

a grant for a key research project from the State Science and Technology Commission, and the National Science Foundation of the People's Republic of China.

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## Structures of Hexachloroniobate(V) Salts of the 1-Methylimidazole/1-Methylimidazolium and 2-Methylimidazolium Cations

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(Received 11 May 1992; accepted 9 December 1992)

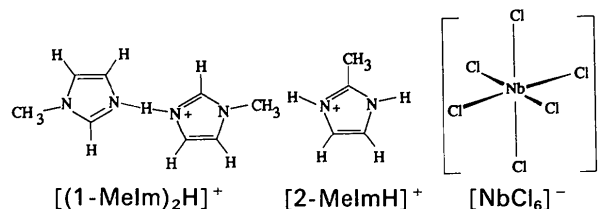
### Abstract

Both salts contain approximately octahedral  $[\text{NbCl}_6]^-$  anions with Nb—Cl bond lengths ranging from 2.326 (2) to 2.378 (2) Å. The 1-methylimidazole salt (I) contains the proton-bridged 1-methylimidazole/1-methylimidazolium cation, whereas the fully N-protonated 2-methylimidazolium ion is present in the 2-methylimidazole compound (II). Cohesion in the crystals is achieved by dipolar interactions between Cl atoms of  $[\text{NbCl}_6]^-$  and imidazole C—H groups for (I) and (II), as well as N—H...Cl hydrogen bonds for (II).

### Comment

The reactions of  $\text{NbCl}_5$  with N-heterocycles are currently being investigated in this laboratory. Two reaction pathways have been identified with pyridine (McCarley, Hughes, Boatman & Torp, 1963) and 7-azaindole (Poitras & Beauchamp, 1992), namely the formation of  $\text{Nb}^{\text{V}}$  adducts  $\text{NbCl}_5(L)$  and the reduction to  $\text{Nb}^{\text{IV}}$  with concomitant ligand oxidation. The two title compounds, (I)  $[(1\text{-MeIm})_2\text{H}]^+$

$[\text{NbCl}_6]^-$  and (II)  $[2\text{-MeImH}][\text{NbCl}_6]^-$ , were among the products isolated from the reactions with 1-methylimidazole (1-MeIm) and 2-methylimidazole (2-MeIm). An X-ray investigation was undertaken in order to explain their different stoichiometries despite very similar chemical properties.



These compounds were present in the filtrates from reactions of  $\text{NbCl}_5$  (~1 g) with the imidazole ligand in a 2:7 ratio in ~50 ml of benzene (I) or toluene (II). The reactions were run under a dry argon atmosphere in a Schlenk system, from  $\text{NbCl}_5$  (Aldrich, stored in glove box) and 1-MeIm (Aldrich, dried over molecular sieves) or 2-MeIm (Aldrich, sublimed). Solvents were dried by distillation over Na. Red crystals of the 1-MeIm compound (I) appeared after two weeks in the benzene filtrate. Brown crystals of the 2-MeIm compound (II) were isolated after two months from the toluene filtrate. Both compounds are extremely moisture sensitive.

The single  $[\text{NbCl}_6]^-$  anion in (I) occupies the inversion center at the cell origin. In (II), the eight anions are distributed over equipoints 4(e)  $[\text{Nb}(1)$ , twofold axis] and 4(c)  $[\text{Nb}(2)$ , inversion center]. These three independent  $[\text{NbCl}_6]^-$  anions have a nearly octahedral geometry. The octahedron is very regular for the two types of anions sitting on inversion centers: the *cis* Cl—Nb—Cl angles are in the region of 90.0 (5)°, whereas the *trans* angles are 180° by symmetry. The anion lying on a twofold axis  $[\text{Nb}(1)$  of (II)] is slightly more distorted, with *cis* angles ranging from 87.80 (6) to 91.98 (6)° and *trans* angles of 177.55 (6) and 177.46 (6)°. The Nb—Cl distances, ranging from 2.326 (2) to 2.378 (2) Å (mean 2.349 Å), compare well with literature values (Hubert-Pfalzgraf, Postel & Riess, 1987; von Dübgen, Müller, Weller & Dehnicke, 1980; Preiss, 1971; Preiss & Reich, 1971; Shibaeva & Lobkovskaya, 1985).

Compound (I) contains the 1-methylimidazole/1-methylimidazolium cation shown in Fig. 1. The two nearly coplanar 1-MeIm units are related by an inversion center. The bridging H(3) proton, whose position was deduced from a  $\Delta F$  map, is disordered over two sites slightly off the inversion center. Thus, each of the imidazole units about the inversion center actually corresponds to equal populations of the neutral and monocationic forms. Attempts to refine a non-disordered model in space group *P1*

failed. The imidazole ring is planar to within 0.011 (14) Å and the H(3) atom lies in this plane, very close to the N(3)⋯N(3') vector [N(3)—H(3)⋯N(3') = 174°]. Similar proton-bridged N-heterocyclic pairs are known for pyridines (Villarreal-Salinas & Schlemper, 1978; Brenčić, Čeh & Leban, 1986, 1987), benzimidazole (Quick & Williams, 1976*a*) and unsubstituted imidazole (Quick & Williams, 1976*b*). The N⋯N separations in these compounds (2.71–2.79 Å) are below the normal range (2.88–3.38 Å) proposed by Stout & Jensen (1968) for N—H⋯N hydrogen bonds. The still shorter N⋯N distance found in (I) [2.645 (14) Å] is evidence for strong hydrogen bonding. Protonation normally affects appreciably the geometry of the imidazole ring, especially the angles near N(3): the smaller size of the protonated N(3) 'lone pair' increases the C(2)—N(3)—C(4) angle, whereas the adjacent angles at C(2) and C(4) undergo opposite variations keeping the ring planar. This is well illustrated by the angles at C(2), N(3) and C(4) in 1-MeIm [112.2 (3), 104.9 (3) and 110.1 (3)°, respectively (Wang & Craven, 1979*b*)] and those in 1-MeImH<sup>+</sup> [108.3 (2), 109.4 (2) and 106.7 (2)°, respectively (Wang & Craven, 1979*a*)]. The intermediate values observed here [109.2 (11), 107.0 (11) and 109.9 (12)°, respectively] are consistent with these two patterns being averaged by disorder.

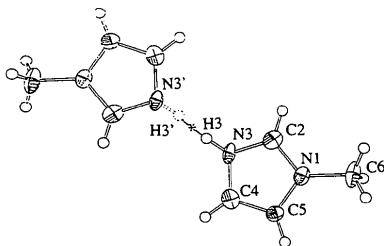


Fig. 1. ORTEP (Johnson, 1965) drawing of the 1-methylimidazolium/1-methylimidazole cation. The two units are related by a crystallographic inversion center (\*) and H(3) is disordered over two sites about this center. Primed atoms correspond to  $1-x$ ,  $2-y$ ,  $1-z$ . Ellipsoids are drawn at 50% probability level. H atoms are shown as spheres of arbitrary size.

A packing diagram is shown in Fig. 2.  $[\text{NbCl}_6]^-$  anions sitting on the origin define a three-dimensional framework in which channels parallel to the  $b$  axis are filled by  $[(1\text{-MeIm})_2\text{H}]^+$  ions centered at  $(\frac{1}{2}, 0, \frac{1}{2})$ . Since the hydrogen-bonding capabilities of the 1-methylimidazole units are satisfied within these dimeric cations, all contacts between anions and cations involve dipolar interactions, mainly between C—H protons and Cl atoms. Table 2 shows that almost all C—H bonds are involved in H⋯Cl contacts shorter than the sum of the van der Waals radii [3.1 Å (Cotton & Wilkinson, 1987)].

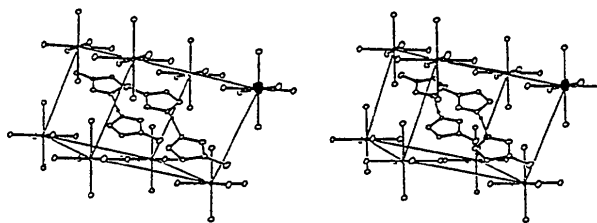


Fig. 2. Stereoview of the unit cell of  $[(1\text{-MeIm})_2\text{H}][\text{NbCl}_6]$ . The origin is indicated by a black dot. The  $a$  (vertical) and  $c$  (horizontal) axes are approximately in the plane of the diagram, whereas  $b$  is pointing away from the reader. Only one of the disordered pair of H(3) atoms is shown. The other H atoms are omitted for clarity.

The 2-methylimidazolium salt (II) contains the normal fully protonated cation. This ion has near  $2mm$  symmetry with the twofold axis running through C(2)—CH<sub>3</sub> and the middle of the C(4)—C(5) bond. The ring is planar to within 0.005 (6) Å and the methyl C(6) atom is displaced by only 0.007 (5) Å from this plane. The distances and angles (Table 3) are normal, although meaningful comparisons cannot be made because the crystallographic data available on this cation (Zalkin, Perry, Tsao & Zhang, 1983; Scheidt, Lee, Tamai & Hatano, 1983) are of low accuracy. Comparisons with the unsubstituted imidazolium cation (Levasseur & Beauchamp, 1991) reveal that the C(2)-bonded methyl group has only a minor effect on the bond lengths, but it decreases the ring angle at C(2) by 3.0°, whereas the adjacent angles at N(1) and N(3) increase by 1.2 and 2.3°, respectively. The structure of 2-MeIm has not been determined, but those of several N(3)-coordinated metal complexes are known.\* Since

\* See deposition footnote.

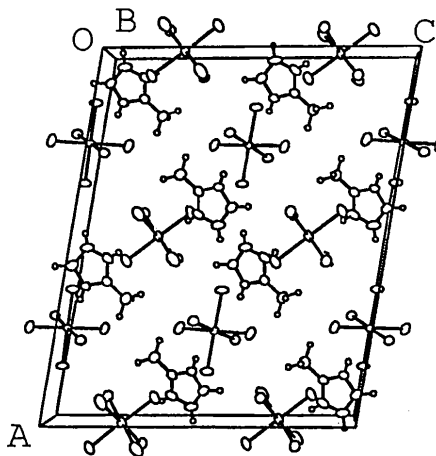


Fig. 3. View of the unit cell of  $[2\text{-MeImH}][\text{NbCl}_6]$  down the  $b$  axis. The Nb atoms lie in planes parallel to the  $bc$  face, at  $x = 0$  and  $\frac{1}{2}$  for Nb(1), and  $x = \frac{1}{4}$  and  $\frac{3}{4}$  for Nb(2).

metal coordination usually affects the ligand geometry to only a small extent, these data can be used to evaluate the effect of protonation. The C(2)—N(3)—C(4) angle is found to be 4.7° greater in the protonated ligand, whereas changes of -4.4 and -2.1° are noted for the angles at C(2) and C(4), respectively. This is similar to the protonation pattern mentioned above for 1-MeIm.

A packing pattern of (II) is given in Fig. 3. Half of the [NbCl<sub>6</sub>]<sup>-</sup> anions are located on twofold axes [Nb(1)], whereas the other half occupy inversion centers [Nb(2)]. Each 2-methylimidazolium cation includes two N—H bonds acting as donors in normal hydrogen bonds to Cl atoms (Table 3). Cohesion in the crystals also involves dipolar contacts of the C—H protons with Cl atoms lying closer than the sum of the van der Waals radii [3.1 Å (Cotton & Wilkinson, 1987)].

## Experimental

### Compound (I)

#### Crystal data

[C<sub>8</sub>H<sub>13</sub>N<sub>4</sub>][NbCl<sub>6</sub>]

*M<sub>r</sub>* = 470.84

Triclinic

*P* $\bar{1}$

*a* = 7.111 (2) Å

*b* = 8.042 (1) Å

*c* = 8.045 (2) Å

$\alpha$  = 78.65 (2)°

$\beta$  = 87.02 (2)°

$\gamma$  = 70.04 (2)°

*V* = 424.0 (2) Å<sup>3</sup>

*Z* = 1

#### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

1716 measured reflections

1490 independent reflections

978 observed reflections

[*I* ≥ 3σ(*I*)]

*R*<sub>int</sub> = 0.025

#### Refinement

Refinement on *F*

Final *R* = 0.056

*wR* = 0.057

*S* = 2.69

978 reflections

88 parameters

H atoms fixed

*D<sub>x</sub>* = 1.844 Mg m<sup>-3</sup>

Mo *K*α radiation

$\lambda$  = 0.71069 Å

Cell parameters from 25 reflections

$\theta$  = 10–12°

$\mu$  = 1.626 mm<sup>-1</sup>

*T* = 200 K

Approximately spherical

0.25 mm (radius)

Red

Crystal source: see *Comment*

$\theta_{\max}$  = 25°

*h* = 0 → 8

*k* = -9 → 9

*l* = -9 → 9

6 standard reflections

frequency: 60 min

intensity variation: 0.8%

$w = 1/[\sigma^2(F) + 0.0001F^2]$

( $\Delta/\sigma$ )<sub>max</sub> = 0.01

Background  $\Delta\rho$  =

±0.88 e Å<sup>-3</sup>

Residual  $\Delta\rho$  =

±|1.0–1.5| e Å<sup>-3</sup> near

Nb and Cl

### Compound (II)

#### Crystal data

[C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>][NbCl<sub>6</sub>]

*M<sub>r</sub>* = 388.74

Mo *K*α radiation

$\lambda$  = 0.71069 Å

Monoclinic

*C*2/*c*

*a* = 21.43 (1) Å

*b* = 6.851 (2) Å

*c* = 17.65 (1) Å

$\beta$  = 99.41 (2)°

*V* = 2555 (2) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 2.02 Mg m<sup>-3</sup>

#### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

4266 (*hkl*, *h* + *k* = 2*n*) measured reflections

2451 independent reflections

1695 observed reflections

[*I* ≥ 3σ(*I*)]

Cell parameters from 19 reflections

$\theta$  = 7–10°

$\mu$  = 2.132 mm<sup>-1</sup>

*T* = 200 K

Approximately spherical

0.17 mm (radius)

Brown

Crystal source: see *Comment*

*R*<sub>int</sub> = 0.022

$\theta_{\max}$  = 25°

*h* = 0 → 25

*k* = -8 → 8

*l* = -21 → 21

5 standard reflections

frequency: 60 min

intensity variation: 0.7%

#### Refinement

Refinement on *F*

Final *R* = 0.030

*wR* = 0.038

*S* = 1.16

1695 reflections

120 parameters

H atoms fixed

$w = 1/[\sigma^2(F) + 0.0001F^2]$

( $\Delta/\sigma$ )<sub>max</sub> = 0.01

$\Delta\rho_{\max}$  = 0.39 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.39 e Å<sup>-3</sup>

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for (I) and (II)

	$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			<i>U</i> <sub>eq</sub>
	<i>x</i>	<i>y</i>	<i>z</i>	
(I)				
Nb(1)	0	1.0000	0	0.018
Cl(1)	0.0626 (5)	0.9580 (4)	0.2905 (4)	0.029
Cl(2)	-0.0608 (5)	0.7263 (4)	0.0407 (4)	0.033
Cl(3)	0.3421 (5)	0.8500 (5)	-0.0422 (4)	0.035
N(1)	0.6986 (14)	0.5693 (13)	0.4194 (12)	0.023
N(3)	0.5970 (15)	0.8275 (13)	0.4994 (13)	0.025
C(2)	0.5913 (19)	0.7467 (17)	0.3747 (16)	0.028
C(4)	0.7067 (19)	0.6987 (18)	0.6276 (16)	0.027
C(5)	0.7696 (18)	0.5373 (16)	0.5810 (15)	0.023
C(6)	0.7271 (21)	0.4340 (17)	0.3131 (17)	0.037
(II)				
Nb(1)	0	0.3378 (1)	0.2500	0.028
Nb(2)	0.2500	0.2500	0	0.020
Cl(1)	0.0666 (1)	0.3302 (2)	0.1569 (1)	0.036
Cl(2)	-0.0641 (1)	0.5737 (2)	0.1817 (1)	0.036
Cl(3)	0.0617 (1)	0.0877 (2)	0.3194 (1)	0.051
Cl(4)	0.1434 (1)	0.1780 (2)	0.0002 (1)	0.036
Cl(5)	0.2802 (1)	-0.0459 (2)	0.0647 (1)	0.029
Cl(6)	0.2547 (1)	0.4106 (2)	0.1183 (1)	0.041
N(1)	0.3688 (2)	0.2153 (6)	0.4371 (2)	0.028
N(3)	0.4418 (2)	0.3341 (7)	0.3842 (3)	0.036
C(2)	0.3804 (2)	0.2993 (7)	0.3731 (3)	0.027
C(4)	0.4695 (3)	0.2704 (8)	0.4543 (3)	0.040
C(5)	0.4243 (2)	0.1959 (8)	0.4882 (3)	0.035
C(6)	0.3335 (3)	0.3461 (9)	0.3041 (3)	0.047

Table 2. Bond lengths (Å), bond angles (°) and hydrogen-bond geometry (Å, °) for (I)

Nb(1)—Cl(1)	2.339 (3)	C(2)—N(3)	1.307 (16)
Nb(1)—Cl(2)	2.343 (3)	N(3)—C(4)	1.363 (17)
Nb(1)—Cl(3)	2.358 (4)	C(4)—C(5)	1.343 (18)
N(1)—C(2)	1.353 (16)	N(1)—C(6)	1.467 (16)
N(1)—C(5)	1.363 (15)		

Cl(1)—Nb(1)—Cl(2)	90.5 (1)	C(2)—N(1)—C(6)	125.4 (11)
Cl(1)—Nb(1)—Cl(3)	90.1 (1)	C(5)—N(1)—C(6)	126.1 (11)
Cl(1)—Nb(1)—Cl(2) <sup>j</sup>	89.5 (1)	N(1)—C(2)—N(3)	109.2 (11)
Cl(1)—Nb(1)—Cl(3) <sup>j</sup>	89.9 (1)	C(2)—N(3)—C(4)	107.0 (11)
Cl(2)—Nb(1)—Cl(3)	90.4 (1)	N(3)—C(4)—C(5)	109.9 (12)
Cl(2)—Nb(1)—Cl(3) <sup>j</sup>	89.6 (1)	C(4)—C(5)—N(1)	105.3 (11)
C(2)—N(1)—C(5)	108.5 (10)		

<i>D</i> —H... <i>A</i>	<i>D</i> ... <i>A</i>	H... <i>A</i>	<i>D</i> —H... <i>A</i>
N(3)—H(3)...N(3) <sup>iii</sup>	2.645 (14)	1.86	174
C(2)—H(2)...Cl(3)	3.688 (13)	2.82	161
C(4)—H(4)...Cl(2) <sup>iii</sup>	3.866 (14)	2.99	164
C(5)—H(5)...Cl(1) <sup>iv</sup>	3.690 (12)	2.91	147
C(5)—H(5)...Cl(2) <sup>iv</sup>	3.628 (13)	2.89	142
C(6)—H(63)...Cl(2) <sup>v</sup>	3.557 (14)	2.98	123
C(6)—H(61)...Cl(1) <sup>vi</sup>	3.791 (14)	3.09	133

Symmetry code: (i)  $-x, 2-y, -z$ ; (ii)  $1-x, 2-y, 1-z$ ; (iii)  $1+x, y, 1+z$ ; (iv)  $1-x, 1-y, 1-z$ ; (v)  $1+x, y, z$ ; (vi)  $1+x, -1+y, z$ .

Table 3. Bond lengths (Å), bond angles (°) and hydrogen-bond geometry (Å, °) for (II)

Nb(1)—Cl(1)	2.347 (2)	N(1)—C(2)	1.327 (6)
Nb(1)—Cl(2)	2.326 (2)	N(1)—C(5)	1.377 (7)
Nb(1)—Cl(3)	2.378 (2)	C(2)—N(3)	1.320 (6)
Nb(2)—Cl(4)	2.338 (2)	N(3)—C(4)	1.354 (8)
Nb(2)—Cl(5)	2.365 (2)	C(4)—C(5)	1.322 (9)
Nb(2)—Cl(6)	2.348 (2)	C(2)—C(6)	1.482 (7)

Cl(1)—Nb(1)—Cl(2)	91.56 (6)	Cl(4)—Nb(2)—Cl(5) <sup>ii</sup>	89.50 (6)
Cl(1)—Nb(1)—Cl(3)	89.66 (6)	Cl(4)—Nb(2)—Cl(6) <sup>ii</sup>	90.15 (6)
Cl(1)—Nb(1)—Cl(1) <sup>j</sup>	177.46 (6)	Cl(5)—Nb(2)—Cl(6)	90.21 (6)
Cl(1)—Nb(1)—Cl(2) <sup>j</sup>	90.18 (6)	Cl(5)—Nb(2)—Cl(6) <sup>ii</sup>	89.79 (6)
Cl(1)—Nb(1)—Cl(3) <sup>j</sup>	88.51 (6)	C(2)—N(1)—C(5)	109.7 (4)
Cl(2)—Nb(1)—Cl(3)	177.55 (6)	N(1)—C(2)—N(3)	105.8 (4)
Cl(2)—Nb(1)—Cl(2) <sup>j</sup>	91.98 (6)	C(2)—N(3)—C(4)	110.8 (5)
Cl(2)—Nb(1)—Cl(3) <sup>j</sup>	90.12 (6)	N(3)—C(4)—C(5)	107.1 (5)
Cl(3)—Nb(1)—Cl(3) <sup>j</sup>	87.80 (6)	C(4)—C(5)—N(1)	106.6 (5)
Cl(4)—Nb(2)—Cl(5)	90.50 (6)	N(1)—C(2)—C(6)	126.7 (4)
Cl(4)—Nb(2)—Cl(6)	89.85 (6)	N(3)—C(2)—C(6)	127.5 (5)

<i>D</i> —H... <i>A</i>	<i>D</i> ... <i>A</i>	H... <i>A</i>	<i>D</i> —H... <i>A</i>
N(3)—H(3)...Cl(1) <sup>iii</sup>	3.474 (5)	3.10	112
N(3)—H(3)...Cl(3) <sup>iv</sup>	3.448 (5)	2.73	151
N(1)—H(1)...Cl(5) <sup>v</sup>	3.380 (4)	2.59	171
N(1)—H(1)...Cl(6) <sup>vi</sup>	3.387 (4)	3.05	108
C(4)—H(4)...Cl(4) <sup>vii</sup>	3.699 (7)	2.82	166
C(5)—H(5)...Cl(2) <sup>viii</sup>	3.855 (6)	2.96	173
C(6)—H(61)...Cl(5) <sup>ix</sup>	3.700 (5)	2.99	124
C(6)—H(62)...Cl(2) <sup>x</sup>	3.810 (5)	2.82	151

Symmetry code: (i)  $-x, y, \frac{1}{2}-z$ ; (ii)  $\frac{1}{2}-x, \frac{1}{2}-y, -z$ ; (iii)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iv)  $\frac{1}{2}+x, \frac{1}{2}+y, z$ ; (v)  $x, -y, \frac{1}{2}+z$ ; (vi)  $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ; (vii)  $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ ; (viii)  $\frac{1}{2}+x, -\frac{1}{2}+y, z$ .

An approximately spherical crystal of (I) was quickly introduced in a Lindemann capillary and transferred to the diffractometer, where the temperature was decreased to 200 K by the cooling system. The reduced cell was checked with long exposure axial photographs along the three axes. No symmetry higher than triclinic was consistent with the Niggli matrix. A crystal of (II) was quickly mounted and the reduced cell was obtained and checked at 200 K, as for (I). A *C*-centered monoclinic cell was indicated by the Niggli matrix. The new cell was confirmed by axial photographs. Density could not be measured because of crystal instability in all solvents. For (I) and (II), the data were corrected for Lp effects. No absorption corrections were applied because of nearly spherical shape and poor face definition of (I) and (II). In (I), space groups *P1* and  $\bar{P}1$  were consistent with the triclinic Laue symmetry. The structure solved and refined normally in space group *P1*. The Nb atom was found from a Patterson map and all other non-H atoms were located from a  $\Delta F$  map. These atoms were refined anisotropically by full-matrix least squares. H(2), H(4) and H(5) were fixed at idealized positions ( $C-H = 0.90 \text{ \AA}$ ,  $B_{\text{iso}} = 3.5 \text{ \AA}^2$ ). H(3), located from the  $\Delta F$  map, was

found to be disordered over two positions about the crystallographic inversion center. For the methyl group, one H atom located from the  $\Delta F$  map provided a  $C(2)-N(1)-C(6)-H$  torsion angle, from which idealized positions were calculated for the three methyl H atoms. The H-atom coordinates [except those of H(3)] were recalculated after each cycle. In (II), space groups *C2/c* and *Cc* were consistent with the Laue symmetry and systematic absences (*hkl*,  $h+k$  odd;  $h0l$ ,  $l$  odd). The structure solved and refined normally in the centrosymmetric space group *C2/c*. Nb and Cl atoms were found by the Patterson method. The N and C atoms were located from a  $\Delta F$  map. The H atoms were handled as for structure (I). All non-H atoms were refined anisotropically by full-matrix least squares. The computer programs used are listed elsewhere (Authier-Martin & Beauchamp, 1977). In both cases, atomic scattering factors were taken from Cromer & Liberman (1970) for non-H atoms and from Stewart, Davidson & Simpson (1965) for H atoms, with anomalous-dispersion terms for Nb and Cl from Cromer (1965).

The authors wish to thank M. Simard and F. Bélanger-Gariépy for assistance in collecting the X-ray data. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes data, as well as a comparison of distances and angles in various N(3)-bonded metal complexes, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55910 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1013]

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### Structure of $[\text{As}(\text{C}_6\text{H}_5)_4]_2\text{-}[\text{Sn}\{\text{Se}_2\text{C}=\text{C}(\text{CN})_2\}_3]^{2-}$

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(Received 29 June 1992; accepted 3 December 1992)

#### Abstract

In the complex anion  $[\text{Sn}\{\text{Se}_2\text{C}=\text{C}(\text{CN})_2\}_3]^{2-}$  in bis(tetraphenylarsonium) tris(2,2-diselenido-1,1-ethylenedicarbonitrile-*Se, Se'*)stannate(IV), the Sn atom is at the center of a distorted octahedron formed of six Se atoms of the chelate ligands with an average Sn—Se bond length of 2.661 (3) Å. The bis(selenium) chelates show only small deviations from planarity and the average Se—C distance is 1.88 (1) Å.

#### Comment

Up to now only a few tris(chelate) complexes with unsaturated 1,1-diselenolato ligands have been structurally characterized. For these transition-metal complexes two different coordination geometries have been found. Whereas the central ion,  $\text{Ni}^{\text{IV}}$  in  $[\text{Ni}\{\text{Se}_2\text{CN}(\text{C}_4\text{H}_9)_2\}_3]\text{Br}$  (Beurskens & Cras, 1971) and  $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Ni}\{\text{Se}_2\text{C}=\text{C}(\text{CN})_2\}_3]$  (Kaiser, Dietzsch, Richter, Golič & Šiftar, 1980) has a distorted octahedral arrangement, the complex  $[\text{Fe}\{\text{Se}_2\text{CN}(\text{CH}_2\text{Ph})_2\}_3]\text{BF}_4$  has  $D_3$  macrosymmetry with a coordination polyhedron intermediate between the idealized trigonal prismatic and trigonal antiprismatic geometries (Deplano, Trogu, Bigoli, Leporati, Pellinghelli, Perry, Saxton & Wilson, 1983). Here we describe the X-ray crystal structure

analysis of the main-group metal tris(chelate) complex bis(tetraphenylarsonium) tris(2,2-diselenido-1,1-ethylenedicarbonitrile-*Se, Se'*)stannate(IV).

The geometry of the anion (Fig. 1) is comparable with  $[\text{Ni}\{\text{Se}_2\text{C}=\text{C}(\text{CN})_2\}_3]^{2-}$ ; the six Se atoms define an irregular octahedron and the average distance to the central metal is 2.661 (3) Å. The coordination around the  $\text{Sn}^{\text{IV}}$  is distorted octahedral. The average projected twist angle of the two  $\text{Se}_3$  triangles (Fig. 2) of the  $\text{SnSe}_6$  polyhedron is  $43.2^\circ$ , intermediate between the  $60$  and  $0^\circ$  expected for octahedral and trigonal prismatic geometry, respectively.

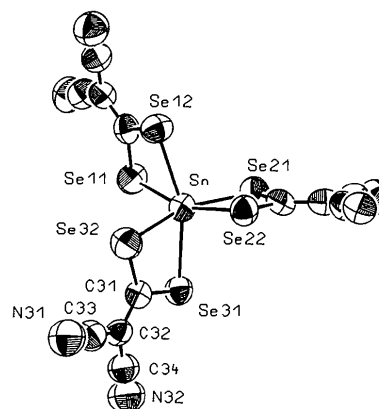


Fig. 1. Structure of the  $[\text{Sn}\{\text{Se}_2\text{C}=\text{C}(\text{CN})_2\}_3]^{2-}$  complex anion.

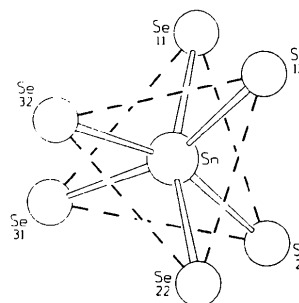


Fig. 2.  $\text{SnSe}_6$  core with the two  $\text{Se}_3$  triangles.

The average Se—Sn— $\text{Se}'$  angle involving two different chelate ligands is  $160.4(1)^\circ$  ( $180^\circ$  in the perfect octahedron) while the intra-chelate angles Se—Sn—Se are in the narrow range  $73.7(1)$ – $74.0(1)^\circ$  and reflect the rigid chelate geometry with Se—C—Se of about  $116^\circ$ .

The three selenolato ligands are nearly planar ( $\Delta_{\text{max}} = 0.3$  Å) and the system of bond lengths and angles compares well with values expected for covalent coordinated diselenolates (Dietzsch, Franke, Hoyer, Grubb & Hummel, 1991).