

Table 3. Bond lengths (Å) and angles (°) for  $\text{Tl}(\text{C}_6\text{H}_4\text{N}_2\text{O})_2\text{Cl}_3$ 

E.s.d.'s of values involving C and N are 0.03 Å and 2°.

Tl—Cl(1)	2.452 (4)	Cl(1)—Tl—Cl(2)	140.2 (2)
—Cl(2)	2.403 (4)	Cl(1)—Tl—Cl(3)	112.9 (2)
—Cl(3)	2.364 (5)	Cl(2)—Tl—Cl(3)	106.6 (2)
—O(1)	2.36 (1)	Cl(1)—Tl—O(1)	88.4 (3)
—O(11)	2.40 (1)	Cl(1)—Tl—O(11)	82.3 (3)
		Cl(2)—Tl—O(1)	92.7 (3)
		Cl(2)—Tl—O(11)	90.6 (3)
		Cl(3)—Tl—O(1)	95.2 (4)
		Cl(3)—Tl—O(11)	93.9 (3)
		O(1)—Tl—O(11)	168.9 (5)
		Tl—O(1)—N(1)	120.1 (9)
		Tl—O(11)—N(11)	111.5 (9)
$x=0$	$x=1$	$x=0$	$x=1$
N(x1)—O(x1)	1.31 1.34	O(x1)—N(x1)—C(x1)	120 122
C(x1)	1.34 1.29	O(x1)—N(x1)—C(x6)	119 120
C(x6)	1.29 1.40	C(x1)—N(x1)—C(x6)	121 118
C(x1)—C(x2)	1.38 1.40	N(x1)—C(x1)—C(x2)	120 125
C(x3)—C(x2)	1.36 1.38	C(x1)—C(x2)—C(x3)	120 115
C(x4)	1.43 1.46	C(x2)—C(x3)—C(x4)	119 119
C(x5)	1.39 1.38	C(x4)—C(x3)—C(x5)	122 117
C(x5)—C(x6)	1.40 1.36	C(x3)—C(x5)—C(x6)	117 116
N(x2)—C(x4)	1.13 1.15	N(x1)—C(x6)—C(x5)	122 122
		C(x2)—C(x3)—C(x5)	119 124
		N(x2)—C(x4)—C(x3)	177 178

168.9 (5)°] and by the difference in Tl—Cl lengths and Cl—Tl—Cl angles. Packing effects are probably responsible for the distortion. As can be seen in Fig. 2, the two Tl—O bonds bend toward the line through Cl(1) and Cl(2) and are a little nearer Cl(1). This is consistent with the opening of the Cl(1)—Tl—Cl(2) angle and with the elongation of the Tl—Cl(1) and Tl—Cl(2) bonds

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## Bis(tetraphenylarsonium) Tris(2,2-diselenido-1,1-ethylenedicarbonitrile-*Se,Se'*)nickelate(IV)

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**Abstract.**  $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Ni}\{\text{Se}_2\text{C}=\text{C}(\text{CN})_2\}_3]$ ,  $2\text{C}_{24}\text{H}_{20}\text{As}^+\cdot\text{C}_{12}\text{N}_6\text{NiSe}_6^{2-}$ , triclinic,  $P\bar{1}$ ,  $a = 14.434$  (2),  $b = 14.567$  (2),  $c = 16.869$  (2) Å,  $\alpha = 105.48$  (1),  $\beta = 101.90$  (1),  $\gamma = 113.42$  (1)°,  $D_o = 1.72$  (1),  $Z = 2$ ,  $D_c = 1.729$  Mg m<sup>-3</sup>;  $R = 0.054$  for 3643 reflexions with  $I > 3\sigma(I)$ . The six Se atoms surround the Ni atom in a distorted octahedral coordination. Some average distances are Ni—Se 2.387 (1), Se—Se (intra-ligand)

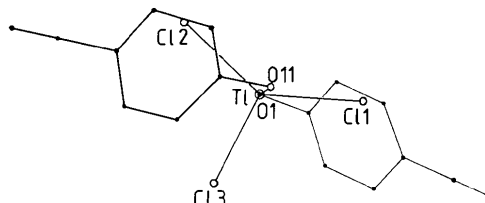


Fig. 2. Projection of the molecule on the equatorial plane showing the distortion of the coordination polyhedron around the Tl atom.

with respect to the other Tl—Cl bond. Another feature which could also be attributed to packing effects is the difference in the Tl—O(1)—N(1) and Tl—O(11)—N(11) angles (120.1 and 111.5°, respectively).

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trigonal-prismatic coordination geometry (Pierpont & Eisenberg, 1971), the central ion Ni<sup>IV</sup> in [Ni{Se<sub>2</sub>CN-(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>}]<sub>3</sub>Br has a distorted octahedral arrangement (Beurskens & Cras, 1971). For the 2,2-diselenido-1,1-ethylenedicarbonitrile ligand a further type of Ni<sup>IV</sup> tris-chelate was found. The spectral properties suggested a distorted octahedral coordination geometry (Dietzsch, Kirmse, Hoyer, Marov & Belyaeva, 1978). For an estimation of the actual distortion of the octahedral coordination geometry and for an evaluation of the difference from the cationic Ni<sup>IV</sup> tris(diseleno-carbamates) the structure of bis(tetraphenylarsonium) tris(2,2-diselenido-1,1-ethylenedicarbonitrile-*Se, Se'*)-nickelate(IV) has been determined. The compound was prepared as described by Dietzsch, Kirmse, Hoyer, Marov & Belyaeva (1978). Black needles were grown by slow evaporation from an acetone/2-propanol solution under vacuum.

The cell parameters were obtained by least squares from the  $2\theta$  values of 45 high-order reflexions measured on a diffractometer. The intensities were collected with an Enraf-Nonius CAD-4 diffractometer. Experimental conditions were: graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ),  $\omega$ - $2\theta$  scan,  $\theta_{\min} = 3^\circ$ ,  $\theta_{\max} = 28^\circ$ ,  $2\theta$  scan width ( $^\circ$ ):  $0.6 + 0.2 \tan \theta$ , aperture (mm):  $2.4 + 0.9 \tan \theta$ , maximum scan time 30 s, background: one quarter of the scan time at each of the scan limits. 14 524 independent reflexions were recorded and 3643 of these with  $I > 3.0\sigma(I)$  were used in the analysis. Corrections were applied for Lorentz and polarization effects but not for absorption. The structure was solved with *MULTAN 77* (Main, Woolfson, Lessinger, Germain & Declercq, 1977) and refined with anisotropic thermal parameters for all heavy atoms and with anomalous-dispersion corrections for Se, As, Ni, N and C. The best  $E$  map (CFOM = 2.514) obtained with unit weights (ABSFOM = 0.983,  $\psi_0 = 122$  and RESID = 13.06 for 250  $E$ 's) revealed the positions of the Se, Ni and As atoms. The function minimized was  $\sum w(|F_o| - K|F_c|)^2$  where the weighting function was determined empirically:  $w = w_F w_S$  where  $w_F (|F_o| < A) = (|F_o|/A)^C$ ,  $w_F (|F_o| > B) = (B/|F_o|)^D$ ,  $w_F (A < |F_o| < B) = 1.0$  and  $w_S (\sin \theta < E) = (\sin \theta/E)^H$ ,  $w_S (\sin \theta > G) = (G/\sin \theta)^J$ ,  $w_S (E < \sin \theta < G) = 1.0$ . The weighting-function parameters were:  $A = 40.0$ ,  $B = 100.0$ ,  $C = 1.0$ ,  $D = 1.0$ ,  $E = 0.20$ ,  $G = 0.27$ ,  $H = 1.0$ ,  $J = 1.0$ . The positional parameters of the H atoms were calculated and included with  $U = 0.06 \text{ \AA}^2$ , but were not refined. The final  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.054$  and  $R_w = 0.066$  for 3643 reflexions and 661 parameters. The final difference map was featureless.

All calculations were performed on the CDC Cyber 172 computer of RRC Ljubljana with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Scattering factors for the non-hydrogen atoms were from Cromer & Mann (1968), anomalous-

Table 1. Final positional parameters ( $\times 10^4$  for Ni and Se,  $\times 10^3$  for N and C) for the atoms of the anion with *e.s.d.*'s in parentheses

	x	y	z
Ni(1)	4197 (2)	7770 (2)	2821 (1)
Se(1)	5430 (2)	7445 (2)	3742 (1)
Se(2)	5068 (1)	9638 (2)	3783 (1)
Se(3)	2941 (1)	7237 (2)	3547 (1)
Se(4)	5462 (1)	7853 (2)	2092 (1)
Se(5)	3419 (2)	8518 (2)	1964 (1)
Se(6)	2890 (2)	5970 (2)	1810 (1)
N(1)	819 (1)	759 (1)	452 (1)
N(2)	14 (1)	339 (1)	105 (1)
N(3)	325 (2)	1098 (2)	161 (1)
N(4)	45 (1)	517 (2)	374 (1)
N(5)	807 (1)	782 (1)	195 (1)
N(6)	545 (2)	1249 (2)	435 (2)
C(49)	622 (1)	766 (1)	300 (1)
C(50)	720 (1)	768 (1)	313 (1)
C(51)	774 (1)	764 (1)	389 (1)
C(52)	62 (1)	415 (2)	171 (1)
C(53)	119 (1)	510 (1)	248 (1)
C(54)	372 (2)	1090 (2)	219 (1)
C(55)	432 (1)	1080 (2)	291 (1)
C(56)	213 (1)	593 (1)	257 (1)
C(57)	430 (1)	986 (1)	291 (1)
C(58)	73 (1)	512 (1)	317 (1)
C(59)	766 (1)	775 (1)	248 (2)
C(60)	494 (2)	1174 (2)	368 (2)

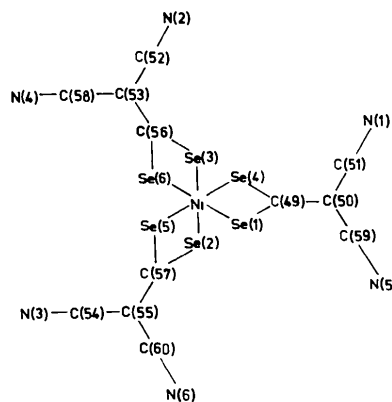


Fig. 1. Numbering of the atoms.

dispersion corrections from Cromer & Liberman (1970), and H atom scattering factors from Stewart, Davidson & Simpson (1965). The positional parameters of the atoms of the anion are listed in Table 1.\* Important distances and angles are in Table 2. The numbering of the atoms is shown in Fig. 1 and a stereoscopic drawing (Johnson, 1965) in Fig. 2.

\* Lists of structure factors, anisotropic thermal parameters and H atom parameters, and the atomic parameters, distances and angles of the cation have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34757 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) for the anion with *e.s.d.*'s in parentheses

Ni(1)—Se(1)	2.391 (4)	N(3)—C(54)	1.14 (4)
Ni(1)—Se(2)	2.388 (3)	N(4)—C(58)	1.11 (3)
Ni(1)—Se(3)	2.385 (3)	N(5)—C(59)	1.18 (3)
Ni(1)—Se(4)	2.387 (4)	N(6)—C(60)	1.17 (3)
Ni(1)—Se(5)	2.385 (4)	C(49)—C(50)	1.36 (3)
Ni(1)—Se(6)	2.387 (2)	C(50)—C(51)	1.40 (3)
Se(1)—C(49)	1.86 (2)	C(50)—C(59)	1.39 (3)
Se(2)—C(57)	1.83 (2)	C(52)—C(53)	1.40 (2)
Se(3)—C(56)	1.86 (1)	C(53)—C(56)	1.36 (3)
Se(4)—C(47)	1.86 (2)	C(53)—C(58)	1.45 (2)
Se(5)—C(57)	1.87 (1)	C(54)—C(55)	1.41 (3)
Se(6)—C(56)	1.85 (2)	C(55)—C(57)	1.36 (3)
N(1)—C(51)	1.16 (3)	C(55)—C(60)	1.40 (3)
N(2)—C(52)	1.17 (2)		
Se(1)—Ni(1)—Se(2)	91.4 (1)	N(1)—C(51)—C(50)	179 (2)
Se(1)—Ni(1)—Se(3)	91.4 (1)	N(5)—C(59)—C(50)	178 (2)
Se(1)—Ni(1)—Se(4)	77.9 (1)	Se(3)—C(56)—Se(6)	107 (1)
Se(1)—Ni(1)—Se(6)	101.8 (1)	Se(3)—C(56)—C(53)	125 (1)
Se(2)—Ni(1)—Se(3)	93.3 (1)	Se(6)—C(56)—C(53)	128 (1)
Se(2)—Ni(1)—Se(4)	98.6 (1)	C(56)—C(53)—C(52)	121 (2)
Se(2)—Ni(1)—Se(5)	77.7 (1)	C(56)—C(53)—C(58)	122 (1)
Se(3)—Ni(1)—Se(5)	100.7 (1)	N(2)—C(52)—C(53)	177 (3)
Se(3)—Ni(1)—Se(6)	77.5 (1)	N(4)—C(58)—C(53)	176 (2)
Se(4)—Ni(1)—Se(5)	92.1 (1)	Se(2)—C(57)—Se(5)	108 (1)
Se(4)—Ni(1)—Se(6)	93.1 (1)	Se(2)—C(57)—C(55)	129 (1)
Se(5)—Ni(1)—Se(6)	91.0 (1)	Se(5)—C(57)—C(55)	124 (2)
Se(1)—C(49)—Se(4)	108 (1)	C(57)—C(55)—C(54)	125 (2)
Se(1)—C(49)—C(50)	126 (2)	C(57)—C(55)—C(60)	119 (2)
Se(4)—C(49)—C(50)	126 (2)	N(3)—C(54)—C(55)	180 (2)
C(49)—C(50)—C(51)	121 (2)	N(6)—C(60)—C(55)	176 (3)
C(49)—C(50)—C(59)	120 (2)		

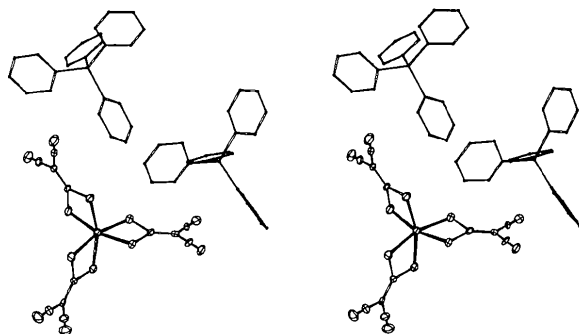


Fig. 2. Stereoscopic drawing of the molecule.

**Discussion.** The geometry of the [As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sup>+</sup> cation is tetrahedral, in good agreement with other determinations (*e.g.* Cowie & Bennett, 1976) and is not further discussed. In the anion six Se atoms are located around the central metal at an average distance of 2.387 (1) Å, forming a slightly distorted octahedron. Each ligand is planar. Surprisingly, in the anion the C=C (1.36 Å) and C≡N (1.15 Å) distances are very similar to those in (H<sub>3</sub>CS)<sub>2</sub>C=C(CN)C<sub>6</sub>H<sub>4</sub>-*p*-Br (1.37 and 1.14 Å) (Abrahamsson, Rehnberg, Liljefors & Sandström, 1974). This shows that the stabilization of the Ni<sup>IV</sup> chelate cannot arise from an extended

Table 3. Selected structural parameters of complexes with MSe<sub>6</sub> cores and geminal ligands

	[Ni{Se <sub>2</sub> C=C(CN) <sub>2</sub> } <sub>3</sub> ] <sup>2-</sup>	[Ni{Se <sub>2</sub> CN(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> } <sub>3</sub> ] <sup>+</sup>
M—Se	2.387 (1) Å	2.391 (5) Å
Se...Se(intra)	2.995 (1)	3.00 (1)
Se...Se(inter)	3.515 (1)	3.515 (5)
Se—C	1.86 (1)	1.78 (3)
C≡N		1.48 (8)
C=C	1.36 (2)	
Se—M—Se	77.67 (7)°	77.4 (4)°
Se—C—Se'	107.5 (5)	114 (1)
<i>s/h</i>	1.29	1.18

delocalization of charge on the ligands. Therefore, the oxidation of complexes containing such ligands should be described as loss of electrons from the NiSe<sub>6</sub> moiety exclusively (Coucovanis, Hollander & Pedelty, 1977). The ratio *s/h* is 1.29, where *s* is a side of a Se<sub>3</sub> triangle and *h* the perpendicular distance between two triangles of the octahedron (Stiefel & Brown, 1972). The Se<sub>3</sub> triangles are twisted with respect to each other by 49.5°. The average bite angle is 77.67 (7)°. A further useful criterion in the structure discussion is the *trans* Se—Ni—Se' angle (136 ± 1° in the known trigonal prisms and 180° in the perfect octahedron) which was found to be 164.1 (1)°. In [C<sub>7</sub>H<sub>7</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>[Fe{S<sub>2</sub>C=C(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sub>3</sub>], a further tris-chelate with 1,1-disubstituted 2,2-ethylenedichalcogenolate ligands and a central metal in the oxidation state +4 (Coucovanis, Hollander & Pedelty, 1977), *s/h* = 1.29, *θ* = 49.0° and an average *trans* S—Fe—S' angle of 158.97 (4)° were found. The Ni—Se distance and the bite angle Se—Ni—Se in the [Ni{Se<sub>2</sub>C=C(CN)<sub>2</sub>}<sub>3</sub>]<sup>2-</sup> anion are also comparable with the values found for the Ni<sup>IV</sup> tris-chelate of *N,N*-dibutyldiselenocarbamate (Beurskens & Cras, 1971), also having octahedral coordination (Table 3). Further X-ray structure analyses of tris-chelates of such ligands have not yet been published.

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## Tetrahedral and Octahedral Cobalt(II) in Hexaaquacobalt Tetrachlorocobaltate–18-Crown-6–Acetone\*

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**Abstract.** [Co(H<sub>2</sub>O)<sub>6</sub>][CoCl<sub>4</sub>].C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>.C<sub>3</sub>H<sub>6</sub>O, triclinic, *P*1̄, *a* = 10.251 (4), *b* = 11.619 (5), *c* = 13.603 (7) Å, α = 92.64 (4), β = 95.05 (4), γ = 112.38 (3)°, *V* = 1487 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.53 (1), *D<sub>c</sub>* = 1.54 Mg m<sup>-3</sup>, μ(Mo *K*α) = 1.57 mm<sup>-1</sup>. The structure of [Co(H<sub>2</sub>O)<sub>6</sub>][CoCl<sub>4</sub>].18-crown-6.acetone, determined by heavy-atom techniques and refined by least-squares methods using diffractometer data to *R*<sub>1</sub> = 4.3% (4246 observed reflections), includes cobalt(II) in two coordination geometries: a tetrachlorocobaltate anion and a hexaaquacobalt cation. The crown ether ring does not incorporate the metal into its cavity.

**Introduction.** Su & Weiher (1968) reported the isolation of a blue material from acetic acid which they formulated as 2CoCl<sub>2</sub>.dicyclohexyl-18-crown-6, a 2:1 complex. Based on the physical properties of this material, two possible structures were proposed (Fig. 1). A more recent report (Knöchel, Klimes, Oehler & Rudolph, 1975) described the formation of transition-metal complexes of unsubstituted 18-crown-6; these

were 2:1 complexes containing nitrate or chloride. Farago (1977) has reported complexes of varying stoichiometries including a series of five complexes of CoBr<sub>2</sub> and 18-crown-6.

Structural investigations have been limited to: [Mn(H<sub>2</sub>O)<sub>5</sub>(NO<sub>3</sub>)]<sup>+</sup>.18-crown-6.NO<sub>3</sub><sup>-</sup>.H<sub>2</sub>O (Knöchel, Kopf, Oehler & Rudolph, 1978) where octahedral Mn is coordinated to five water molecules and one nitrate ion, and CuCl<sub>2</sub>.12-crown-4 where the metal is directly bound to the polyether O atoms (van Remoortere, Boer & Steiner, 1975). We have determined the structures of a series of transition-metal complexes with crown ethers to examine the structural consequences of change of ring size and metal ion (part II: Vance, Holt, Varie & Holt, 1980; Vance, 1978).

Hexaaquacobalt(II) tetrachlorocobaltate(II)–18-crown-6–acetone (Farago, 1977) was crystallized in a form suitable for X-ray diffraction studies. A crystal (approximately 0.5 × 0.5 × 0.5 mm) was coated with epoxy glue and mounted on a Syntex *P*1̄ diffractometer with graphite-monochromatized radiation (Mo *K*α, λ = 0.71069 Å). Least-squares refinement of the angular coordinates of fifteen independent reflections gave the unit-cell parameters and their standard deviations. The θ/2θ scan mode, at an invariant scan

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