)	119.9 (1)
O(1)—Co(3)—N(4)	98.0 (1)	N(7)—Co(4)—N(9)	116.2 (1)
O(1)—Co(3)—N(10)	100.0 (1)	Co(1)—O(1)—Co(2)	109.3 (1)
O(1)—Co(3)—N(12)	97.7 (1)	Co(1)—O(1)—Co(3)	110.1 (1)
N(4)—Co(3)—N(10)	113.2 (1)	Co(4)—N(9)—N(10)	116.8 (2)
N(4)—Co(3)—N(12)	120.0 (1)	Co(3)—N(10)—N(9)	113.3 (2)
N(10)—Co(3)—N(12)	120.3 (1)	Co(2)—N(11)—N(12)	117.5 (2)
O(1)—Co(4)—N(6)	98.0 (1)	Co(3)—N(12)—N(11)	116.3 (2)
O(1)—Co(4)—N(7)	97.6 (1)	Co(4)—N(7)—N(8)	117.1 (2)
O(1)—Co(4)—N(9)	98.1 (1)	Co(2)—N(8)—N(7)	113.3 (2)

Data collection and structure solution and refinement were carried out using the *TEXSAN* system (Molecular Structure Corporation, 1985). Molecular graphics were prepared using *ORTEP*II (Johnson, 1976). The H atoms were fixed in calculated positions [methyl-group orientations based on observed difference map positions, C—H = 0.98 Å, B(H) = 1.2 × B of the bonded atom]. Four of the 12 methyl groups were twofold orientationally disordered and for each, two sets of H atoms were assigned 50% occupancy. The crystal used for data collection may contain a small amount of zinc, disordered over the four metal-atom positions. The metal atoms were all refined as Co.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and intermolecular distances, least-squares-planes data and torsion angles, and a stereoview of the molecule have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71846 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1047]

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Tetrakis[{μ_3-ethoxy(N-methylimino)methanethiolato}copper(I)]

Takayoshi Kuroda-Sowa,* Megumu Munakata,*
Makoto Miyazaki and Masahiko Maekawa

Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Japan

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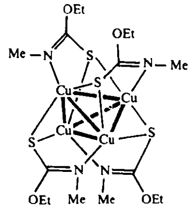
Abstract

Tetrakis[μ_3-ethoxy(N-methylimino)methanethiolato]-1κN,2:4$\kappa^2 S$;2κN,1:3$\kappa^2 S$;3κN,1:4$\kappa^2 S$;4κN,2:3$\kappa^2 S$-tetracopper, $[Cu_2(C_4H_8NOS)_2]_2$, contains a tetrahedral Cu_4 core surrounded by four effectively tridentate ethoxy(N-methylimino)methanethiolato (or O-ethyl N-methylcarbonimidothioato) ligands, $CH_3N{=}C(OC_2H_5)S^-$. Each Cu atom is coordinated by an N atom and two S atoms in a trigonal planar environment. There are two kinds of Cu^I—Cu^I distances (average 2.616 and 2.845 Å), resulting in a butterfly structure for the Cu_4 core.

Comment

Methyl isothiocyanate, $CH_3N{=}C{=}S$, in ethanol reacts with copper(I) to form a tetranuclear compound, $[Cu\{\mu_3\text{-}SC({=}NCH_3)(OC_2H_5)\}]_4$ (I) (Fig. 1). Four Cu atoms define a distorted tetrahedron, the faces of which are capped by four tridentate $CH_3N{=}C(OC_2H_5)S^-$ ligands (formed *in situ*). The N atom and the S atom of each ligand coordinate to one and two Cu atoms, respectively. Although the molecule has *quasi* S_4 symmetry, somewhat different conformations of the terminal ethyl groups reduce the molecular symmetry to C_2.



(I)

The deviation of each Cu atom from the plane of the coordinating atoms is negligible (0.015 Å). The coordination geometry around each Cu atom can be regarded as a regular triangle, though the angle S—Cu—S′ (mean value 123.9°) is slightly greater than the angles N—Cu—S and N—Cu—S′ (mean value 118.0°). The average Cu—N and Cu—S dis-

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tances of 1.983 and 2.283 Å, respectively, are comparable to those reported for three-coordinated copper(I) complexes (Karlin, Gultneh, Hutchinson & Zubieta, 1982; Griffith, Hunt & Amma, 1976; Lawton, Rohrbaugh & Kokotailo, 1972). The short N(1)—C(2) distance of 1.282 (5) Å shows C=N double-bond character, which is also reflected by the ligand structure which is planar except for the ethyl group.

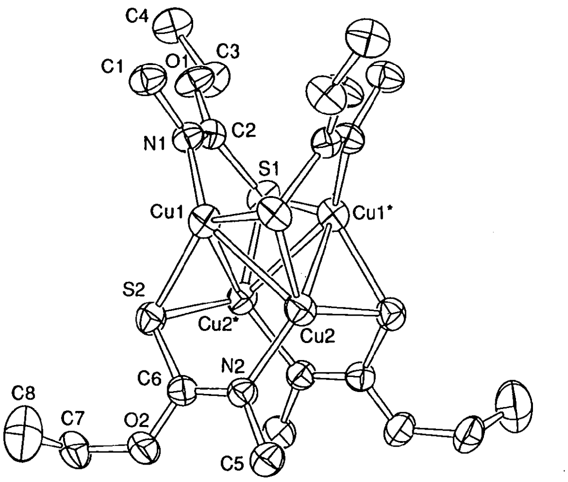

Fig. 1. Molecular structure of the compound viewed from near the *a* axis showing 50% probability displacement ellipsoids. H atoms are omitted for clarity. Only half of the constituent atoms are labelled; others are related by a rotation round a C_2 axis.

The Cu—Cu distances fall into two categories. Those bridged by sulfur (four out of six) average 2.616 Å and those not bridged average 2.845 Å. This clearly shows a butterfly structure for the Cu_4 core. Cu^I—Cu^I distances in other tetrahedral Cu_4 clusters range from 2.74 Å in $Cu_4[({}^iC_3H_7O)_2PS_2]_4$ (Lawton, Rohrbaugh & Kokotailo, 1972) to 3.093 Å in $Cu_4[SC(NH_2)_2]_6^{4+}$ (Griffith, Hunt & Amma, 1976). Although the present value of 2.616 Å is the shortest among those reported in tetrahedral Cu_4 clusters, disputes remain about whether or not a metal–metal interaction between d^{10} metal atoms exists (*e.g.* Merz & Hoffmann, 1988; Cotton, Feng, Matusz & Poli, 1988).

Regarding the *in situ* formation of the iminomethanethiolato ligand, Narasimhamurthy, Samuelson & Manohar (1989) have reported a similar reaction in which PhNCS inserts into a Cu—OPh′ bond giving a hexanuclear copper compound, $[Cu\{\mu\text{-}SC(=NPh)(OPh')\}]_6$ (Ph′ = 4-MeC_6H_4). This compound contains a distorted octahedral Cu_6 core and effectively tridentate SC=N bridging ligands. Each Cu atom shows trigonal-planar coordination as in the title compound, although the Cu atom deviates slightly from the plane of the coordinating atoms (mean value 0.31 Å). Similar skeletons with Cu^I and SC=N bridging ligands can be seen in the hexanuclear Cu^I compounds $[Cu_6(C_5H_4NS)_6]$ (Kitagawa, Munakata, Shimono, Matsuyama & Masuda, 1990) and $[Cu_6(C_9H_6NS)_6]$ (Kitagawa, Kawata, Nozaka & Munakata, 1993).

Experimental

A solution of methyl isothiocyanate (3.9 mg, 0.053 mmol) in ethanol (7 ml) was added to $[Cu(CH_3CN)_4]ClO_4$ (143 mg, 0.044 mmol) under argon and stirred for 1 h. The colorless clear solution was transferred to a glass tube and kept at 258 K. After seven months, crystals suitable for X-ray diffraction were obtained.

Crystal data

$[Cu_2(C_4H_8NOS)_2]$
M_r = 363.44
Monoclinic
$C2/c$
a = 17.699 (1) Å
b = 10.201 (2) Å
c = 15.4469 (9) Å
β = 106.618 (4)°
V = 2672.4 (8) Å^3
Z = 8
D_x = 1.81 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 21.63–23.57°
μ = 3.48 mm^{-1}
T = 296 K
Plate
0.25 × 0.25 × 0.15 mm
Yellow

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.90, T_{max} = 1.0
3342 measured reflections
3235 independent reflections
2255 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.018
θ_{max} = 27.5°
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 13$
$l = -20 \rightarrow 19$
3 standard reflections monitored every 150 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.027
wR = 0.020
S = 1.75
2255 reflections
209 parameters
Coordinates and U_{iso} of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max}$ = 0.17
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu(1)	−0.06192 (2)	0.30654 (4)	0.16846 (3)	3.11 (2)
Cu(2)	−0.05798 (2)	0.14261 (4)	0.29834 (3)	3.13 (2)
S(1)	0.12919 (4)	0.33080 (8)	0.22565 (5)	3.14 (3)

S(2)	−0.05930 (5)	0.11870 (8)	0.09050 (5)	3.14 (3)
O(1)	0.1088 (1)	0.5576 (2)	0.1334 (1)	3.7 (1)
O(2)	−0.1284 (1)	−0.1172 (2)	0.0877 (1)	4.3 (1)
N(1)	−0.0036 (1)	0.4579 (2)	0.1391 (2)	2.9 (1)
N(2)	−0.0985 (1)	−0.0124 (2)	0.2216 (2)	2.9 (1)
C(1)	−0.0448 (3)	0.5732 (4)	0.0911 (3)	4.1 (2)
C(2)	0.0720 (2)	0.4571 (3)	0.1605 (2)	2.8 (1)
C(3)	0.1926 (2)	0.5561 (4)	0.1448 (3)	4.0 (2)
C(4)	0.2091 (3)	0.6628 (4)	0.0880 (3)	4.3 (2)
C(5)	−0.1254 (3)	−0.1309 (4)	0.2577 (3)	4.2 (2)
C(6)	−0.0987 (2)	−0.0118 (3)	0.1384 (2)	2.9 (1)
C(7)	−0.1334 (3)	−0.1248 (4)	−0.0075 (2)	4.4 (2)
C(8)	−0.2107 (3)	−0.0794 (6)	−0.0631 (3)	6.8 (3)

Table 2. *Selected geometric parameters* (Å, °)

Starred atoms are related to the corresponding unstarred atoms by a twofold axis.

Cu(1)—Cu(1*)	2.8270 (7)	S(2)—C(6)	1.761 (3)
Cu(1)—Cu(2)	2.5974 (5)	N(1)—C(1)	1.468 (4)
Cu(1)—Cu(2*)	2.6344 (5)	N(1)—C(2)	1.282 (3)
Cu(1)—S(1*)	2.2953 (8)	N(2)—C(5)	1.467 (4)
Cu(1)—S(2)	2.2706 (9)	N(2)—C(6)	1.283 (3)
Cu(1)—N(1)	1.982 (2)	O(1)—C(2)	1.344 (3)
Cu(2)—Cu(2*)	2.8628 (7)	O(1)—C(3)	1.444 (4)
Cu(2)—S(1*)	2.2680 (9)	O(2)—C(6)	1.345 (3)
Cu(2)—S(2*)	2.2974 (9)	O(2)—C(7)	1.450 (4)
Cu(2)—N(2)	1.983 (2)	C(3)—C(4)	1.479 (5)
S(1)—C(2)	1.766 (3)	C(7)—C(8)	1.467 (6)
N(1)—Cu(1)—S(2)	116.44 (7)	O(1)—C(2)—S(1)	119.0 (2)
N(1)—Cu(1)—S(1*)	119.33 (7)	C(2)—O(1)—C(3)	121.8 (2)
S(2)—Cu(1)—S(1*)	124.22 (3)	Cu(2)—Cu(1)—Cu(2*)	66.34 (2)
N(2)—Cu(2)—S(1*)	119.19 (7)	Cu(2)—Cu(1)—Cu(1*)	57.93 (1)
N(2)—Cu(2)—S(2*)	117.23 (7)	Cu(2)—Cu(1*)—Cu(1)	56.66 (1)
S(1*)—Cu(2)—S(2*)	123.57 (3)	Cu(1)—Cu(2)—Cu(1*)	65.41 (2)
C(2)—N(1)—C(1)	117.8 (3)	Cu(1)—Cu(2)—Cu(2*)	57.45 (1)
C(1)—N(1)—Cu(1)	121.6 (2)	Cu(1)—Cu(2*)—Cu(2)	56.21 (1)
C(2)—N(1)—Cu(1)	120.6 (2)	Cu(1*)—S(1)—Cu(2*)	69.39 (3)
N(1)—C(2)—O(1)	118.5 (3)	Cu(1)—S(2)—Cu(2*)	70.44 (3)
N(1)—C(2)—S(1)	122.5 (2)		
Cu(2)—Cu(1)—Cu(1*)—Cu(2*)	81.11 (2)		
Cu(1)—Cu(1*)—Cu(2)—Cu(2*)	66.06 (2)		
Cu(1)—Cu(2)—Cu(2*)—Cu(1*)	80.40 (2)		
Cu(2)—Cu(1)—Cu(2*)—Cu(1*)	64.31 (2)		
Cu(1)—N(1)—C(2)—O(1)	175.2 (2)		
S(1)—C(2)—N(1)—C(1)	175.0 (3)		
Cu(1)—N(1)—C(2)—S(1)	−6.0 (3)		
Cu(2)—N(2)—C(6)—O(2)	−178.4 (2)		
S(2)—C(6)—N(2)—C(5)	−173.9 (3)		
Cu(2)—N(2)—C(6)—S(2)	3.4 (3)		

The unit cell was found to be *C*-centred monoclinic. Based on the systematic absences (*hkl*, $h + k = 2n$; *h*0*l*, $l = 2n$), packing considerations, a statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be *C*2/*c*. The structure was solved by direct methods (Gilmore, 1990) and expanded using Fourier techniques (Beurskens *et al.*, 1992).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: OH1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[{PtCl(dmso)}$_2$(μ-OH)$_2$]

Zivadin Bugarcic, Karin Lövqvist
and Åke Oskarsson*

*Inorganic Chemistry 1, Chemical Center,
University of Lund, PO Box 124, S-221 00 Lund,
Sweden*

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Abstract

The crystal structure of di-μ-hydroxo-bis[chloro(dimethyl sulfoxide)platinum(II)], $[Pt_2Cl_2(\mu\text{-}OH)_2(C_2H_6OS)_2]$, has been determined from X-ray intensity data. The compound contains a hydroxo-bridged dinuclear *cis* complex, *i.e.* the Cl atoms are in *cis* positions in [Cl(dmso)Pt$(OH)_2$Pt(dmso)Cl]. Each Pt atom has pseudo square-planar coordination composed of one dmso molecule, one Cl atom and two hydroxo groups. The complexes are linked by a hydrogen-bond network parallel to the *ab* plane.

Comment

The title compound (I) was obtained in an attempt to synthesize [PtCl$_2$(dmso)(H$_2$O)] in aqueous solution by abstracting one Cl$^-$ in K[PtCl$_3$(dmso)] by AgF in the following way: 0.03 g AgF in 5 ml water was