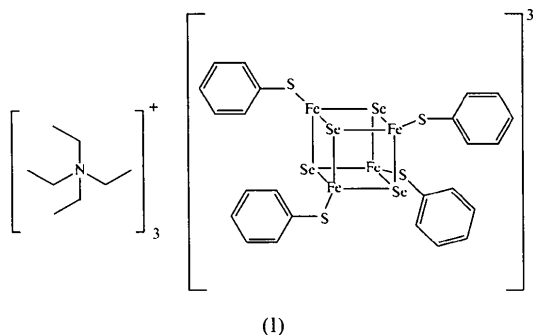


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During our investigations of iron–selenide–thiolate complexes, we were able to synthesize  $[Et_4N]_3[Fe_4Se_4(SPh)_4]$ , (I), by reaction of  $[Et_4N]_2[FeCl_4]$  with sodium thiophenolate and lithium selenide. In this mixed-



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### Tris(tetraethylammonium) tetra- $\mu_3$ -selenido-tetrakis[(thiophenolato-S)iron]

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#### Abstract

The title compound,  $[Et_4N]_3[Fe_4Se_4(SPh)_4]$ , comprises a mixed iron–selenium cubane unit, which is slightly elongated. The  $[Fe_4Se_4(SPh)_4]^{3-}$  anion contains iron in the mean oxidation state +2.25.

#### Comment

Iron–sulfide–thiolate complexes of general formula  $[Fe_4S_4(SR)_4]^{n-}$  ( $n = 1, 2$ , and  $3$ ) have been studied extensively due to their importance in many biological processes (Holm *et al.*, 1990; Krebs & Henkel, 1991; Holm, 1992; Harris, 1989). In view of their interesting electrochemical and magnetic properties, the analogous iron–chalcogenide–chalcogenolate complexes were also investigated (Bobrik *et al.*, 1978; Carney *et al.*, 1988; Henkel *et al.*, 1989). The characteristic feature of these compounds is a central cubane-like  $Fe_4E_4$  core ( $E = S, Se$  or  $Te$ ).

valence electronically delocalized compound, the mean oxidation state of iron is +2.25. The crystal structure consists of discrete  $[Fe_4Se_4(SPh)_4]^{3-}$  anions and  $[Et_4N]^+$  counter-cations in their expected geometries. There are two independent cations in the structure, one of which sits across a twofold axis. The N—C distances occur in the range 1.49 (1)–1.52 (1) Å. The anion has a crystallographically imposed twofold axis, which passes through the centroids of opposite non-planar  $Fe_2Se_2$  faces of the  $\{Fe_4Se_4\}^+$  core. The Fe atoms are coordinated by three Se and one S atom in a distorted tetrahedral manner. The central cubane unit is slightly elongated, with eight shorter and four longer Fe—Se distances. The average of the shorter ones, which occur in the range 2.396 (1)–2.425 (1) Å, is 2.408 (5) Å. The longer Fe—Se distances are 2.488 (1) ( $2 \times$ ) and 2.522 (1) Å ( $2 \times$ ), giving an average of 2.505 (9) Å. This value is very close to that observed in the tetramethylammonium salt determined at ambient temperature (Carney *et al.*, 1988), but is significantly larger than in the oxidized  $[Fe_4Se_4(SPh)_4]^{2-}$  complex anion (Bobrik *et al.*, 1978), where the mean Fe—Se distances are 2.385 (2) and 2.417 (5) Å. This result is expected because the mean oxidation state of iron is raised from +2.25 to +2.50. In contrast to the  $\{Fe_4E_4\}^{2+}$  cores ( $E = S, Se$  or  $Te$ ), which are compressed in all cases known so far, the stereochemistry of  $\{Fe_4E_4\}^+$  units in the crystalline state is much more complicated. In the literature, compressed as well as elongated cubanes of the latter type have been described (Ciurli *et al.*, 1990; Yu *et al.*, 1991). In our case, the  $\{Fe_4Se_4\}^+$  core is elongated. The Fe—Fe distances range from 2.675 (1) to 2.780 (2) Å, giving an average of 2.740 (19) Å. This value is virtually identical to the value observed in the tetramethylammonium salt. The mean Fe—S bond length involving the terminal thiolate groups [2.296 (2) Å] is comparable to that observed in the  $[Me_4N]^+$  salt [2.302 (8) Å], but is significantly longer than that found in the oxidized species [2.273 (7) Å].

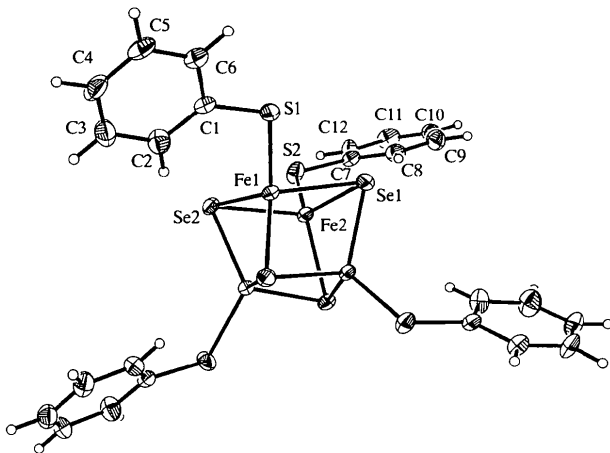


Fig. 1. The structure of the  $[\text{Fe}_4\text{Se}_4(\text{SPh})_4]^{3-}$  anion with atom labels and 50% probability displacement ellipsoids. H atoms are shown as circles.

## Experimental

All operations were performed under a dinitrogen atmosphere in a glove-box.  $[\text{Et}_4\text{N}]_2[\text{FeCl}_4]$  (3.66 g, 8 mmol) and sodium thiophenolate (4.20 g, 32 mmol) were suspended in  $\text{CH}_3\text{CN}$  (30 ml) and stirred for 1 h. A solution of lithium selenide (6 mmol) in THF (50 ml), prepared *in situ* from selenium and lithium triethylborohydride, was added and the reaction mixture refluxed for 8 h. The dark-brown slurry was filtered at room temperature. Black crystals of the title compound were obtained by storing the filtrate at 275 K. One of these crystals was mounted on a glass capillary with silicone grease and quickly put into the cold nitrogen stream of the cooling device of the goniometer.

### Crystal data

$(\text{C}_8\text{H}_{20}\text{N})_3[\text{Fe}_4\text{Se}_4(\text{C}_6\text{H}_5\text{S})_4]$	Mo $K\alpha$ radiation
$M_r = 1366.63$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 18 reflections
$Fdd2$	$\theta = 10\text{--}20^\circ$
$a = 24.490 (5) \text{ \AA}$	$\mu = 3.74 \text{ mm}^{-1}$
$b = 39.314 (8) \text{ \AA}$	$T = 150 \text{ K}$
$c = 11.808 (2) \text{ \AA}$	Needle
$V = 11369 (4) \text{ \AA}^3$	$0.73 \times 0.26 \times 0.22 \text{ mm}$
$Z = 8$	Black
$D_x = 1.597 \text{ Mg m}^{-3}$	
$D_m$ not measured	

### Data collection

Siemens P3 diffractometer	2839 reflections with $F > 4\sigma(F)$
$\omega$ scans	$\theta_{\text{max}} = 27.05^\circ$
Absorption correction:	$h = 0 \rightarrow 31$
$\psi$ scan (SHELXTL-Plus; Sheldrick, 1990)	$k = 0 \rightarrow 50$
$T_{\text{min}} = 0.484$ , $T_{\text{max}} = 0.613$	$l = 0 \rightarrow 15$
3279 measured reflections	1 standard reflection
3279 independent reflections	every 99 reflections
	intensity decay: none

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = -0.001$
$R(F) = 0.0366$	$\Delta\rho_{\text{max}} = 0.756 \text{ e \AA}^{-3}$
$wR(F^2) = 0.0824$	$\Delta\rho_{\text{min}} = -0.926 \text{ e \AA}^{-3}$
$S = 1.080$	Extinction correction: none
3279 reflections	Scattering factors from SHELXL93 (Sheldrick, 1993)
287 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = $-0.05 (3)$
$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Fe1—S1	2.299 (2)	Fe1—Fe1'	2.780 (2)
Fe1—Se1'	2.396 (1)	Fe2—S2	2.293 (2)
Fe1—Se2	2.425 (1)	Fe2—Se2'	2.405 (1)
Fe1—Se1	2.488 (1)	Fe2—Se1	2.406 (1)
Fe1—Fe2	2.675 (1)	Fe2—Se2	2.522 (1)
Fe1—Fe2'	2.775 (1)	Fe2—Fe2'	2.757 (2)
S1—Fe1—Se1'	119.37 (6)	S2—Fe2—Se2	93.77 (6)
S1—Fe1—Se2	120.65 (6)	Se2'—Fe2—Se2	108.05 (4)
Se1'—Fe1—Se2	102.89 (4)	Se1—Fe2—Se2	112.43 (4)
S1—Fe1—Se1	93.40 (5)	Fe1'—Se1—Fe2	70.61 (4)
Se1'—Fe1—Se1	106.85 (4)	Fe1'—Se1—Fe1	69.38 (4)
Se2—Fe1—Se1	113.01 (4)	Fe2—Se1—Fe1	66.24 (3)
S2—Fe2—Se2'	119.42 (7)	Fe2'—Se2—Fe1	70.15 (3)
S2—Fe2—Se1	119.56 (7)	Fe2'—Se2—Fe2	68.01 (4)
Se2'—Fe2—Se1	103.16 (4)	Fe1—Se2—Fe2	65.43 (3)

Symmetry code: (i)  $-x, -y, z$ .

Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct methods and subsequent difference Fourier synthesis. After anisotropic refinement of this model, H atoms were added at idealized positions. One common isotropic displacement parameter per group was refined for the otherwise riding H atoms. The origin was fixed by constraining the  $z$  coordinate of the Se1 atom. An alternative refinement without this specific constraint produced identical results.

Data collection: P3 (Siemens, 1991a). Cell refinement: P3. Data reduction: XDISK (Siemens, 1991b). Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1065). Services for accessing these data are described at the back of the journal.

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### Sodium copper(II) trimesate, $[NaCu\{C_6H_3(COO)_3\}(H_2O)_4]\cdot 2H_2O$ , a double-sheet coordination polymer with bridging aqua ligands

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#### Abstract

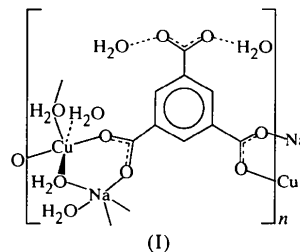
The title compound, poly[[[ $\mu$ -aqua-diaquasodium(I)copper(II)]- $\mu$ -aqua- $\mu$ -trimesate(3-)] dihydrate], contains one-dimensional zigzag polymer strands of trimesate and  $Cu^{2+}$  ions, which are connected into a two-dimensional double-sheet network *via* sodium ions and bridging aqua ligands.

#### Comment

There has been much recent interest in the synthesis of metal coordination polymers (Yaghi & Li, 1995) due to their possible application as microporous hosts for absorption or even as catalysts. Trimesic acid or 1,3,5-benzenetricarboxylic acid (TMA- $H_3$ ) has been of

particular interest since it is capable of articulating polymer networks, and serves as a useful model system for studying coordination polymer formation. We have studied its coordination chemistry in aqueous solution with a wide variety of divalent metal ions (Ca, Sr, Ba, Zn, Cd and Pb) and found a wide variety of coordination modes and polymer arrangements and topologies. These are both metal and pH dependent (Chui & Williams, 1999).

For copper, a one-dimensional  $[Cu(TMA-H)(H_2O)_3]$  coordination polymer containing square-pyramidal  $Cu^{2+}$  centres and monoprotonated trimesate dianions has been reported from neutral solution (Pech & Pickardt, 1988). We were curious to see the effect of pH on this system and the polymer formed from basic conditions. We report herein the formation of  $[NaCu(TMA)(H_2O)_4]\cdot 2H_2O$ , (I), which has one-dimensional zigzag polymer strands similar to the monoprotonated form, but now consisting of Cu and  $TMA^{3-}$  trianions. The asymmetric



unit is shown with the labelling scheme in Fig. 1. Each  $Cu^{2+}$  ion is square pyramidal with two monodentate carboxylates which are stabilized by four hydrogen bonds to aqua ligands of adjacent strands or to extra-framework water molecules. The two O atoms of

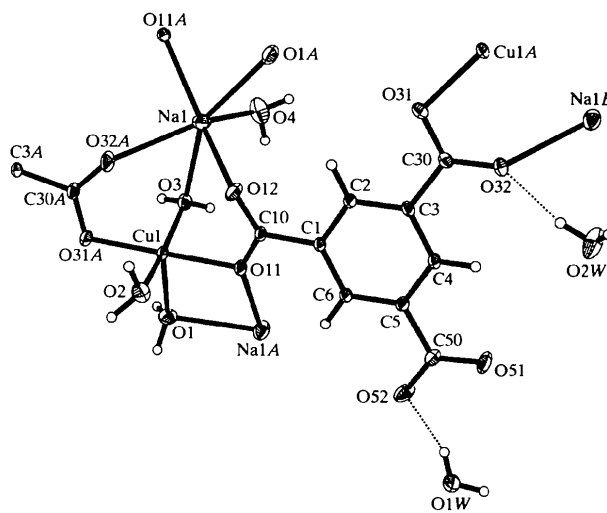


Fig. 1. The molecular structure of the title compound showing 40% probability displacement ellipsoids for non-H atoms. H atoms are shown as spheres of arbitrary radii.