

**Bis( $\mu$ -diselenido- $\mu$ -Se, $\mu$ -Se')-bis[dichlorobis(tetrahydrothiophene)niobium(IV)](Nb–Nb),  
[Nb<sub>2</sub>Cl<sub>4</sub>Se<sub>4</sub>(C<sub>4</sub>H<sub>8</sub>S)<sub>4</sub>]**

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(Received 12 April 1984; accepted 11 May 1984)

**Abstract.**  $M_r = 995.95$ , triclinic,  $P\bar{1}$ ,  $a = 8.678$  (7),  $b = 8.293$  (9),  $c = 11.103$  (10) Å,  $\alpha = 102.9$  (1),  $\beta = 101.6$  (1),  $\gamma = 103.5$  (1)°,  $V = 729.84$  Å<sup>3</sup>,  $Z = 1$ ,  $D_m = 2.20$  (5),  $D_x = 2.27$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 71.9$  cm<sup>-1</sup>,  $F(000) = 478$ ,  $T = 298$  K. Final  $R = 0.101$  for 1384 observed reflections. In the binuclear complex the two Nb atoms are bridged by two diselenide bridges [Nb–Se 2.618 (4), 2.643 (4), 2.646 (4) and 2.638 (4) Å] with Se–Se 2.260 (5) Å. There is an interaction between the two Nb atoms [Nb...Nb 2.972 (5) Å]. The coordination sphere around each Nb atom is completed by two terminal Cl atoms [Nb–Cl 2.490 (7) and 2.481 (8) Å] and two S atoms of the tetrahydrothiophene ligands [Nb–S 2.717 (7) and 2.745 (7) Å].

**Introduction.** In a previous paper (Drew, Rice & Williams, 1984) we describe the reactions of the niobium selenidohalides NbX<sub>3</sub>Se ( $X = \text{Cl}$  or Br) with thioether ligands. The structure of one of the products, a niobium(IV) species Nb<sub>2</sub>Cl<sub>4</sub>Se<sub>4</sub>·4(Me<sub>2</sub>S) was described. The formation of these niobium(IV) compounds in which two metal centres were bridged by two Se<sub>2</sub> groups from the niobium(V) compound NbCl<sub>5</sub>Se was somewhat surprising.

In order to confirm the structural reproducibility of the Nb<sub>2</sub>Cl<sub>4</sub>Se<sub>4</sub> core, we report here the formation and structure of the corresponding tetrahydrothiophene (tht) adduct Nb<sub>2</sub>Cl<sub>4</sub>Se<sub>4</sub>·4tht (I), obtained by recrystallization in CH<sub>2</sub>Cl<sub>2</sub> of the soluble product from the reaction of NbCl<sub>5</sub>S with tht. Experimental details are as previously described (Drew *et al.*, 1984).

**Experimental.** Density measured by flotation. Crystal: approximate size 0.8 × 0.35 × 0.15 mm, mounted on a Stoe STADI2 diffractometer to rotate around the  $a$  axis. The crystal was of poor quality and several superimposed reciprocal lattices were observed; we chose the most intense lattice for measurement. Cell dimensions obtained by measurement of 20 high-angle axial reflections. Intensity data collected *via* variable-width  $\omega$  scan, background counts 20s, step-scan rate of 0.033° s<sup>-1</sup> applied to a width of  $(1.5 + \sin \mu/\tan \theta)$ °,  $2\theta_{\text{max}} = 50$ °. One standard reflection measured every 20 measurements for each layer, rechecked at end

of data collection but no significant change in intensity observed. 3341 independent reflections measured ( $h -11 \rightarrow 10$ ,  $k -11 \rightarrow 10$ ,  $l 0 \rightarrow 14$ ); in order to minimize the effect of the weaker reciprocal lattices only 1386 reflections with  $I > 5\sigma(I)$  used in subsequent calculations. Absorption correction applied using SHELX76 (Sheldrick, 1976), min. and max. transmission factors 0.101 and 0.374 respectively. Structure determined *via* Patterson and Fourier methods using SHELX76 (Sheldrick, 1976). Non-H atoms refined anisotropically. H atoms positioned in tetrahedral sites, atoms in the same ligand given a common (refined) thermal parameter. Structure then refined by full-matrix least squares on  $F$  to  $R = 0.101$  ( $R_w = 0.104$ ). Two reflections for which  $F_o \gg F_c$  given zero weight in the refinement. Calculations carried out using SHELX76 (Sheldrick, 1976) at the University of Manchester Regional Computing Centre. Scattering factors from *International Tables for X-ray Crystallography* (1974). Weighting scheme chosen to give similar values of  $w\Delta^2$  over ranges of  $\sin \theta/\lambda$  and  $F_o$ ;  $w = 1/[\sigma^2(F) + 0.002F^2]$ ,  $\sigma(F)$  from counting statistics.  $(\Delta/\sigma)_{\text{max}} = 0.2$ . Difference Fourier maps showed no significant peaks.

**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters for (I) are given in Table 1\* and molecular dimensions in Table 2.

The structure of (I) consists of discrete centrosymmetric dimers [ $\{(tht)_2Cl_2Nb\}_2(\mu\text{-Se})_2$ ] as shown in Fig. 1. The two Nb atoms are bridged by two diselenide groups with Nb–Se distances of 2.618 (4), 2.643 (4), 2.646 (4) and 2.638 (4) Å. The coordination sphere of each Nb atom is completed by two Cl atoms [Nb–Cl(1) 2.490 (7), Nb–Cl(2) 2.481 (8) Å] and two S atoms [Nb–S(1) 2.717 (7), Nb–S(2) 2.745 (7) Å]. The two S atoms, the two Cl atoms and the two mid-points of the diselenide groups [called Se(A)] provide an approximately octahedral environment for the metal.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39482 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of (I) is thus analogous to that of the corresponding dimethyl sulphide adduct, Nb<sub>2</sub>Cl<sub>4</sub>Se<sub>4</sub>.4(Me<sub>2</sub>S) (II) (Drew *et al.*, 1984) and both are related to that of the parent chalcogenide halide NbCl<sub>2</sub>Se<sub>2</sub> (III) (Rijnsdorp, de Lange & Wiegers, 1979) which also contains [Nb<sub>2</sub>(Se<sub>2</sub>)<sub>2</sub>]<sup>4+</sup> units but these are linked into chains *via* bridging Cl atoms rather than existing as discrete molecules as (I) and (II).

The metal–metal distance of 2.972 (5) Å in (I) is long compared with that of the single bond in NbCl<sub>2</sub>S<sub>2</sub> 2.871 (4) Å (von Schnering & Beckmann, 1966) but is equivalent to those in (II) 2.962 (3) Å and (III) 2.973 (4) Å, suggesting a general trend of bond lengthening on going from the bridging disulphide to the larger bridging diselenide groups. A bonding interaction in (I) can be inferred from the displacement of the Cl atoms from the metal–metal vector [Nb...Nb<sup>I</sup>–Cl 112.6 (2), 113.6 (2)°].

The mean Nb–Se distances in (I) and (II) are equivalent at 2.636 (4) and 2.633 (3) Å. The Se–Se distance in (I) [2.260 (5) Å] is shorter than that observed in (II) [2.289 (3) Å] and (III) [2.272 (5) Å]. The Se–Se distance is sensitive to the degree of Se<sub>2</sub>π\*–Nb d<sub>π</sub> donation and hence to factors that affect the Lewis acidity of the Nb<sup>IV</sup> centre. From a comparison of (I), (II), (III), it would appear that Me<sub>2</sub>S is more effective at reducing Lewis acidity than the bridging halogen atoms of (III) which in turn are more effective than tht. The effect of Lewis acidity is also seen in the Nb–Cl distances which are shorter in (I) [2.490 (7), 2.481 (8) Å] than in (II) [2.527 (5), 2.510 (5) Å]. However, the Nb–S distances are equivalent in (I) and (II).

The atoms Nb, S(1), S(2) and Se(A) are not coplanar in (I) as they are in (II). Distances from the least-squares plane incorporating these atoms are –0.075 (1), 0.035 (3), 0.001 (4) and 0.040 (1) Å, respectively.

We thank SERC for their support of this work and A. W. Johans for his help with the crystallographic investigations.

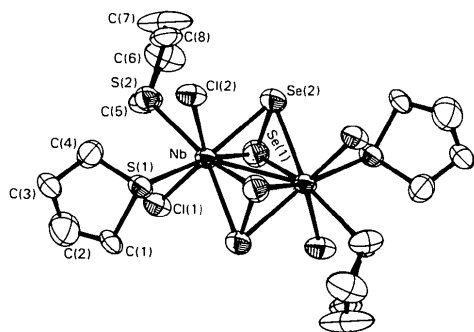


Fig. 1. The structure of (I) together with the atomic-numbering scheme; thermal ellipsoids are shown at 50% probability.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10^3$ ) with *e.s.d.*'s in parentheses

	x	y	z	$\bar{U}^*$ (Å <sup>2</sup> )
Nb	6151 (3)	441 (3)	11292 (2)	63 (3)
Se(1)	7094 (4)	654 (5)	9222 (3)	91 (4)
Se(2)	5882 (4)	2667 (4)	9948 (3)	85 (4)
Cl(1)	8099 (9)	–1335 (10)	11391 (7)	95 (9)
Cl(2)	5719 (9)	2798 (10)	12886 (8)	93 (9)
S(1)	5725 (8)	–677 (9)	13357 (7)	81 (8)
S(2)	9212 (8)	2636 (10)	12642 (7)	80 (9)
C(1)	6178 (35)	–2741 (37)	13386 (30)	92 (39)
C(2)	7446 (54)	–2297 (56)	14534 (33)	152 (65)
C(3)	7755 (40)	–701 (41)	15481 (33)	101 (45)
C(4)	7289 (42)	508 (42)	14759 (27)	88 (44)
C(5)	10852 (34)	2535 (40)	11860 (31)	90 (39)
C(6)	11399 (44)	4235 (51)	11563 (44)	171 (65)
C(7)	10862 (70)	5501 (48)	12286 (41)	212 (87)
C(8)	9459 (38)	4936 (38)	12722 (35)	80 (43)

\* $\bar{U}$  defined as  $\frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ .

Table 2. Bond distances (Å) and angles (°)

Metal-coordination-sphere dimensions		Remaining dimensions	
Nb–Nb <sup>I</sup>	2.972 (5)	Se(1)–Se(2)	2.260 (5)
Nb–Se(1)	2.618 (4)	S(1)–C(1)	1.850 (27)
Nb–Se(2)	2.643 (4)	S(1)–C(4)	1.752 (29)
Nb–Se(A)	2.375 (5)	S(2)–C(5)	1.819 (27)
Nb–Cl(1)	2.490 (7)	S(2)–C(8)	1.848 (31)
Nb–Cl(2)	2.481 (8)	C(1)–C(2)	1.417 (41)
Nb–S(1)	2.717 (7)	C(2)–C(3)	1.424 (46)
Nb–S(2)	2.745 (7)	C(3)–C(4)	1.493 (38)
Nb–Se(1 <sup>I</sup> )	2.646 (4)	C(5)–C(6)	1.510 (45)
Nb–Se(2 <sup>I</sup> )	2.638 (4)	C(6)–C(7)	1.40 (5)
Nb–Se(A <sup>I</sup> )	2.388 (4)	C(7)–C(8)	1.42 (5)
Se(1)–Nb–Se(2)	50.87 (12)	Nb–Se(1)–Nb <sup>I</sup>	68.74 (12)
Se(1)–Nb–Cl(1)	80.43 (19)	Nb–Se(2)–Nb <sup>I</sup>	68.50 (14)
Se(2)–Nb–Cl(1)	128.69 (20)	Nb–Se(A)–Nb <sup>I</sup>	77.20 (13)
Se(1)–Nb–Cl(2)	127.08 (21)	Nb–Se(1)–Se(2)	65.13 (13)
Se(2)–Nb–Cl(2)	79.28 (20)	Nb–Se(2)–Se(1)	64.00 (12)
Cl(1)–Nb–Cl(2)	133.83 (27)	Nb–S(1)–C(1)	115.4 (11)
Se(1)–Nb–S(1)	159.39 (21)	Nb–S(1)–C(4)	112.8 (10)
Se(2)–Nb–S(1)	149.63 (21)	C(1)–S(1)–C(4)	93.3 (14)
Cl(1)–Nb–S(1)	79.45 (22)	Nb–S(2)–C(5)	116.0 (10)
Cl(2)–Nb–S(1)	71.49 (24)	Nb–S(2)–C(8)	114.6 (10)
Se(1)–Nb–S(2)	86.43 (18)	C(5)–S(2)–C(8)	93.1 (15)
Se(2)–Nb–S(2)	87.54 (17)	S(1)–C(1)–C(2)	103.8 (24)
Cl(1)–Nb–S(2)	72.54 (25)	C(1)–C(2)–C(3)	119.5 (32)
Cl(2)–Nb–S(2)	73.33 (24)	C(2)–C(3)–C(4)	105.5 (27)
S(1)–Nb–S(2)	91.78 (22)	S(1)–C(4)–C(3)	109.3 (22)
Cl(1)–Nb–Se(A)	104.84 (24)	S(2)–C(5)–C(6)	107.5 (22)
Cl(2)–Nb–Se(A)	103.23 (25)	C(5)–C(6)–C(7)	110.7 (32)
S(1)–Nb–Se(A)	174.72 (22)	C(6)–C(7)–C(8)	117.7 (32)
S(2)–Nb–Se(A)	86.67 (21)	S(2)–C(8)–C(7)	106.4 (26)
Cl(1)–Nb–Se(A <sup>I</sup> )	103.69 (20)		
Cl(2)–Nb–Se(A <sup>I</sup> )	104.88 (21)		
S(1)–Nb–Se(A <sup>I</sup> )	78.87 (17)		
S(2)–Nb–Se(A <sup>I</sup> )	170.49 (25)		
Se(A)–Nb–Se(A <sup>I</sup> )	102.80 (14)		

Symmetry code: (i) 1–x, –y, 2–z.

## References

- DREW, M. G. B., RICE, D. A. & WILLIAMS, D. M. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1087–1093.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

RIJNSDORP, J., DE LANGE, G. J. & WIEGERS, G. A. (1979). *J. Solid State Chem.* **30**, 365–373.

SCHNERING, H. G. VON & BECKMANN, W. (1966). *Z. Anorg. Allg. Chem.* **347**, 231–239.

SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1984). **C40**, 1549–1551

## The Structure of Tetramethylammonium Tris[tetracarbonylcobalt(–I)]mercurate(II), [N(CH<sub>3</sub>)<sub>4</sub>][Hg{Co(CO)<sub>4</sub>}<sub>3</sub>]

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(Received 16 January 1984; accepted 22 May 1984)

**Abstract.**  $M_r = 787.7$ , monoclinic,  $P2_1/a$ ,  $a = 16.286$  (3),  $b = 16.460$  (3),  $c = 19.213$  (4) Å,  $\beta = 96.84$  (1)°,  $V = 5113.6$  (17) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.05$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 79.7$  cm<sup>-1</sup>,  $F(000) = 2976$ , 293 K,  $R = 0.048$  for 4470 symmetrically independent reflections. The title compound is prepared by the reaction of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  with  $\text{Co}(\text{CO})_4^-$ . The two independent  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  anions in the unit cell consist of an  $\text{Hg}^{2+}$  cation coordinated by three  $\text{Co}(\text{CO})_4^-$  anions. The geometry at mercury is trigonal planar with an average Hg–Co bond distance of 2.686 Å. The cobalt atoms have a distorted trigonal bipyramidal geometry with an average Hg–Co–C (equatorial) angle of 80.9°.

**Introduction.** The anion  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  has been known for several years, but the structure remained unknown. This complex was first postulated to be a radical anion  $\text{Hg}[\text{Co}(\text{CO})_4]_2^-$  (Vizi-Orosz, Papp & Marko, 1969), and later correctly identified as a tetrametallic cluster by several groups (Burlitch, Petersen, Conder & Robinson, 1970; Conder & Robinson, 1972; Cleland, Fieldhouse, Freeland, Mann & O'Brien, 1970).

There have been several reported examples of structures which contain trigonal planar mercury(II) (see Petersen, Ragosta, Whitwell & Burlitch, 1983, for references), including several which contain mercury coordinated to three transition metals (Erner *et al.*, 1983; Duffy, Mackey, Nicholson & Robinson, 1981; and a preliminary report of this work, Petersen *et al.*, 1983). The tetramethylammonium salt of  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  was found to give crystals suitable for X-ray single-crystal analysis, and the results are presented here.

**Experimental.** Title compound prepared from  $\text{N}(\text{CH}_3)_4^+\text{Co}(\text{CO})_4^-$  and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  (Petersen *et al.*, 1983). Single crystals prepared by cooling a methylene chloride solution. Single crystal mounted in capillary tube under nitrogen, rhombohedral with faces (001) 0.15, (00 $\bar{1}$ ) 0.15, (110) 0.10, ( $\bar{1}\bar{1}0$ ) 0.10, (1 $\bar{1}0$ ) 0.175, ( $\bar{1}10$ ) 0.175 mm (distances from each face to crystal center given). Lattice constants refined from 15 reflections with  $15 < 2\theta < 25^\circ$  measured on a Syntex  $P2_1$  diffractometer. 6007 reflections in the range  $-16 \leq h \leq 16$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 19$  ( $2\theta < 42^\circ$ ) measured with graphite monochromator, Mo  $K\alpha$  radiation,  $\omega$ -scan technique, scan speed  $1.0^\circ \text{ min}^{-1}$ , scan range  $1.0^\circ$ , background time equal to scan time, three standard reflections every 50 reflections (intensity variation  $< \pm 6\%$ ). Data reduction on a Prime 850 computer: data reduction and Lorentz and polarization corrections – *REDUCE* and *UNIQUE* (Leonowicz, 1978), absorption correction – *ABSORB* (Templeton & Templeton, 1973) using optically measured crystal dimensions listed above (transmission range 0.084 to 0.244). Direct-methods structure solution – *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), plotting – *PLUTO78* (Motherwell, 1978) and *ORTEP* (Johnson, 1965). All other calculations carried out using *CRYSTALS* (Watkin & Carruthers, 1981). Rejection of reflections with  $|F| < 2\sigma(F)$ , with  $\sigma(F)$  from counting statistics, gave 4470 symmetrically independent observed reflections. Atomic scattering factors and anomalous-dispersion coefficients (real and imaginary) for Hg, Co, O, N and C from *International Tables for X-ray Crystallography* (1974). Structure solved by direct methods. Both mercury atoms and all cobalt atoms of the two independent anions found in *E* map using set with highest combined figure of merit. All carbonyl carbons and oxygens, except two, found in first difference

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