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Key indicators

Single-crystal X-ray study
T = 291 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in main residue
R factor = 0.038
wR factor = 0.072
Data-to-parameter ratio = 31.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1,4-Dimethylpyridinium bis(2-oxo-1,3-dithiole-4,5-dithiolato)diphenylantimonate(V)

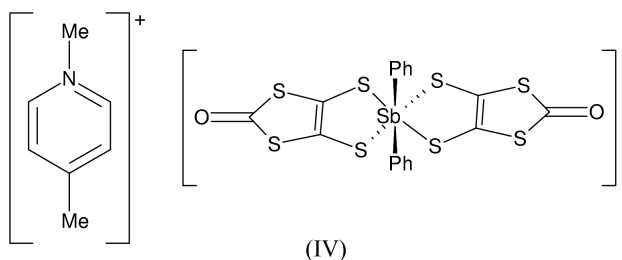
The title compound, $(\text{C}_7\text{H}_{10}\text{N})[\text{Sb}(\text{C}_6\text{H}_5)_2(\text{C}_3\text{OS}_4)_2]$, is a further example of a salt containing Sb^{V} of the form $[\text{Q}][\text{R}_2\text{Sb}(\text{dmio})_2]$, with Q an onium counter-cation and $\text{R} = \text{aryl}$. It is compared, particularly in terms of the packing of the ions in the unit cell, with other members of the series.

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Comment

The 1,3-dithiol-2-one-4,5-dithiolate (represented here as dmio, although the acronym dmid is sometimes used) and 1,3-dithiole-2-thione-4,5-dithiolate (dmit) dianions are well known ligand species and, especially the latter, have been much studied in the form of complexes of transition and main group metals. Many of the main group metal complexes also contain alkyl or aryl ligands. Until comparatively recently, one of the less studied areas of the this very broad field was that of complex salts containing Sb^{V} , of the form $[\text{Q}][\text{R}_2\text{SbX}_2]$ with Q an onium counter-cation, $\text{R} = \text{alkyl}$ or aryl and $\text{X} = \text{dmit}$ or dmio .

Preliminary work in this field has been carried out by Howie *et al.* (1997), hereinafter designated H, and extended further, as part of a wider study, by Avarvari & Formigué (2003), hereinafter A & F. Between them, these authors have reported structures for several compounds, categorized as follows in terms of the anions because, in every case, $\text{Q} = \text{NEt}_4$. The list comprises $[(p\text{-tolyl})_2\text{Sb}(\text{dmit})_2]^-$, (I) [Cambridge Structural Database (CSD), version 5.24 (Allen, 2002), reffcode NIJJIZ; Howie *et al.*, 1997], $[\text{Ph}_2\text{Sb}(\text{dmit})_2]^-$, (II) (CSD reffcode NIJJEV; Howie *et al.*, 1997), a relatively poor structure determination badly compromised by disorder (H), now augmented by a much improved redetermination by A & F], $[\text{Ph}_2\text{Sb}(\text{dmio})_2]^-$, (III) (with polymorphs *a* and *b* - see below), and $[\text{Ph}_2\text{Sb}(\text{dmit})(\text{dmio})]^-$, these last two both A & F. In order to extend the series further, we now present the structure of $[\text{1,4-dimethylpyridinium}][\text{Ph}_2\text{Sb}(\text{dmio})_2]$, (IV), with $\text{Q} = \text{dmp}$.



The asymmetric unit of (IV), which differs from (III) only in the replacement of the NEt_4 counter-cation by dmp, is shown in Fig. 1. The polymorphs of (III) are then clearly the most relevant species for comparison purposes. The coordination of

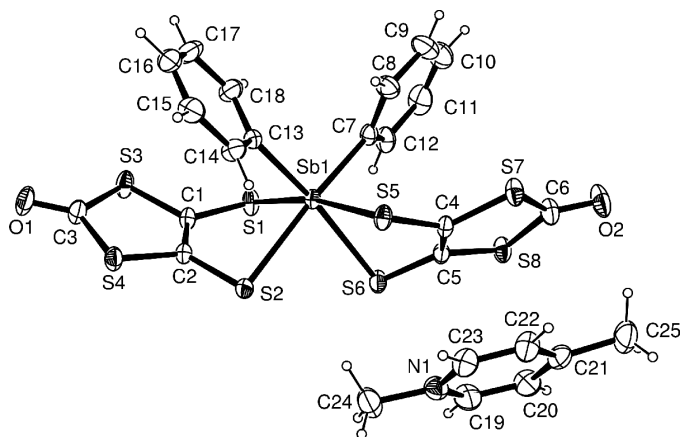


Figure 1

The asymmetric unit of (IV), showing the atom-labelling scheme. Non-H atoms are shown as 30% probability displacement ellipsoids and H atoms as small spheres of arbitrary radii. Only those triplets of the ideally disordered methyl H atoms in which one member of the set is involved in weak hydrogen-bond formation is shown.

Sb in the polymorphs of (III) and in (IV), as given in Table 1, is much the same in all three cases, *i.e.* Sb is in a distorted octahedral environment with *cis* aryl groups and asymmetrically chelating dmio ligands. For each ligand, the longer Sb—S bond is *trans* to an Sb—C bond. The coordinative saturation of the Sb centres precludes the occurrence of additional secondary Sb···S or Sb···O bonds, which are therefore not observed. There is also little significant variation in the internal geometry of the ligands (Table 2). The bond lengths and angles in the dmp counter-cation of (IV) are entirely as expected and are not discussed further.

Perhaps suprisingly, there is no evidence of disorder between the site of the N atom and that of the C atom *para* to it. The H atoms of the terminal methyl groups, however, could only be modelled in an ideally disordered manner (see the refinement details section below).

Of the polymorphs of (III) (A & F) mentioned briefly above, one, (IIIa), is orthorhombic with space group *Pbca*, while the other, (IIIb), is monoclinic with space group *P2₁/c*. The most obvious structural difference between the polymorphs (IIIa) and (IIIb), aside from the differing crystal systems and space groups, is the overall shape of the anions. The anions in (IIIa) and (IV) can be perceived as short and squat, as against the comparatively tall and narrow configuration observed in (IIIb) and indeed in all the other compounds in the list above. The difference is entirely due to the orientation of the dmio ligands relative to the remainder of the anion. The effect is clearly, if crudely, demonstrated by the values of the O1—Sb1—O2 angles (Table 1). In all three cases, the Sb atom is displaced by about 1.5 Å from the plane defined by the C=C bond and the four S atoms associated with it in a manner which, as already noted by A & F, can be envisaged as a tilt of the ligand brought about by rotation of

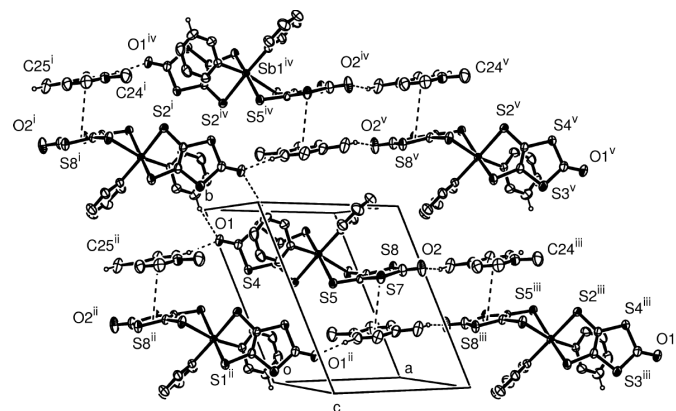


Figure 2

Part of a layer in the structure of (IV). The intra-layer C—H···O and π - π interactions mentioned in the text are shown by dashed lines. Only those H atoms involved in the former are shown, and for the latter the line joins the centroids of the rings concerned. Selected atoms are labelled. The representation is otherwise the same as Fig. 1. [Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $2-x, 1-y, 2-z$; (iv) $x, y+1, z$; (v) $2-x, 2-y, 2-z$.]

the entire ligand about the line joining the thiol S atoms bonded to Sb. For (IIIa) and (IV), the rotation is towards the aryl groups, and for (IIIb) away from them.

The consequences of this, discernible in the data given in Table 1, are apparent in the values for the dihedral angles between the ligand planes, designated 'Twist', which are much smaller for (IIIb), and, to a lesser extent, in the somewhat greater Sb1—S—C angles for (IIIb) as opposed to those for (IIIa) and (IV). The compound [dmp][Sb(dmit)₃] (Spencer *et al.*, 1996) provides a more elaborate example of this same effect because, within the tris-chelate complex, ligands in one pair are related in the tall and narrow manner and in another pair in the short and squat mode, while the third pair provides an intermediate case. The O—Sb—O angles in this example are 64.86 (5), 175.18 (4) and 110.38 (5)°, respectively, with corresponding dihedral angles of 5.93 (6), 56.97 (6) and 62.08 (6)°.

In (II), in both polymorphs of (III) and in (IV), the constituent ions are found packed together in admixture in comparatively well defined layers. In (IIIa), the layers, although somewhat corrugated, are parallel to (010). In (IIIb) and, as noted by A & F, in isostructural (II), as refined by them in the space group *P2₁/c*, the layers are parallel to (100). For the original, rather problematic, refinement of (II) by H employing a different unit cell with space group *P2₁/n*, the layers are parallel to (101). In (IV), the layers (Fig. 2) are parallel to (10 $\bar{2}$).

Within these layers, each dmp cation (ring 1 with centroid Cg1) is found face-to-face with a five-membered ring of one of the dmio ligands (S7, C4, C5, S8 and C6—ring 2 with centroid Cg2). For this contact, clearly a π - π interaction, the distance between the ring centroids (vector **A**), the perpendicular

distance from Cg1 to ring 2 (vector **B**) and the perpendicular distance from Cg2 to ring 1 (vector **C**) are, respectively, 3.684, 3.561 and 3.505 Å. The dihedral angle between the least-squares planes of the rings, and the angles between vectors **A** and **B** at Cg1, and between vectors **A** and **C** at Cg2, are 4.23, 17.90 and 14.83°, respectively.

Also present within the layers are weak C—H···O hydrogen bonds, two of which involve aryl H atoms with atom O1 as acceptor and the third, of a rather dubious nature, involving a methyl H atom of dmp and atom O2 as acceptor (Table 3). There is very little interaction between the layers in (IV) but it is here that the only remotely significant interanion S···S interaction occurs [S1···S1^{vi} = 3.6013 (13) Å; symmetry code: (vi) 1 - x, 2 - y, 1 - z], along with a weak, and again rather dubious, C—H···S6 hydrogen bond (Table 3), in which the other methyl group of the dmp cation is the donor species.

In the case of (IV), a major contributor to the dubiety associated with the C—H···X (X = O2 or S6) contacts noted above is the fact that the methyl groups could only be refined in an ideally disordered manner. Based upon the solid state NMR studies of Riddell & Rogerson (1996, 1997), there is currently a body of opinion (Baddeley *et al.*, 2003) that not all C—H···X contacts involving methyl H atoms are above suspicion. However, examples of apparently structurally significant C—H···O contacts, involving in this case methyl H and nitro group O atoms, are found in the work of Tafeenko *et al.* (2003).

It is noted here that the S···S contact of 3.638 (6) Å described by H in their refinement of (I) is between ligands which, although related by symmetry, are attached to the same Sb atom, and it is therefore an intramolecular contact. The packing of the ions in (I) is, in any case, completely different. In this case it is most readily perceived as taking the form of distinct columns parallel to *b*, with cations in one set of columns and anions in the other.

Experimental

Compound (IV) was obtained as the product of the reaction of Ph₂SbCl₃·2H₂O (0.40 g, 1.0 mmol) and KSCN (0.30 g, 3.10 mmol) in acetone (30 ml), to which was added a solution of [dmp]₂[Zn(dmio)₂] (0.64 g, 1.0 mmol) in acetone (30 ml). After stirring for 15 min at room temperature (295 K), the reaction mixture was filtered and the filtrate reduced in volume to 10 ml. On standing with cooling (273 K), dark crystals of (IV) were obtained. These were recrystallized from acetone (m.p. 434–435 K). Analysis, found: C 40.7, H 2.4, N 2.1%; calculated for C₂₅H₂₀N₂O₂S₈Sb: C 40.8, H 2.5, N 1.9%. Spectroscopic analysis: ¹H NMR (DMSO-*d*₆, 250 MHz, p.p.m.): 2.52 (*s*, 3H, Me—C), 4.31 (*s*, 3H, Me—N), 7.4–7.6 (*m*, 10H, Ph), 7.92 (*d*, 2H, pyridinium H), 8.78 (*d*, 2H, pyridinium H); ¹³C NMR (DMSO-*d*₆, 63 MHz, p.p.m.): 21.3 (Me—C), 40.6 (Me—N), 122.8 (C=C), 128.1, 132.0, 144.5 (all phenyl C), 132.2 (pyridinium C), 151.7 (C_{ipso}—phenyl), 158.3 (pyridinium C), 191.2 (C=O); IR (KBr, *v*, cm⁻¹): 3062, 3048, 1661, 1610, 1517, 1475, 1430, 1295, 1184, 1060, 901, 824, 731, 691; IR (CsI, *v*, cm⁻¹): 489, 468, 451, 380, 372, 330, 279 (*sh*), 268, 249, 225, 210, 191, 161.

Crystal data

(C₇H₁₀N)[Sb(C₆H₅)₂(C₃OS₄)₂]
M_r = 744.65
 Triclinic, *P* $\bar{1}$
a = 10.7513 (5) Å
b = 12.0130 (6) Å
c = 13.5273 (6) Å
 α = 94.063 (1)°
 β = 112.126 (1)°
 γ = 108.137 (1)°
V = 1502.53 (12) Å³

Z = 2
D_x = 1.646 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 4647 reflections
 θ = 2.2–30.8°
 μ = 1.50 mm⁻¹
T = 291 (2) K
 Plate, dark red
 0.39 × 0.21 × 0.04 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.845, *T_{max}* = 0.928
 15 605 measured reflections

10 417 independent reflections
 6570 reflections with *I* > 2σ(*I*)
R_{int} = 0.021
 θ_{max} = 32.5°
h = -10 → 16
k = -18 → 17
l = -20 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.038
wR(*F*²) = 0.072
S = 0.88
 10 417 reflections
 334 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0267P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 $\Delta\rho_{max} = 0.69 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.32 \text{ e } \text{Å}^{-3}$

Table 1

Coordination of Sb (Å, °) in (IV), (IIIa) and (IIIb).

Bond and angle designations wholly consistent with Fig. 1 are extended to bonds and angles of corresponding type in columns 2 and 3. Twist is the dihedral angle between the ligand planes defined, as noted in the text, by the C=C bond and the four S atoms associated with it.

	(IV)	(IIIa)	(IIIb)
Sb1—S1	2.5376 (6)	2.5569 (11)	2.5404 (14)
Sb1—S2	2.5929 (7)	2.6083 (11)	2.6277 (15)
Sb1—S5	2.5561 (6)	2.5291 (10)	2.5339 (14)
Sb1—S6	2.6081 (7)	2.5771 (11)	2.6404 (14)
Sb1—C7	2.163 (3)	2.153 (3)	2.158 (5)
Sb1—C13	2.165 (2)	2.165 (3)	2.170 (5)
S1—Sb1—S2	80.03 (2)	79.25 (4)	80.11 (5)
S1—Sb1—S5	169.05 (3)	171.39 (4)	166.88 (5)
S1—Sb1—S6	91.48 (2)	92.36 (4)	89.69 (5)
S1—Sb1—C7	92.69 (7)	92.46 (10)	92.46 (13)
S1—Sb1—C13	94.08 (7)	91.55 (9)	96.83 (14)
S2—Sb1—S5	92.89 (2)	94.70 (3)	90.69 (5)
S2—Sb1—S6	81.83 (2)	80.71 (3)	86.30 (5)
S2—Sb1—C7	169.47 (7)	169.00 (11)	171.97 (14)
S2—Sb1—C13	89.91 (7)	89.52 (9)	89.74 (14)
S5—Sb1—S6	79.17 (2)	80.55 (4)	80.33 (5)
S5—Sb1—C7	93.13 (7)	92.72 (10)	96.14 (13)
S5—Sb1—C13	94.26 (7)	94.54 (9)	92.42 (14)
S6—Sb1—C7	90.82 (7)	92.52 (10)	90.67 (14)
S6—Sb1—C13	169.12 (7)	168.61 (9)	171.68 (14)
C7—Sb1—C13	98.25 (9)	98.00 (12)	94.18 (19)
Sb1—S1—C1	93.54 (8)	93.44 (13)	96.30 (19)
Sb1—S2—C2	92.58 (9)	92.89 (13)	94.54 (19)
Sb1—S5—C4	93.28 (8)	93.04 (12)	97.52 (18)
Sb1—S6—C5	92.66 (9)	92.46 (12)	95.18 (19)
O1—Sb1—O2	177.93 (3)	179.24 (4)	66.29 (6)
Twist	67.67 (3)	71.51 (5)	10.43 (8)

Table 2

Bond lengths and angles (\AA , $^\circ$) for the dmio ligands in (IV), (IIIa) and (IIIb).

Bond and angle designations wholly consistent with the ligand shown in Fig. 1 are extended to bonds and angles of corresponding types in the remaining columns. Subscript oop denotes quantities which are the out-of-plane displacements (planes as defined in Table 1 and the text) of the atoms with which it is associated.

(a) Bond lengths

	(IV)		(IIIa)		(IIIb)	
	Lig 1	Lig 2	Lig 1	Lig 2	Lig 1	Lig 2
S1—C1	1.744 (2)	1.746 (2)	1.742 (4)	1.747 (4)	1.737 (6)	1.733 (5)
S2—C2	1.731 (2)	1.729 (2)	1.732 (4)	1.732 (4)	1.712 (6)	1.726 (6)
C1—C2	1.355 (3)	1.359 (3)	1.347 (5)	1.352 (5)	1.366 (8)	1.349 (7)
C1—S3	1.753 (3)	1.748 (2)	1.745 (4)	1.749 (4)	1.744 (6)	1.743 (5)
C2—S4	1.749 (2)	1.746 (2)	1.751 (4)	1.742 (4)	1.748 (6)	1.756 (6)
S3—C3	1.764 (3)	1.768 (3)	1.767 (5)	1.771 (4)	1.765 (7)	1.768 (7)
S4—C3	1.756 (3)	1.766 (3)	1.762 (5)	1.760 (5)	1.768 (7)	1.757 (7)
C3—O1	1.212 (3)	1.209 (3)	1.210 (4)	1.210 (4)	1.213 (7)	1.212 (7)
C3 _{oop}	0.054 (3)	0.045 (4)	−0.136 (4)	0.055 (4)	0.092 (7)	−0.101 (7)
O1 _{oop}	0.092 (3)	0.034 (3)	−0.247 (4)	0.084 (3)	0.169 (5)	−0.195 (5)
Sb1 _{oop}	1.5944 (9)	1.6447 (10)	−1.6484 (2)	1.5893 (2)	1.4819 (3)	−1.4056 (3)

(b) Bond angles

	(IV)		(IIIa)		(IIIb)	
	Lig 1	Lig 2	Lig 1	Lig 2	Lig 1	Lig 2
C2—C1—S1	124.24 (19)	123.83 (19)	124.0 (3)	124.3 (3)	124.4 (4)	125.1 (4)
C2—C1—S3	116.66 (19)	116.64 (19)	117.0 (3)	116.8 (3)	117.5 (4)	117.4 (4)
S1—C1—S3	118.76 (15)	119.20 (14)	118.5 (2)	118.4 (2)	117.7 (3)	117.1 (3)
C1—C2—S2	123.81 (19)	123.74 (19)	124.2 (3)	123.9 (3)	124.9 (4)	125.1 (4)
C1—C2—S4	116.72(19)	116.78(19)	116.8(3)	117.0(3)	115.6(4)	116.1(4)
S2—C2—S4	119.20(14)	119.12(14)	118.4(2)	118.9(2)	119.1(3)	118.4(3)
C1—S3—C3	96.89(13)	97.27(13)	96.86(19)	96.71(19)	97.1(3)	97.1(3)
C2—S4—C3	97.18(12)	97.33(13)	96.88(19)	97.15(19)	97.7(3)	97.5(3)
O1—C3—S3	123.4(2)	124.3(2)	124.1(4)	123.5(4)	124.3(6)	123.2(6)
O1—C3—S4	124.1(2)	123.7(2)	123.6(4)	124.2(3)	123.7(6)	124.8(6)
S4—C3—S3	112.54(16)	111.93(16)	112.3(2)	112.3(2)	112.0(3)	112.0(3)

Table 3

Bond lengths and angles (\AA , $^\circ$) for the dmio ligands in (IV), (IIIa) and (IIIb).

	C—H	H...A	C...A	C—H...A
C17—H17...O1 ⁱ	0.93	2.46	3.336 (4)	158
C23—H23...O1 ⁱⁱ	0.93	2.28	3.204 (4)	172
C25—H25A...O2 ⁱⁱⁱ	0.96	2.54	3.457 (4)	159
C24—H24D...S6 ^{vii}	0.96	2.87	3.790 (4)	162

Symmetry codes: (i), (ii) and (iii) as given in the caption of Fig. 2; (vii) $1-x, 1-y, 1-z$.

In the final stages of refinement, H atoms were introduced in calculated positions, with C—H distances of 0.93 and 0.96 \AA for aryl and methyl H, respectively, and refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (aryl H) or $1.5U_{\text{eq}}(\text{C})$ (methyl H). Methyl H atoms were ideally disordered over two sets of three H atoms rotated by 60° . All disordered H atoms were of equal occupancy.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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