N(3)	0.4933 (14)	0.7409 (10)	0.3425 (5)	0.065 (4)
C(1)	0.7145 (11)	0.0542 (11)	0.4437 (5)	0.041 (4)
C(2)	0.7026 (11)	0.1425 (11)	0.5133 (5)	0.038 (3)
C(3)	0.8573 (12)	0.1974 (12)	0.5532 (5)	0.040 (3)
C(4)	0.7661 (11)	0.0272 (11)	0.2989 (4)	0.038 (3)
C(5)	0.8425 (12)	0.0825 (13)	0.2352 (5)	0.046 (4)
C(6)	1.0178 (15)	0.0718 (14)	0.2503 (6)	0.055 (4)
C(7)	0.6526 (10)	0.3416 (11)	0.3442 (4)	0.033 (3)
C(8)	0.6867 (12)	0.5017 (11)	0.3877 (5)	0.044 (4)
C(9)	0.5748 (11)	0.6359 (11)	0.3621 (5)	0.038 (2)

Table 2. *Selected geometric parameters* (Å, °) *for polymorphs* (1) *and* (2)

Polymorph (1)			
Au—Cl	2.295 (3)	Au—P(1)	2.225 (3)
P(1)—C(1)	1.832 (11)	P(1)—C(4)	1.827 (12)
P(1)—C(7)	1.833 (11)	N(1)—C(3)	1.143 (18)
N(2)—C(6)	1.132 (20)	N(3)—C(9)	1.125 (16)
C(1)—C(2)	1.522 (17)	C(2)—C(3)	1.490 (19)
C(4)—C(5)	1.546 (16)	C(5)—C(6)	1.449 (18)
C(7)—C(8)	1.500 (16)	C(8)—C(9)	1.473 (16)
Cl—Au—P(1)	177.8 (1)	Au—P(1)—C(1)	115.2 (4)
Au—P(1)—C(4)	113.6 (4)	C(1)—P(1)—C(4)	105.3 (5)
Au—P(1)—C(7)	113.9 (4)	C(1)—P(1)—C(7)	100.9 (5)
C(4)—P(1)—C(7)	106.7 (5)	P(1)—C(1)—C(2)	115.9 (8)
C(1)—C(2)—C(3)	112.9 (10)	N(1)—C(3)—C(2)	178.8 (14)
P(1)—C(4)—C(5)	113.0 (8)	C(4)—C(5)—C(6)	113.3 (10)
N(2)—C(6)—C(5)	178.2 (14)	P(1)—C(7)—C(8)	114.2 (7)
C(7)—C(8)—C(9)	112.7 (9)	N(3)—C(9)—C(8)	178.5 (13)
Polymorph (2)			
Au—Cl	2.315 (2)	Au—P(1)	2.243 (2)
P(1)—C(1)	1.842 (10)	P(1)—C(4)	1.830 (9)
P(1)—C(7)	1.843 (8)	N(1)—C(3)	1.154 (13)
N(2)—C(6)	1.124 (18)	N(3)—C(9)	1.112 (13)
C(1)—C(2)	1.518 (13)	C(2)—C(3)	1.475 (12)
C(4)—C(5)	1.536 (14)	C(5)—C(6)	1.480 (16)
C(7)—C(8)	1.522 (12)	C(8)—C(9)	1.463 (13)
Cl—Au—P(1)	177.1 (1)	Au—P(1)—C(1)	114.1 (3)
Au—P(1)—C(4)	113.8 (3)	C(1)—P(1)—C(4)	102.9 (4)
Au—P(1)—C(7)	114.9 (3)	C(1)—P(1)—C(7)	107.0 (4)
C(4)—P(1)—C(7)	102.9 (4)	P(1)—C(1)—C(2)	118.3 (6)
C(1)—C(2)—C(3)	113.5 (8)	N(1)—C(3)—C(2)	179.3 (9)
P(1)—C(4)—C(5)	114.9 (6)	C(4)—C(5)—C(6)	112.6 (8)
N(2)—C(6)—C(5)	177.9 (13)	P(1)—C(7)—C(8)	112.9 (6)
C(7)—C(8)—C(9)	112.2 (7)	N(3)—C(9)—C(8)	178.0 (11)

Table 3. *Comparison of bond lengths and angles* (Å, °) *for mononuclear gold*(I) *triorganophosphine chloride complexes*

Phosphine	Au—Cl	Au—P	P—Au—Cl	References
PPh_3	2.279	2.235	179.6	Baenziger, Bennet & Soboroff (1976)
(*o*-MePh)$_3$P	2.281	2.243	179.4	Harker & Tiekink (1990)
(*m*-MePh)$_3$P	2.288	2.235	175.1	Harker & Tiekink (1991)
Cy$_2$PhP	2.281	2.234	178.3	Muir, Cuadrado & Muir (1991)
(2-pyridyl)$_3$P (*A*)	2.277	2.214	179.4	Lock & Turner (1987)
(*B*)	2.272	2.218	176.5	Lock & Turner (1987)
Cy$_3$P	2.279	2.242	177.0	Muir, Muir, Pulgar, Jones & Sheldrick (1985)
Et$_3$P	2.305	2.232	178.5	Tiekink (1989)
	2.306	2.231	178.9	
CEP (1)	2.295	2.225	177.8	This work
(2)	2.315	2.243	177.1	This work
Average for all	2.289	2.2232	178.0	

A small colorless crystal was mounted on a glass fiber in a random orientation. Monoclinic symmetry of both polymorphs was suggested on the basis of symmetry in axial photographs. Data were corrected for Lp factors. The Au atom was found by direct methods; the remaining non-H atom positions were located by Fourier techniques. H atoms were placed in idealized positions (C—H 0.96 Å) and the isotropic displacement parameters were fixed as $1.2 \times U_{eq}$ of the parent C atom. All computation was carried out using the *SHELXTL* crystallographic program package (Sheldrick, 1986).

These studies were supported by the Welch Foundation and the National Science Foudation (grant CHE-8708625).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1000). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BK1000]

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μ_4-Oxo-hexakis(μ-3,5-dimethylpyrazolato-*N*,*N′*)tetracobalt(II)

Martin K. Ehlert, Steven J. Rettig, Alan Storr,* Robert C. Thompson* and James Trotter*

Department of Chemistry,
University of British Columbia, 2036 Main Mall,
Vancouver, BC, Canada V6T 1Z1

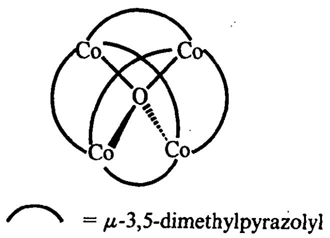
(*Received* 16 *February* 1993; *accepted* 26 *November* 1993)

Abstract

The title compound, $[Co_4O(C_5H_7N_2)_6]$, consists of a central O atom coordinated by four Co^{II} atoms which are themselves bridged in a pairwise fashion by six exobidentate 3,5-dimethylpyrazolate ligands. The coordination geometry about each Co^{II} atom is that of a distorted tetrahedron.

Comment

During attempts to synthesize the mixed cobalt/zinc 3,5-dimethylpyrazolate analogue $[Co_{1/3}Zn_{2/3}(4\text{-}Hdmpz)_2]_x$, where 4-Hdmpz is the 3,5-dimethylpyrazolato ligand, of the cobalt(II) polymer $[Co(4\text{-}Hdmpz)_2]_x$ (Ehlert, Storr & Thompson, 1993; Singh, Satpathy & Sahoo, 1973; Bagley, Nicholls & Warburton, 1970), a tetrametallic cobalt(II) 3,5-dimethylpyrazolate species was prepared unexpectedly. $[Zn(4\text{-}Hdmpz)_2(4\text{-}HdmpzH)]_2$ (Ehlert, Rettig, Storr, Thompson & Trotter, 1990) was reacted with $[Co(CH_3CN)_6][BF_4]_2$ (Hathaway, Holah & Underhill, 1962) and excess triethylamine in the hope of obtaining $[Co_{1/3}Zn_{2/3}(4\text{-}Hdmpz)_2]_x$, but instead the reaction yielded two products, a light purple powder which, on the basis of infrared spectroscopy and elemental analysis, is thought to be impure $[Co_{1-n}Zn_n(4\text{-}Hdmpz)_2]_x$, and a small amount of well formed macroscopic blue–purple crystals of $[Co_4\text{-}Hdmpz)_6O]$ (I). Crystals of the tetrametallic compound, $[Co_4(4\text{-}Hdmpz)_6O]$, were difficult to separate in quantity from the insoluble purple powder, so characterization of the complex was limited to a single-crystal X-ray diffraction structure determination and the recording of the infrared spectrum of the compound. The diffraction study revealed the presence of oxygen in $[Co_4(4\text{-}Hdmpz)_6O]$ in spite of the fact that the reaction was performed under anhydrous anaerobic conditions. The most likely source of oxygen in the reaction was the starting material, $[Co(CH_3CN)_6][BF_4]_2$. This complex was prepared according to a literature method (Hathaway, Holah and Underhill, 1962) and it is a very thermally sensitive and hygroscopic compound. Although C, H and N analyses of $[Co(CH_3CN)_6][BF_4]_2$ indicated it to be pure, its infrared spectrum exhibited a weak band in the ν_{OH} region suggesting the presence of a small amount of H_2O in the complex. Crystals of $[Co_4(4\text{-}Hdmpz)_6O]$ are stable in air and the complex is sparingly soluble in CH_3CN and acetone.



(I)

The structure of $[Co_4(4\text{-}Hdmpz)_6O]$ with atomic labelling is depicted in Fig. 1 and consists of a central O atom around which the four Co^{II} ions are pseudo-tetrahedrally arrayed; the six edges of the tetrahedron are bridged by $4\text{-}Hdmpz^-$ ligands. The bond lengths from the Co^{II} ions to the central atom range from 1.936 (2) to 1.953 (2) Å (average 1.944 Å) and the Co—O—Co angles range from 108.1 (1) to 111.8 (1)°. The Co^{II} centres are separated by an average non-bonding distance of 3.17 Å (range 3.148–3.209 Å). Co—N bond lengths range from 1.987 (3) to 2.017 (3) Å (average 1.998 Å). The average O—Co—N bond angle is 98.3° and the average N—Co—N bond angle is 118.0°, thus, the coordination geometry about the co^{II} centres is best described as distorted tetrahedral. The $[Co_4(4\text{-}Hdmpz)_6O]$ complex was synthesized using $[Zn(4\text{-}Hdmpz)_2(4\text{-}HdmpzH)]_2$ as a starting material and as a result Zn atoms may be present in some of the molecules *via* isomorphous replacement of the Co^{II} ions. If Zn^{II} ions are randomly distributed over the Co^{II} sites in the lattice, it is estimated that as many as 10–20% of the Co^{II} sites could be occupied by Zn^{II} before the diffraction data would indicate the presence of Zn^{II}.

The structure of $[Co_4(4\text{-}Hdmpz)_6O]$ is strongly reminiscent of the well known basic beryllium carboxylates, $[Be_4(O_2CR)_6O]$ (where R is an alkyl group) (Bragg & Morgan, 1923; Cotton & Wilkinson, 1988). Zn^{II} is also known to form complexes of the type $[Zn_4(O_2CR)_6O]$ (Koyama & Saito, 1954). The basic beryllium acetates are quite resistant to hydrolysis while the zinc analogues are readily hydrolyzed. It is believed that this reactivity difference is due to the fact that Be^{II} in a tetrahedral environment is coordinatively saturated while Zn^{II} can exhibit coordination numbers higher than four. The limited observations that have been made on $[Co_4(4\text{-}Hdmpz)_6O]$ seem to indicate that it is moderately

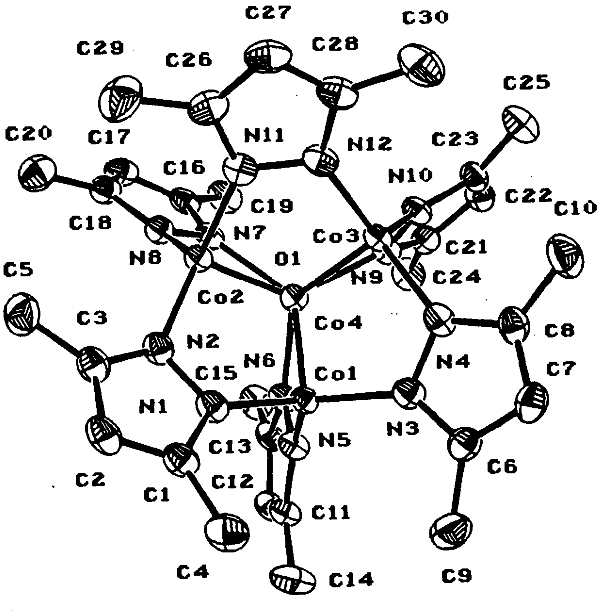


Fig. 1. Structure of $[Co_4(4\text{-}Hdmpz)_6O]$ with the atom-labelling scheme and 33% probability displacement ellipsoids. Co(4) is directly below O(1).

resistant to hydrolysis in spite of the fact that it is coordinatively unsaturated. The structure of this compound provides a clue to this behaviour (Fig. 1) in that the open coordination site on each Co^{II} centre is blocked by the three methyl groups of the 4-$Hdmpz^-$ ligands.

Experimental

$[Co(CH_3CN)_6][BF_4]_2$ (0.148 g, 0.309 mmol), prepared by the method of Hathaway, Holah & Underhill (1962), and triethylamine (0.304 g, 3.00 mmol) were combined in 5 ml of dry acetonitrile. To this solution was added a slurry of $[Zn(4\text{-}Hdmpz)_4(4\text{-}HdmpzH)]_2$(0.211 g, 0.300 mmol) in 20 ml of dry acetonitrile. The mixture was then stirred for 2 h at room temperature which resulted in the formation of a dark blue-purple solution and a small amount of light purple solid. The mixture was left standing for four days at room temperature in a closed vessel. During this time large blue-purple crystals grew in the solution. All manipulations were performed in a nitrogen atmosphere.

Crystal data

$[Co_4O(C_5H_7N_2)_6]$
M_r = 822.47
Triclinic
$P\bar{1}$
a = 12.270 (2) Å
b = 14.785 (1) Å
c = 11.970 (2) Å
α = 103.143 (9)°
β = 118.462 (9)°
γ = 77.154 (9)°
V = 1842.4 (4) Å^3
Z = 2
D_x = 1.482 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 39.5–54.0°
μ = 1.491 mm^{-1}
T = 294 K
Prism
0.30 × 0.12 × 0.08 mm
Blue-purple

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.57, T_{max} = 1.00 (relative)
7891 measured reflections
7521 independent reflections
4952 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.029
θ_{max} = 77.5°
$h = 0 \rightarrow 15$
$k = -18 \rightarrow 18$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 200 reflections intensity variation: negligible

Refinement

Refinement on F
R = 0.034
wR = 0.035
S = 1.97
4952 reflections
425 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Extinction correction: secondary (Zachariasen, 1963)
Extinction coefficient: 1.49 (7) × 10^{-6}
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}
Co(1)	0.53196 (5)	0.24038 (4)	0.66342 (5)	2.80 (2)
Co(2)	0.24761 (5)	0.25656 (4)	0.45631 (5)	2.77 (2)
Co(3)	0.32039 (5)	0.25714 (4)	0.75194 (5)	2.83 (2)
Co(4)	0.34998 (5)	0.43101 (3)	0.66234 (5)	2.69 (2)
O(1)	0.3621 (2)	0.2945 (2)	0.6333 (2)	3.0 (1)
N(1)	0.4901 (3)	0.1564 (2)	0.4959 (3)	3.6 (1)
N(2)	0.3706 (3)	0.1775 (2)	0.3983 (3)	3.6 (1)
N(3)	0.5817 (3)	0.1833 (2)	0.8197 (3)	3.7 (1)
N(4)	0.4867 (3)	0.1843 (2)	0.8525 (3)	3.7 (1)
N(5)	0.5972 (3)	0.3587 (2)	0.6836 (3)	3.6 (1)
N(6)	0.5134 (3)	0.4408 (2)	0.6719 (3)	3.4 (1)
N(7)	0.1955 (3)	0.4555 (2)	0.5021 (3)	3.4 (1)
N(8)	0.1640 (3)	0.3817 (2)	0.4011 (3)	3.4 (1)
N(9)	0.3297 (3)	0.4543 (2)	0.8222 (3)	3.4 (1)
N(10)	0.2900 (3)	0.3827 (2)	0.8464 (3)	3.5 (1)
N(11)	0.1449 (3)	0.1896 (2)	0.4940 (3)	3.7 (1)
N(12)	0.1769 (3)	0.1896 (2)	0.6224 (3)	3.9 (1)
C(1)	0.5515 (4)	0.0871 (3)	0.4448 (4)	4.1 (2)
C(2)	0.4742 (4)	0.0623 (3)	0.3156 (4)	4.6 (2)
C(3)	0.3628 (4)	0.1207 (3)	0.2904 (4)	4.2 (2)
C(4)	0.6817 (4)	0.0456 (3)	0.5256 (5)	6.0 (2)
C(5)	0.2478 (5)	0.1267 (3)	0.1668 (4)	6.0 (2)
C(6)	0.6878 (4)	0.1417 (3)	0.9085 (4)	4.1 (2)
C(7)	0.6632 (4)	0.1158 (3)	0.9970 (4)	4.6 (2)
C(8)	0.5376 (4)	0.1441 (3)	0.9605 (4)	4.1 (2)
C(9)	0.8100 (4)	0.1329 (4)	0.9044 (5)	6.2 (2)
C(10)	0.4613 (5)	0.1370 (4)	1.0234 (5)	6.7 (3)
C(11)	0.7015 (4)	0.3797 (3)	0.6896 (4)	3.9 (2)
C(12)	0.6857 (4)	0.4743 (3)	0.6823 (4)	4.2 (2)
C(13)	0.5677 (4)	0.5099 (3)	0.6711 (4)	3.6 (2)
C(14)	0.8102 (4)	0.3074 (4)	0.7021 (5)	6.3 (2)
C(15)	0.5013 (4)	0.6073 (3)	0.6583 (4)	4.8 (2)
C(16)	0.1112 (4)	0.5309 (3)	0.4604 (4)	3.6 (2)
C(17)	0.0266 (4)	0.5077 (3)	0.3349 (4)	4.2 (2)
C(18)	0.0617 (3)	0.4139 (3)	0.3005 (4)	3.8 (2)
C(19)	0.1173 (4)	0.6217 (3)	0.5476 (5)	5.0 (2)
C(20)	0.0054 (4)	0.3533 (3)	0.1746 (5)	5.7 (2)
C(21)	0.3314 (3)	0.5291 (3)	0.9113 (4)	3.6 (1)
C(22)	0.2930 (4)	0.5080 (3)	0.9924 (4)	4.1 (2)
C(23)	0.2668 (4)	0.4169 (3)	0.9485 (4)	3.8 (2)
C(24)	0.3738 (4)	0.6173 (3)	0.9141 (4)	4.8 (2)
C(25)	0.2161 (4)	0.3596 (3)	0.9967 (5)	5.6 (2)
C(26)	0.0436 (4)	0.1452 (3)	0.4222 (4)	4.5 (2)
C(27)	0.0081 (4)	0.1163 (3)	0.5006 (5)	5.2 (2)
C(28)	0.0939 (4)	0.1453 (3)	0.6249 (5)	4.5 (2)
C(29)	−0.0152 (5)	0.1333 (4)	0.2796 (5)	7.4 (3)
C(30)	0.1023 (5)	0.1300 (4)	0.7477 (6)	7.0 (3)

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

Co(1)—O(1)	1.946 (2)	Co(3)—N(12)	1.994 (3)
Co(1)—N(1)	1.999 (3)	Co(4)—O(1)	1.953 (2)
Co(1)—N(3)	1.996 (3)	Co(4)—N(6)	1.990 (3)
Co(1)—N(5)	2.001 (3)	Co(4)—N(7)	1.987 (3)
Co(2)—O(1)	1.936 (2)	Co(4)—N(9)	1.989 (3)
Co(2)—N(2)	1.993 (3)	N(1)—N(2)	1.394 (4)
Co(2)—N(8)	1.995 (3)	N(3)—N(4)	1.393 (4)
Co(2)—N(11)	2.017 (3)	N(5)—N(6)	1.392 (4)
Co(3)—O(1)	1.939 (2)	N(7)—N(8)	1.394 (4)
Co(3)—N(4)	2.012 (3	N(9)—N(10)	1.394 (4)
Co(3)—N(10)	2.001 (3)	N(11)—N(12)	1.393 (4)
O(1)—Co(1)—N(1)	97.9 (1)	Co(1)—O(1)—Co(4)	109.4 (1)
O(1)—Co(1)—N(3)	98.4 (1)	Co(2)—O(1)—Co(3)	118.8 (1)
O(1)—Co(1)—N(5)	98.1 (1)	Co(2)—O(1)—Co(4)	108.1 (1)
N(1)—Co(1)—N(3)	118.5 (1)	Co(3)—O(1)—Co(4)	108.1 (1)
N(1)—Co(1)—N(5)	116.7 (1)	Co(1)—N(1)—N(2)	115.6 (2)
N(3)—Co(1)—N(5)	118.9 (1)	Co(2)—N(2)—N(1)	115.3 (2)
O(1)—Co(2)—N(2)	98.8 (1)	Co(1)—N(3)—N(4)	116.2 (2)
O(1)—Co(2)—N(8)	100.2 (1)	Co(3)—N(4)—N(3)	116.6 (2)
O(1)—Co(2)—N(11)	96.6 (1)	Co(1)—N(5)—N(6)	116.5 (2)

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.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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

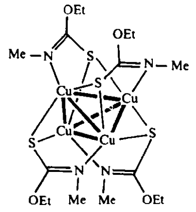
(*Received* 16 *July* 1993; *accepted* 22 *November* 1993)

Abstract

Tetrakis[μ_3-ethoxy(N-methylimino)methanethiolato]-$1\kappa N,2{:}4\kappa^2 S;2\kappa N,1{:}3\kappa^2 S;3\kappa N,1{:}4\kappa^2 S;4\kappa N,2{:}3\kappa^2 S$-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-

Acta Crystallographica Section C
ISSN 0108-2701 ©1994