

## Tris(2-methylquinoline-8-selenolato- $\kappa^2N,Se$ )antimony(III)

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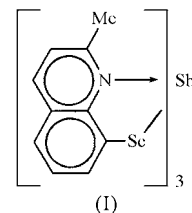
The title complex,  $[Sb(C_{10}H_8NSe)_3]$ , has a 3Se+3N distorted octahedral geometry at the Sb atom. The structure is stabilized by weak intermolecular C—H $\cdots\pi$ (arene) interactions.

### Comment

This work represents a continuation of our systematic investigations of internal complexes of *p* elements in the partial-valence state ( $M = As^{III}$ ,  $Sb^{III}$  or  $Bi^{III}$ ) with the bidentate ligands 8-hydroxyquinoline (8-Oq), 8-mercaptoquinoline (8-Sq) and 8-hydroselenoquinoline (8-Seq). The coordination polyhedra of the central atoms are different in the molecular structures of 8-mercaptoquinolinates  $M(8-Sq)_3$ : As is defined as 3S+N with only one bidentate ligand (Matjuhina *et al.*, 1984), Sb is a 3S+3N distorted octahedron (Pech *et al.*, 1973), and Bi is a distorted 3S+3N pentagonal pyramid with an apical S atom (Silina *et al.*, 2000).

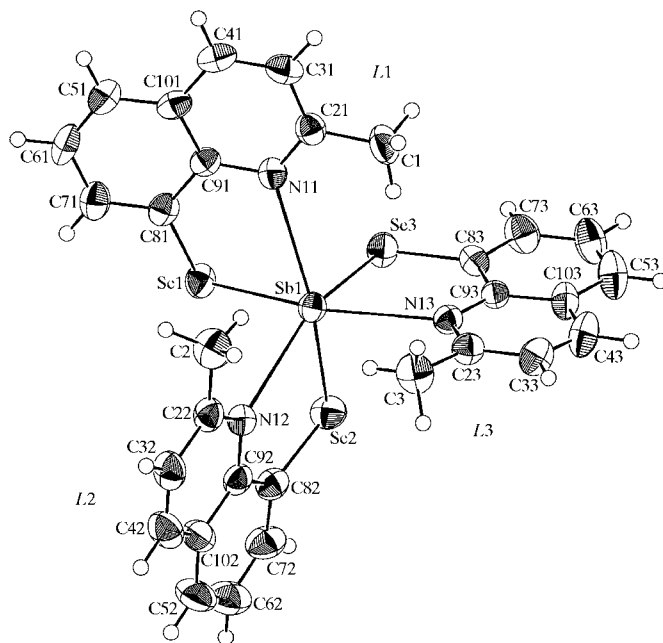
These molecular structures lead to the suggestion that the unshared metal electron pair (*E*) is directed between the  $M-N$  vectors corresponding to the direction of weak  $M-N$  coordination bonds. However, the As (Silina *et al.*, 2004), Sb (Silina *et al.*, 1997) and Bi 2-methyl-8-mercaptoquinolinates,  $M[2-CH_3(8-Sq)]_3$ , are isostructural. The central metal atom occurs in a 3S+3N octahedral geometry with approximate  $C_3$  symmetry. In accordance with the  $M[2-CH_3(8-Sq)]_3$  geometries and in the context of the  $M(8-Sq)_3$  structures, we consider the electrostatic interaction of the unpaired electrons (*E*) of the As, Sb and Bi atoms with one H atom from each methyl group as the reason for the occurrence of isostructural compounds. Such an interaction is interpreted as a weak branched locking intramolecular hydrogen bond (see scheme). This interaction evidently plays a determining role in the formation of the  $As[2-CH_3(8-Sq)]_3$  complex, where the As—N bonds are in the range 2.641 (3)–2.719 (4) Å, but can hardly be the reason for the *M*-containing rings closing in. Diffraction studies of the title complex,  $Sb[2-CH_3(8-Seq)]_3$ , (I), should quantify the effect of changing the ligand atom

from S to Se on the molecular and crystal structures of (I) and the analogous complex,  $Sb[2-CH_3(8-Sq)]_3$ , (II).



The molecular structure of (I) is depicted in Fig. 1. The dihedral angle between the 2-methyl-8-hydroselenoquinoline ligand planes *L1* and *L2* is 58.40 (3)°, that between planes *L1* and *L3* is 96.94 (4)°, and that between planes *L2/L3* is 96.02 (4)° (*L1*–*L3* are defined in Fig. 1). The  $Sb^{III}$  atom possesses a distorted 3Se+3N octahedral coordination geometry, with an average Sb—Se bond length of 2.6097 (7) Å (Table 1), similar to  $Sb(8-Seq)_3$ , (III), and data from the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002). The Se—Sb—Se angles have an average value of 87.14 (2)°.

The Se and N atoms of the three bidentate ligands form five-membered metal-containing rings. The Se—Sb—N chelate angles [mean 71.4 (1)°] are smaller than the Sb—Se—C angles [mean 104.9 (2)°]. The three chelate rings have dihedral angles between the Se/Sb/N and Se/C/C/N planes of 29.04 (4)° (*L1*), 7.40 (5)° (*L2*) and 0.83 (6)° (*L3*). The Sb atom deviates from the SeCCN planes by  $-1.0787$  (4) (envelope conformation, *L1*), 0.2893 (3) (*L2*) and 0.0294 (4) Å (*L3*), whereas in (II), the corresponding angles are 4.3, 17.6 and



**Figure 1**

The molecular structure of (I), showing the ligands and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. *L1*, *L2* and *L3* represent the ligand planes used in the *Comment*.

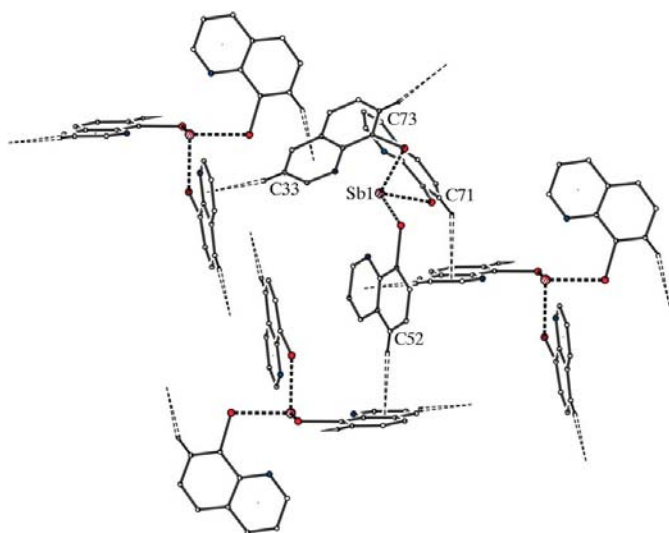
17.9°. The Se/Sb/N coordination planes in (I) are almost perpendicular to one another, with dihedral angles between these planes in the range 83.44 (2)–90.15 (3)° [84.45 (4)–90.78 (4)° in (II)].

The Sb–N bonds [mean 2.826 (4) Å] are longer than and *trans* to the Sb–Se bonds, slightly longer than those in (II) and (III), and *ca* 30% longer than the sum of the covalent radii ( $\Sigma_{CR}$ ) of Se and N (Campbell, 1975). The mean value of the N–Sb–N angles is 112.06 (14)°, with N11–Sb1–N12 = 120.75 (14)°, or 13° greater than the other two angles. The equatorial Se–Sb–N interligand angles are close to 90°. In (I), the quinolinyl bond lengths and angles of the ligand are normal (Allen, 2002).

In (I), the intramolecular Sb···C distances are 3.764 (8) (C1), 3.698 (7) (C2) and 3.667 (7) Å (C3), and these are greater than the Sb···C distances in (II) [mean 3.655 (7) Å]. Therefore, quantitative changes in the geometry of the complex due to an S→Se substitution in group VI have resulted in subtle changes in (I) compared with (II).

Differences in the nature of the ligand atoms in (I) and (II) appear in the crystal packing in different space groups, with (I) in *C2/c* and (II) in *P2<sub>1</sub>/c*. Intermolecular interactions corresponding to  $\pi$ – $\pi$  interactions cause different bending of the metal-containing rings, and consequently a different spatial disposition of the quinoline rings in (I). Quinoline ring *L1* partially overlaps ring *L1<sup>i</sup>* of a symmetry-related molecule at ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ), with a centroid-to-centroid distance of 3.639 Å. There are four C–H··· $\pi$ (arene) interactions of note and details of these are given in Table 2 and Fig. 2.

The main result of this study is that an S→Se substitution of the group VI ligand atoms does not change the nearest order for the central atom of (I) compared with (II). However, the overall crystal structure of (I) differs from (II).



**Figure 2**

Part of the crystal structure of compound (I), showing the three shortest C–H··· $\pi$ (arene) interactions (double dashed lines) from Table 2. Heavy dashed lines indicate the Se–Sb bonds. For the sake of clarity, H atoms and transannular N–Sb bonds have been omitted.

## Experimental

2,2'-Dimethyl-8,8'-diquinolyl diselenide (0.1 g) was dissolved in 3 M HCl (1 ml). Ethanol (5 ml) and 50% aqueous H<sub>3</sub>PO<sub>4</sub> (0.5 ml) were added, and the mixture was kept for 5 min at room temperature. A saturated aqueous Na(O<sub>2</sub>CCMe) solution (2 ml) and a solution (2 ml) containing K(SbO)C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> (0.045 g) were added. The resulting amorphous pale-yellow precipitate was filtered off, washed with water and dried in air (yield 0.1 g, 85%). Single crystals of (I) were grown from a solution in CHCl<sub>3</sub>.

### Crystal data

[Sb(C <sub>10</sub> H <sub>8</sub> NSe) <sub>3</sub> ]	Z = 8
<i>M<sub>r</sub></i> = 785.16	<i>D<sub>x</sub></i> = 1.857 Mg m <sup>-3</sup>
Monoclinic, <i>C2/c</i>	Mo <i>K</i> α radiation
<i>a</i> = 40.0004 (7) Å	$\mu$ = 4.89 mm <sup>-1</sup>
<i>b</i> = 8.8672 (1) Å	<i>T</i> = 293 K
<i>c</i> = 16.9706 (4) Å	Plate, yellow
$\beta$ = 111.0625 (8)°	0.34 × 0.18 × 0.07 mm
<i>V</i> = 5617.17 (18) Å <sup>3</sup>	

### Data collection

Nonius KappaCCD area-detector diffractometer	24753 measured reflections
$\varphi$ and $\omega$ scans	8183 independent reflections
Absorption correction: Gaussian integration based on 12 indexed crystal faces (NUMABS; Coppens, 1970)	5183 reflections with <i>I</i> > 2σ( <i>I</i> )
<i>T<sub>min</sub></i> = 0.287, <i>T<sub>max</sub></i> = 0.726	<i>R<sub>int</sub></i> = 0.074
	$\theta_{max}$ = 30.0°

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0913P)^2]$
$wR(F^2) = 0.170$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 1.06	( $\Delta/\sigma$ ) <sub>max</sub> = 0.005
8183 reflections	$\Delta\rho_{max} = 0.64 \text{ e \AA}^{-3}$
334 parameters	$\Delta\rho_{min} = -0.60 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Sb1–Se1	2.6069 (7)	Sb1–N11	2.829 (4)
Sb1–Se2	2.6081 (7)	Sb1–N12	2.865 (4)
Sb1–Se3	2.6140 (7)	Sb1–N13	2.785 (5)
Se1–Sb1–Se2	88.94 (2)	Se2–Sb1–Se3	81.71 (2)
Se1–Sb1–Se3	90.78 (2)		

**Table 2**

Hydrogen-bond geometry (Å, °).

*Cg1*, *Cg2* and *Cg3* are the pyridine ring centroids of the quinoline systems containing atoms N11, N12 and N13, respectively.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C33–H33··· <i>Cg2</i> <sup>i</sup>	0.93	2.62	3.512 (7)	161
C52–H52··· <i>Cg3</i> <sup>ii</sup>	0.93	2.71	3.629 (9)	170
C71–H71··· <i>Cg3</i> <sup>iii</sup>	0.93	2.81	3.587 (8)	142
C73–H73··· <i>Cg1</i> <sup>iv</sup>	0.93	2.84	3.686 (8)	151

Symmetry codes: (i)  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (ii)  $x, -y - 1, z + \frac{1}{2}$ ; (iii)  $x + \frac{1}{2}, y + \frac{1}{2}, z - 1$ ; (iv)  $x, y + 1, z$ .

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C–H = 0.93 Å for aromatic rings or 0.96 Å for methyl groups, and refined with  $U_{iso}(H) = 1.2U_{eq}(C)$  for aromatic rings or  $1.5U_{eq}(C)$  for methyl groups.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3054). Services for accessing these data are described at the back of the journal.

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