A tetranuclear copper(I) cluster complex with a benzeneselenolate ligand, (Me4N)2-[Cu4(SePh)6]·CH3OH

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Abstract

The structure of bis(tetramethylammonium) hexakis-(μ-benzeneselenolato)tetracuprate(I) methanol solvate, $(C_4H_{12}N)_2[Cu_4(C_6H_5Se)_6]\cdot CH_3OH$, is composed of a Cu_4Se_6 adamantane-type cluster anion and a bulky cation. The cluster anion, $[Cu_4(SePh)_6]^{2-}$, can be considered as a tetrahedron of Cu atoms inscribed in a distorted octahedron of Se atoms. The Cu atoms are in a distorted trigonal–planar coordination, which includes three μ_2-Se atoms.

Comment

The monothiolate or selenolate ion RE^- (E = S, Se) is a fundamental ligand type. Uncharged copper(I) or silver(I) thiolates or selenolates $[(REM)_n; M = Cu, Ag]$, in which R is not bulky, are frequently insoluble in inert solvents, forming non-molecular aggregates. But in the presence of excess ligand ions, it is possible to obtain solutions containing anionic complexes and to crystallize discrete anionic cluster complexes with suitable cations. A number of copper(I) or silver(I) thiolate anionic complexes of the formula $[M_x(SR)_y]^{x-y}$ ($y > x$) have been structurally characterized (Dance, 1986). However, very few copper(I) or silver(I) selenolate complexes have been reported. This may be because selenolates are more air sensitive than thiolates. Recently, we reported the synthesis and crystal structure of a tetranuclear silver cluster complex with a benzeneselenolate ligand, $(Me_4N)_2[Ag_4(SePh)_6]\cdot CH_3OH$ (Jin *et al.*, 1999). We present here the structure of the copper analog, (I).
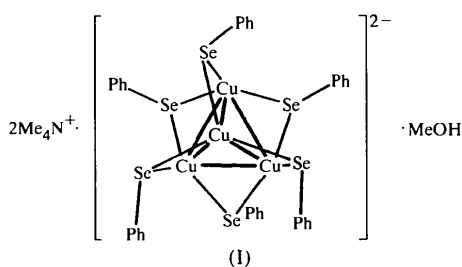
In the structure of the $[Cu_4(SePh)_6]^{2-}$ anion, the six (SePh)$^-$ ligands, which are in a distorted octahedral arrangement, bridge the edges of a tetrahedron defined by the four Cu atoms (Fig. 1). The coordination about each Cu atom is distorted trigonal and nearly planar. The structure of the $[Cu_4Se_6]$ core is very similar to that of the $[Cu_4S_6]$ core in $[Me_4N]_2[Cu_4(SPh)_6]$ (Dance & Calabrese, 1976; Dance *et al.*, 1983) and $(Ph_4P)_2$-$[Cu_4(SPh)_6]$ (Coucouvanis *et al.*, 1980; Baumgartner *et al.*, 1987), and to that of the $[Ag_4Se_6]$ core in $(Me_4N)_2$-$[Ag_4(SePh)_6]\cdot CH_3OH$ (Jin *et al.*, 1999). The Cu—Cu distances in the title complex range from 2.7210 (15) to 2.8116 (16) Å, with a mean of 2.75 Å, which is close to that in $[Cu_4S_6]$ (2.76 Å). The Cu—Se distances average 2.3970 Å [2.3708 (15)–2.4337 (15) Å], which is longer than the Cu—S distance of 2.28 Å in $(Ph_4P)_2$-$[Cu_4(SPh)_6]$.
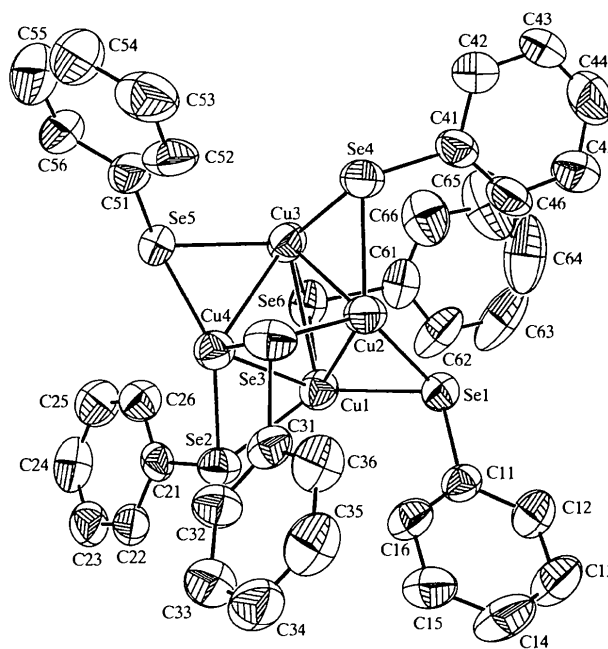

Fig. 1. The structure of the $[Cu_4(SePh)_6]^{2-}$ anion and the atomic numbering scheme (50% probability ellipsoids).

(I)

Experimental

The title compound was prepared from the reaction of CuCl, PhSeH (Horning, 1955), Et3N and Me4NCl (in a 1:4:3 molar ratio for CuCl:PhSeH:Me4NCl) in dimethylform-amide–methanol under a nitrogen atmosphere using Schlenk techniques. Pale-yellow block crystals of (I) were formed by diffusion of ethanol into the reaction solution.

Crystal data

$(C_4H_{12}N)_2[Cu_4(C_6H_5Se)_6]\cdot$CH4O	Mo $K\alpha$ radiation
$M_r = 1370.85$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
	$\theta = 5–10°$

$a = 12.346\,(3)$ Å
$b = 20.167\,(7)$ Å
$c = 11.269\,(3)$ Å
$\alpha = 97.49\,(2)°$
$\beta = 101.12\,(2)°$
$\gamma = 106.44\,(2)°$
$V = 2589.1\,(13)$ Å^3
$Z = 2$
$D_x = 1.758$ Mg m^{-3}
D_m not measured

$\mu = 5.871$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.50 \times 0.20 \times 0.15$ mm
Pale yellow

Data collection

Rigaku AFC-6S diffractometer
ω–2θ scans
Absorption correction: ψ scan (Coppens et al., 1965)
$T_{min} = 0.247$, $T_{max} = 0.415$
9529 measured reflections
9114 independent reflections

4557 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0253$
$\theta_{max} = 25°$
$h = 0 \rightarrow 14$
$k = -23 \rightarrow 22$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.043$
$wR(F^2) = 0.108$
$S = 0.957$
9114 reflections
535 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.2158P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.475$ e Å^{-3}
$\Delta\rho_{min} = -0.484$ e Å^{-3}
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected bond lengths (Å)

Se1—C11	1.923 (7)	Se5—C51	1.920 (9)
Se1—Cu2	2.3844 (14)	Se5—Cu4	2.3848 (14)
Se1—Cu1	2.3875 (14)	Se5—Cu3	2.4283 (14)
Se2—C21	1.922 (8)	Se6—C61	1.940 (8)
Se2—Cu1	2.3708 (15)	Se6—Cu3	2.3812 (15)
Se2—Cu4	2.4005 (14)	Se6—Cu1	2.3995 (15)
Se3—C31	1.936 (8)	Cu1—Cu4	2.7086 (15)
Se3—Cu4	2.3927 (14)	Cu1—Cu2	2.7320 (15)
Se3—Cu2	2.4337 (15)	Cu1—Cu3	2.8116 (16)
Se4—C41	1.918 (8)	Cu2—Cu3	2.7210 (15)
Se4—Cu3	2.3741 (14)	Cu2—Cu4	2.7663 (15)
Se4—Cu2	2.4263 (14)	Cu3—Cu4	2.7884 (17)

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1994). Cell refinement: MSC/AFC Diffractometer Control Software. Data reduction: TEXSAN (Molecular Structure Corporation, 1997). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXS97 (Sheldrick, 1997b). Molecular graphics: XP (Siemens, 1990). Software used to prepare material for publication: SHELXL97.

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Bis(pyrimidine-2-thiolato-N,S)bis(trimethyl phosphite-P)cobalt(III) hexafluorophosphate

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Abstract

The title complex, $[Co(C_4H_3N_2S)_2\{P(OCH_3)_3\}_2]PF_6$, with mixed N-heterocyclic thiolate and trimethyl phosphite ligands, was synthesized and characterized by X-ray crystallography and spectroscopic measurements. The Co^{III} ion is six-coordinated and has a slightly distorted octahedral geometry, being coordinated to two pairs of N and S atoms of two monoanionic bidentate pyrimidine-2-thiolate ligands and the P atom of each of two monodentate trimethyl phosphite ligands,