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[Bis(1,3-dithiole-2-thione-4,5-dithiolato)diarylantimonate(1-)], $[Ar_2Sb(dmit)_2]^-$, complexes. Crystal structures of $[NEt_4][Ar_2Sb(dmit)_2]$ (Ar = Ph or *p*-tolyl)

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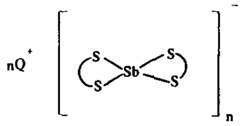
Abstract—The ionic complexes $[Q][Ph_2Sb(dmit)_2]$ (**4**; Q = NEt_4 or 1,4-Me_2-pyridinium) and $[Net_4][(p\text{-tolyl})_2Sb(dmit)_2]$ (**5**) have been prepared from $[Q]_2[Zn(dmit)_2]$ and Ar_2SbCl_3 in the presence of KSCN (H_2-dmit = 4,5-dimercapto-1,3-dithiole-2-thione). As shown by X-ray crystallography for **4** (Q = NEt_4) and **5**, these complexes contain distorted octahedral anions with *cis*-aryl groups: the C—Sb—C angles in **4** (Q = NEt_4) and **5** are 93.1(2) and 95.3(5)°, respectively. The dmit chelates are unsymmetrically bonded to antimony in both **4** (Q = NEt_4) and **5** with the longer bonds *trans* to the aryl groups (for both compounds, the Sb—S bond lengths are in the ranges, 2.614 to 2.636 and 2.530–2.550 Å). © 1997 Elsevier Science Ltd

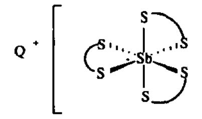
Keywords: crystallography; organoantimony; dmit.

Complexes of the 1,3-dithiole-2-thione-4,5-dithiolato (**1**, dmit) ligand with various metals have been studied and, in many cases, crystal structures have been determined [1]. For antimony, the crystal structures of the inorganic complexes $[Q][Sb^{III}(dmit)_2]$ [**2**, Q = NEt_4 or 1,4-Me_2-pyridinium)] [2] and [3] [1,4-Me_2-pyridinium]$[Sb^V(dmit)_3]$ (**3**) have recently been reported. In both types of complexes **2** and **3**, interanionic contacts involving sulfur atoms at separations less than the sum of the appropriate van der Waals radii were clearly evident (van der Waals radii of Sb and S are taken to be 2.2 and 1.85 Å). In solid **3**, interanionic S---S contacts were found to be between 3.450(2) and 3.583(2) Å. For **2**, in addition to similar S---S contacts, there were also stronger Sb—S interanionic contacts at *ca* 3.3 Å. Both sets of secondary interanionic interactions in **2** were found to vary with the cation [Q]; most significantly, the different number of Sb—S interanionic contacts in the two complexes with [Q] = 1,4-Me_2-pyridinium and NEt_4 resulted in different coordination numbers for antimony. We have now studied some organoantimony(V)-dmit derivatives, namely $[Q][Ar_2Sb(dmit)_2]$ (**4**: Q = NEt_4 or 1,4-Me_2-pyridinium; Ar = Ph) and **5** (Q = NEt_4; Ar = *p*-tolyl), and have determined the crystal structures of **4** (Q = NEt_4) and (**5**). We now report our findings.

(1)



(2)



(3)

EXPERIMENTAL

NMR spectra were obtained on a Bruker 250 MHz instrument; IR spectra were recorded on Philips Ana-

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lytical PU9800 and Nicolet 205 Fourier-transform spectrometers. X-ray data were collected on a Nicolet P3 instrument. The salts $[NEt_4]_2[Zn(dmit)_2]$ (m.pt 186–188°C) and $[1,4\text{-}Me_2\text{-pyridinium}]_2[Zn(dmit)_2]$ (m.pt 231–233°C) were produced from carbon disulfide, sodium, zinc sulfate and either $[NEt_4]Br$ or $[1,4\text{-}Me_2\text{-pyridinium}]I$, using a general method [4].

Preparation of $Ph_2SbCl_3 \cdot H_2O$

Tetraphenyltin (42.8 g, 0.1 mol) was heated to reflux in CCl_4 (300 cm^3). A solution of antimony pentachloride (30 g, 0.1 mol) in CCl_4 (30 cm^3) was added dropwise; reflux was continued for 2 h after addition was complete. On cooling, the white precipitate was filtered off and the filtrate concentrated to 30 cm^3 to yield further solid. The combined solids were recrystallised from 5 M HCl (600 cm^3) to yield a white crystalline solid, m.pt 173–174°C [lit. [5] m.pt 175°C].

Preparation of (p-*tolyl*)$_2$SbCl$_3$

The compound was similarly prepared from (*p*-tolyl)$_4$Sn and antimony pentachloride. The compound, (*p*-tolyl)$_2$SbCl$_3$ was obtained as a non-hydrated material. Found. C, 40.8; H, 3.3. $C_{14}H_{14}Cl_3Sb$ required: C, 41.0; H, 3.4%.

Preparation of $[NEt_4]Ph_2Sb(dmit)_2]$ (4: Q = NEt_4)

The compound $Ph_2SbCl_3 \cdot H_2O$ (0.40 g, 1 mmol) and KSCN (0.3 g, 3.1 mmol) were mixed in acetone (30 cm) in the ultrasonic bath for 10 min. The solution was added to a solution of $[NEt_4]_2[Zn(dmit)_2]$ (0.719 g, 1 mmol) in acetone (50 cm^3) and stirred for 10 min to give a brown solution. This was filtered and the filtrate was concentrated and cooled to give a black crystalline solid, which was recrystallized twice from acetone, m.pt 174–175°C; yield 0.568 g, 71%. Found: C, 38.6; H, 3.6; N, 1.75. $C_{26}H_{30}NS_{10}Sb$ requires: C, 39.1; H, 3.8; N, 1.75%. IR (KBr, cm^{-1}): 3042, 2975–2963, 1508, 1502, 1476, 1429, 1391, 1169, 1057, 1034, 995, 731, 692. ^1H NMR (Me_2CO-d_6, 250 MHz) δ: 1.39 [t,t, 12H, J(H—H) = 7.3 Hz, Me], 3.49 [q, 8H, J(H—H) = 7.3 Hz, CH_2N], 7.36 (m, 6H, *m*- + *p*-phenyl-H), 7.74 (m, 4H, *o*-phenyl-H).

Preparation of [1,4-Me$_2$-*pyridinium*][Ph$_2$Sb(dmit)$_2$] (4: Q = 1,4-Me$_2$-*pyridinium*)

This was prepared by the same method as used for the tetraethylammonium salt from $Ph_2SbCl_3 \cdot H_2O$ (0.400 g, 1 mmol), KSCN (0.3 g, 3.1 mmol) and $[1,4\text{-}Me_2\text{-pyridinium}]_2[Zn(dmit)_2]$ (0.647 g, 1 mmol). Dark brown crystals were obtained, m.pt 152–154°C. Found: C, 38.5; H, 2.4; N, 1.5. $C_{25}H_{20}NS_{10}Sb$ requires: C, 38.7; H, 2.6; N, 1.8%. IR (KBr, cm^{-1}): 3040–3005, 1570, 1473, 1468, 1429, 1059, 1030, 1015, 995, 907, 889, 812, 739, 733, 691. ^1H NMR (Me_2CO-d_6, 250 MHz) δ: 2.74 (s, 3H, Me), 4.57 (s, 3H, Me—N), 7.35 (m, 6H, *m*- + *p*-phenyl-H), 7.76 (m, 4H, *o*-phenyl-H), 8.09 [d, 2H, J(H—H) = 6.2 Hz, cation], 8.95 [d, 2H, J(H—H) = 6.6 Hz, cation].

Preparation of [NEt$_4$][(p-*tolyl*)$_2$Sb(dmit)$_2$] (5)

This was prepared by the same method as used for $[NEt_4][Ph_2Sb(dmit)_2]$, from (*p*-tolyl)$_2$SbCl$_3$ (0.205 g, 0.5 mmol), KSCN (0.15 g, 1.55 mmol) and $[NEt_4]_2[Zn(dmit)_2]$ (0.360 g, 0.5 mmol). Black crystals were obtained, m.pt 159–160°C. Found: C, 40.8; H, 3.9; N, 1.6. $C_{28}H_{3}4NS_{10}Sb$ requires: C, 40.7; H, 4.1; N, 1.7%. IR (KBr, cm^{-1}): 3045, 2994–2855, 1489, 1480, 1445, 1435, 1412, 1387. ^1H NMR (Me_2SO-d_6, 250 MHz) δ: 1.40 [t,t, 12H, J(H—H) = 7.2 Hz, Me of cation], 2.33 (s, 6H, Me of tolyl group), 3.50 [q, 8H, J(H—H) = 7.2 Hz, CH_2N], 7.16 [d, 4H, J(H—H) = 7.6 Hz, *m*-aryl-H], 7.76 [d, 4H, J(H—H) = 8.0 Hz, *o*-aryl-H]. ^{13}C NMR (Me_2CO-d_6, 62.9 MHz) δ: 7.55 (Me of cation), 21.2 (Me of tolyl group), 129.3, 133.4, 135.2, 139.8, 141.9, 150.0, 211.7 (C═S).

Crystal structure determinations

General. Nicolet P3 software [6] was used for data collection and cell refinement: data collection used 2θ scan rates of 5.33 ($Ip < 150$) to 58.6 ($Ip > 2500$)° min^{-1}, where Ip was the prescan intensity. Scan widths were 2.4 to 2.7° 2θ. Cell dimensions were determined using 14 reflections at 8.3–9.5° in θ. Data reduction utilized the program [7] RDNIC. Refinements were by full-matrix least-squares. All computations were performed on the SUN SPARCserver (Unix operating system) of the Computing Centre of the University of Aberdeen. Structure solution [8] and refinement [9] software: SHELXS86 and SHELX76. Molecular diagrams were obtained by the programs PLOTAID [10] and ORTEX [11]. XPUB software was used to prepare data for publication [12].

$[NEt_4][Ph_2Sb(dmit)_2]$. The crystal used in the structure determination was grown from Me_2CO solution. The Sb and S atoms, as well as C(1), C(3), C(4) and C(6), were refined anisotropically. All other atoms were refined with isotropic thermal vibration parameters. Phenyl groups were refined as rigid bodies with C—C and C—H fixed at 1.395 and 0.95 Å, respectively, and a common group U_{iso} for phenyl H atoms. Methylene and methyl H atoms were placed in calculated positions with C—H = 0.95 Å and refined riding on the C to which they were attached with separate common group U_{iso}s. The methyl groups were also refined as rigid bodies. The disorder of the dmit ligands of the anions arising from the superposition of pairs of stereoisomers was modelled on the basis of pairs of atoms as S(3)/S(3A), S(4)/S(4A), S(8)/S(8A), S(9)/S(9A), C(2)/C(2A) and C(5)/C(5A) with site occupancy factors which refined to 0.516(4) for the series S(3), S(4), etc., and 0.484(4) for the series S(3A), etc. The remaining dmit atoms, S(1), S(2), S(5), S(6), S(7), S(10), C(1), C(3), C(4) and C(6), were treated as being common to both stereoisomers. As a result the detailed geometry of the ligands is only approximate. Crystal data and structure refinement data are listed in Table 1.

$[NEt_4][(p\text{-tolyl})_2Sb(dmit)_2]$. The crystal used in the structure determination was grown from Me_2CO solution. Both ions in this structure lie on two-fold crystallographic axes. The asymmetric unit consisted of N and two ethyl groups for the cation and Sb, one dmit unit and one tolyl group for the anion. All non-H atoms were refined anisotropically. H atoms were placed in calculated positions with C—H = 0.95 Å and refined riding upon the C atoms to which they were attached with separate group U_{iso}s for phenyl H, methylene H and methyl H atoms. Methyl groups were treated as rigid bodies. Crystal data and structure refinement data are listed in Table 1.

RESULTS AND DISCUSSION

The black complexes $[Q][Ar_2Sb(dmit)_2]$ were obtained from the reactions of $[Q]_2[Zn(dmit)_2]$ with premixed solutions of Ar_2SbCl_3 and KSCN in acetone [eq. (1)].

$$KSCN + Ar_2SbCl_3 + [Q]_2[Zn(dmit)_2] \rightarrow [Q][Ar_2Sb(dmit)_2] \quad (1)$$

(**4**: Q = NEt_4 or 1,4-Me_2-pyridinium; Ar = Ph)

(**5**: Q = NEt_4; Ar = *p*-tolyl)

Reactions in the absence of the KSCN resulted in the formation of mixtures of products, which proved difficult to separate. The NMR and IR spectra of the

Table 1. Crystal data and structure refinement

	4 (Q = NEt_4)	**5**
Formula	$C_{26}H_{30}NS_{10}Sb$	$C_{28}H_{34}NS_{10}Sb$
Formula weight	798.92	826.98
Temperature (K)	298	298
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2/n$
Unit-cell dimensions		
a (Å)	16.839(14)	13.135(15)
b (Å)	11.733(15)	9.228(12)
c (Å)	17.152(15)	14.412(15)
β (°)	95.75(7)	91.76(9)
Volume ($Å^3$)	3372(6)	1746(3)
Z	4	2
D_x ($Mg\ m^{-3}$)	1.573	1.573
Absorption coefficient (mm^{-1})	1.44	1.39
F(000)	1616	840
Crystal size (mm)	0.6 × 0.36 × 0.3	0.3 × 0.3 × 0.2
Colour	Black	Black
Theta range for data collection (°)	25 (max)	25 (max)
Index range		
h	$-20 \leqslant h \leqslant 20$	$-15 \leqslant h \leqslant 15$
k	$0 \leqslant k \leqslant 13$	$0 \leqslant k \leqslant 10$
l	$0 \leqslant l \leqslant 20$	$0 \leqslant l \leqslant 17$
Reflections collected	6500	3433
Independent reflections	5963 [R_{int} = 0.026]	3087 [R_{int} = 0.034]
Observed reflections	4236 [$F > 4\sigma(F)$]	1946 [$F > 4\sigma(F)$]
Refinement method	Full-matrix least-squares on *F*	Full-matrix least-squares on *F*
Number of parameters	264	194
Final *R* indices [$F > 4\sigma(F)$]	*R* = 0.068	*R* = 0.073
R indices (all data)	*wR* = 0.068	*wR* = 0.065
Final weighting scheme	[a]	[b]
Residual diffraction (e $Å^{-3}$) max. (min.)	1.4(−0.72)	2.22[c](−1.43)

[a] $w = 1/[\sigma^2(F) + 0.000418F^2]$.

[b] $w = 1/[\sigma^2(F) + 0.000514F^2]$.

[c] *ca* 1 Å from Sb.

dmit groups in these complexes were similar to those observed for the dmit ligands in the inorganic Sb-dmit complexes **2** and **3**.

Solid state structures

The compounds **4** (Q = NEt$_4$) and **5** are the first organoantimony-dmit derivatives to be structurally analysed in the solid state. Both are ionic compounds. Selected bond lengths and angles are displayed in Tables 2 and 3; the atom arrangements for **4** (Q = NEt$_4$) and **5** are illustrated in Figs 1 and 2, respectively.

As well as the arrangement for the anion of **5** shown in Fig. 2, there is also its mirror image generated by the operation of a crystallographic centre of symmetry (see Fig. 3). The dmit chelate arrangements in **4** (Q = NEt$_4$) are more complex as a consequence of the partial disorder which results in the occupation of two sets of atom positions: C(2), S(3), S(4), C(5), S(8) and S(9) [occupancy 0.516(4)] as well as C(2A), S(3A), S(4A), C(5A), S(8A) and S(9A) [occupancy 0.484(4)]. Positions which are not disordered are the Sb and remaining dmit atom positions, i.e. the four sulfur atoms, S(1), S(2), S(6) and S(7), bonded to antimony, and C(1), C(3), C(4), C(6), S(5) and S(10). This disorder is interpreted as indicating the presence of stereoisomers, A and B, see Fig. 1. The two stereoisomers differ only in the connectivity and orientation of the dmit ligands with respect to the diphenylantimony portion of the anions. In stereoisomer A, the dmit ligands are defined by the atoms of full occupancy common to both isomers, i.e. S(1), S(2), C(1), C(3) and S(5) (dmit 1) and S(6), S(7), C(4), C(6) and S(10) (dmit 2) and completed by "disordered" atoms in sites with occupancy factors of 0.516(4), i.e. C(2), S(3) and S(4) (dmit 1) and C(5), S(8) and S(9) (dmit 2). In stereoisomer B, the dmit ligands are defined by the atoms of full occupancy common to both isomers: S(1), S(7), C(1), C(3) and S(5) (dmit 1) and S(2), S(6), C(4), C(6) and S(10) (dmit 2) and completed by "disordered" atoms in sites with occupancy factors of 0.484(4), C(2A), S(3A), and S(4A) (dmit 1) and C(5A), S(8A) and S(9A) (dmit 2). These stereoisomers A and B are basically of opposite hand, but cannot be truly described as being enantiomers due to the differences in comparable bond angles and lengths within the dmit moieties. However, both the A and B stereoisomers are subject to the operation of a crystallographic centre of symmetry, which does generate the true enantiomers, A′ and B′, respectively (symmetry operation; $-x$, $-y$, $-z$). In broad terms, there are present in **4** (Q = NEt$_4$) one stereoisomer set made up of A and B′ species and another comprised of A′ and B, each set being present to the same extent, see Fig. 3.

The antimony atoms in the anions of both **4** (Q = NEt$_4$) and **5** have distorted octahedral geometries, with *cis* aryl groups. The angle between

Table 2. Selected bond lengths (Å) and angles (°) for **4** (Q = NEt$_4$)

Sb—S(1)	2.536(3)	Sb—S(2)	2.614(2)
Sb—S(6)	2.550(3)	Sb—S(7)	2.636(2)
Sb—C(12)	2.139(6)	Sb—C(18)	2.146(7)
C(1)—S(1)	1.711(13)	C(2)—S(2)	1.888(19)
C(5A)—S(2)	1.803(17)	C(1)—S(3)	1.663(14)
C(3)—S(3)	1.785(16)	C(1)—S(3A)	1.584(14)
C(3)—S(3A)	1.694(15)	C(2)—S(4)	1.719(19)
C(3)—S(4)	1.654(14)	C(2A)—S(4A)	1.727(19)
C(3)—S(4A)	1.849(12)	C(3)—S(5)	1.618(12)
C(4)—S(6)	1.691(11)	C(2A)—S(7)	1.739(12)
C(5)—S(7)	1.729(17)	C(4)—S(8)	1.616(13)
C(6)—S(8)	1.623(14)	C(4)—S(8A)	1.585(15)
C(6)—S(8A)	1.760(13)	C(5)—S(9)	1.773(18)
C(6)—S(9)	1.798(12)	C(5A)—S(9A)	1.781(17)
C(6)—S(9A)	1.830(11)	C(6)—S(10)	1.605(10)
C(2)—C(1)	1.57(2)	C(2A)—C(1)	1.63(2)
C(5)—C(4)	1.78(2)	C(5A)—C(4)	1.48(2)
S(2)—Sb—S(1)	84.7(1)	S(6)—Sb—S(1)	164.1(1)
S(6)—Sb—S(2)	83.0(1)	S(7)—Sb—S(1)	84.6(1)
S(7)—Sb—S(2)	86.6(1)	S(7)—Sb—S(6)	84.7(1)
C(12)—Sb—S(1)	95.0(2)	C(12)—Sb—S(2)	177.5(2)
C(12)—Sb—S(6)	96.9(2)	C(12)—Sb—S(7)	91.0(2)
C(18)—Sb—S(1)	96.9(2)	C(18)—Sb—S(2)	89.3(2)
C(18)—Sb—S(6)	92.9(2)	C(18)—Sb—S(7)	175.5(2)
C(18)—Sb—C(12)	93.1(2)		

Table 3. Selected bond lengths (Å) and angles (°) for **5**

Sb—S(1)	2.530(3)	Sb—S(2)	2.636(3)
Sb—C(4)	2.158(12)	C(1)—S(1)	1.717(12)
C(2)—S(2)	1.745(13)	C(1)—S(3)	1.769(11)
C(3)—S(3)	1.723(13)	C(2)—S(4)	1.734(12)
C(3)—S(4)	1.731(12)	C(3)—S(5)	1.640(13)
C(2)—C(1)	1.337(12)		
S(2)—Sb—S(1)	81.1(1)	C(4)—Sb—S(1)	96.7(3)
S(1^{i})—Sb—S(1)	166.9(1)	S(2^{i})—Sb—S(1)	89.4(1)
C(4^{i})—Sb—S(1)	92.1(3)	C(4)—Sb—S(2)	89.6(3)
S(2^{i})—Sb—S(2)	86.2(1)	C(4^{i})—Sb—S(2)	172.0(3)
C(4^{i})—Sb—C(4)	95.3(5)	C(1)—S(1)—Sb	97.1(4)
C(2)—S(2)—Sb	95.8(4)	C(3)—S(3)—C(1)	98.0(6)
C(3)—S(4)—C(2)	97.5(6)	S(3)—C(1)S(1)	117.7(8)
C(2)—C(1)—S(1)	127.9(9)	C(2)—C(1)—S(3)	114.3(9)
S(4)—C(2)—S(2)	118.5(8)	C(1)—C(2)—S(2)	123.5(9)
C(1)—C(2)—S(4)	117.6(10)	S(4)—C(3)—S(4)	112.3(7)
S(5)—C(3)—S(3)	124.1(7)	S(5)—C(3)—S(4)	123.5(8)
C(5)—C(4)—Sb	123.5(15)	C(9)—C(4)—Sb	118.3(9)

the phenyl groups in **4**, (Q = NEt_4) is 93.1(2)° [C(18)—Sb—C(12)] and that between the *p*-tolyl groups in **5** is 95.3(5)° [C(4)—Sb—C(4)^{i})]. A similar geometry was determined [13] for the anion of $[Ph_4Sb][Ph_2Sb(oxalate)_2]$ (**6**), although in **6** the C—Sb—C angle was greater [102.2(2)°]. The Sb—C bond lengths are 2.139(6) and 2.146(7) Å in **4** (Q = NEt_4) and 2.158(12) Å in **5** and are comparable to those in **6** [2.120(6) and 2.122(5) Å].

The dmit units are unsymmetrically coordinated in both complexes. The longest Sb—S bonds in both compounds are those *trans* to aryl groups, e.g. in **4** (Q = NEt_4) these bond lengths are 2.636(2) and 2.614(2) Å [S(7)—Sb and S(2)—Sb, respectively] with the *trans* bond angles S(7)—Sb—C(18) and S(2)—Sb—C(12) = 175.5(2) and 177.5(2)°, respectively. The remaining *trans* angle in **4** (Q = NEt_4), S(6)—Sb—S(1) [164.1(1)°], shows a considerably greater distortion from linearity; the remaining Sb—S bond lengths in **4** (Q = NEt_4) are 2.536(3) [S(1)—Sb] and 2.550(3) Å [S(6)—Sb].

The Sb—S bond lengths in **5** are 2.636(3) [Sb—S(2)] and 2.530(3) Å [Sb—S(1)], with the *trans* angles equal to 172.0(3) [S(2)—Sb—C(4^{i})] and 166.9(1)° [S(1)—Sb—S(1^{i})]. The Sb—S bond lengths in **3** are in the smaller range 2.504(1)–2.553(1) Å.

The bite angles of the dmit chelates in **5** are 81.1(1)°; the values in **4** (Q = NEt_4) are both 84.7(1)° in A/A′-type species and are 83.0(1) and 84.6(1) in B/B′-type species. The anions in **5** show S- - -S contacts close to twice the van der Waals radius of S (1.85 Å), e.g. S(1)- - -S(2^{ii}) = 3.638(6) and S(3)- - -S(5^{iii}) = 3.671(7) Å, are the shortest interanionic contacts. In **4** (Q = NEt_4), the stereoisomeric anions are related in pairs by the operation of crystallographic centres of symmetry of which those at 0, 0, 0 and 1/2, 1/2, 1/2 provide the shortest interanionic S- - -S contacts. S- - -S contact distances less than twice the van der Waals radius for S of 1.85 Å are observed for all three of the possible anion pairs, i.e. AA′, AB′ and BB′. The shortest S- - -S distances observed for the pairs AA′ and AB′, S(10)- - -S(4A′) at 3.354(7) and S(1)- - -S(4A′) at 3.405(6) Å, respectively, are acceptable given that similar S- - -S interactions have been determined for example in **2** and **3**. The shortest S- - -S distance observed in the case of the BB′ pair, however, is S(9A)- - -S(9A′) at 2.546(7) Å. This distance is impossibly short and therefore the BB′ anion pair cannot exist in the crystal. On this basis the occupancy factors for the "disordered" atoms given above can be taken into account. They suggest that the majority, approximately 97%, of the anion–anion pairs are of the AB′ and A′B types distributed at random over the anion pair sites at 0, 0, 0 and 1/2, 1/2, 1/2 and the remainder, about 3%, of the AA′ type distributed over the same sites.

The "disorder" which is observed in the space group $P2_1/n$ is of course entirely due to the incompatibility between acentric AB′ and A′B anion pairs and the centrosymmetric space group. It is tempting to consider the possibility of adopting a non-centric space group, of which the obvious choices are $P2_1$ and *Pn*. The space group $P2_1$ demands that all of the anions are of the same hand, which is extremely unlikely on thermodynamic grounds. Consider for example the completely ordered and racemic arrangement in the centrosymmetric structure of **5**. The space group *Pn* on the other hand can accommodate the AB′ and A′B anionic pairing, but will only yield an ordered structure if the AB′ and A′B pairs are rigorously ordered on the ion pair sites at 0, 0, 0 and 1/2, 1/2, 1/2, respectively. There are no obvious inter-ionic bonds or

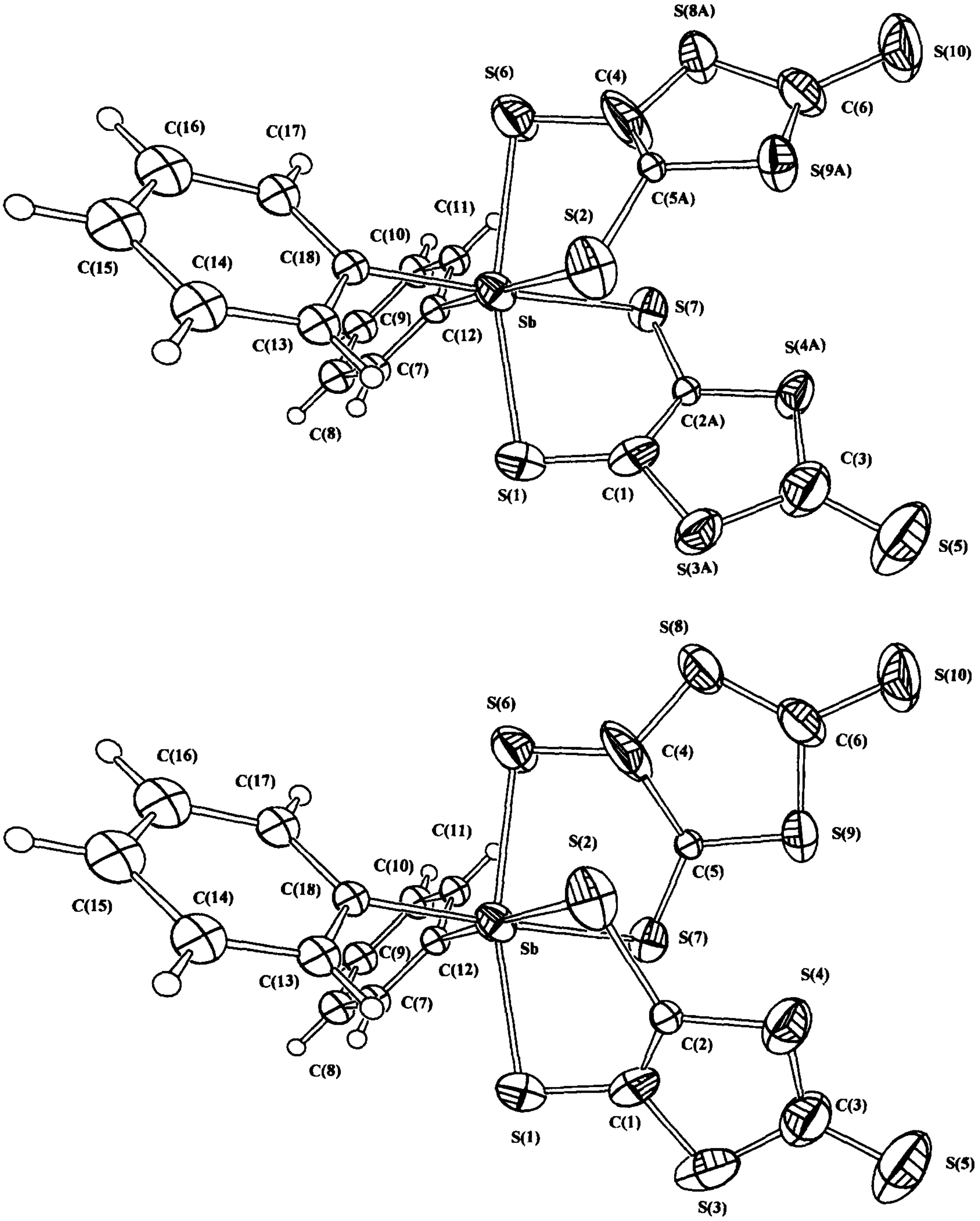

Fig. 1. Perspective views of the cation and anions of **4** (Q = NEt_4) showing the atom labels and 40% probability thermal vibration ellipsoids.

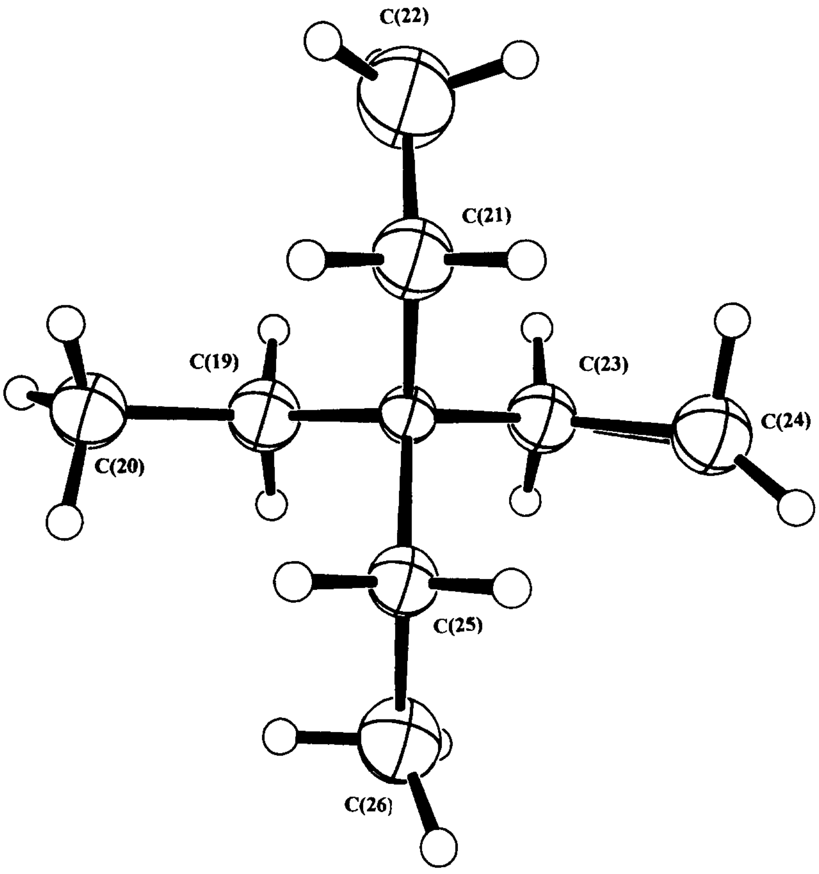

Fig. 1.—*Continued.*

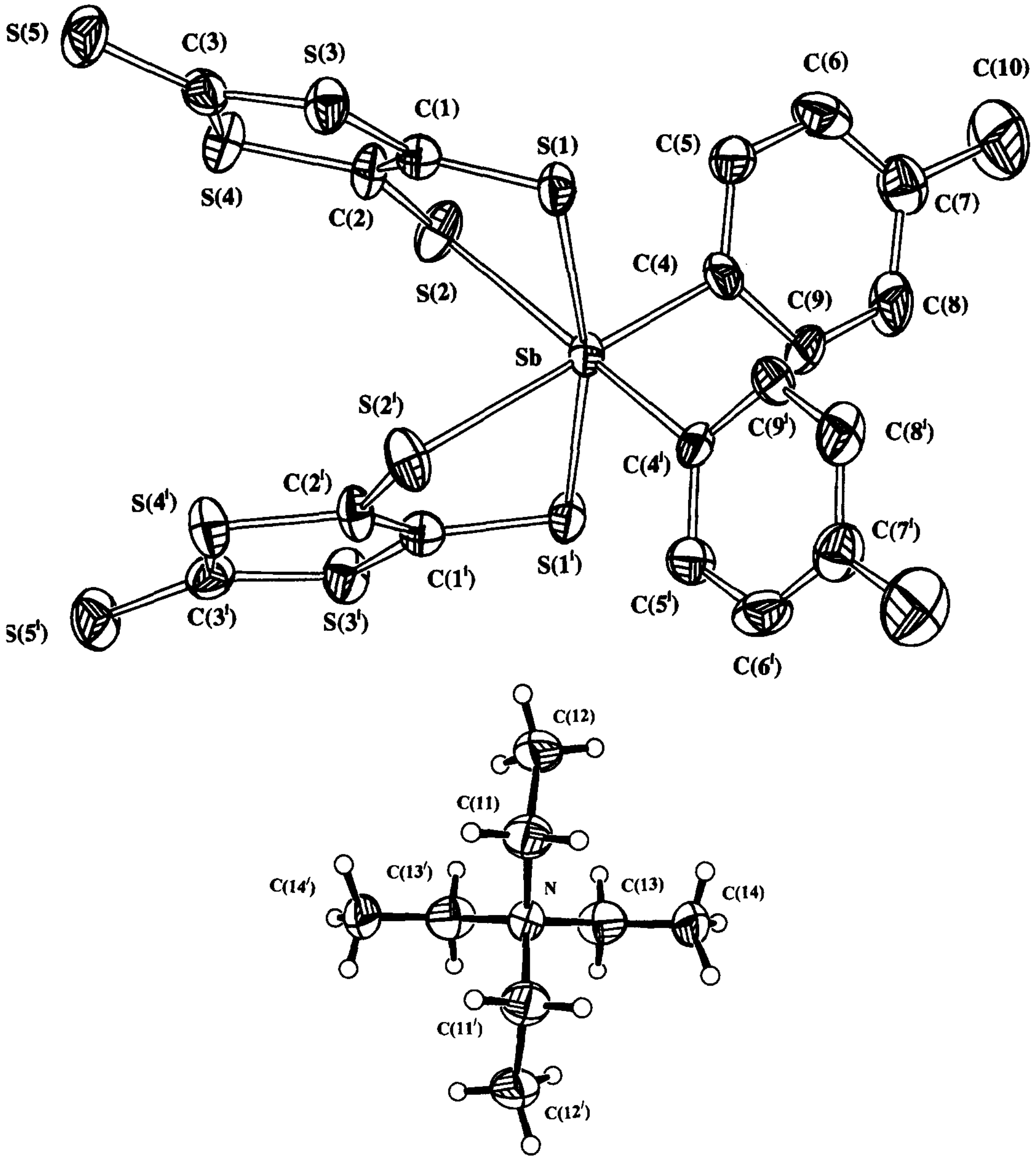

Fig. 2. Perspective views of the cation and anion of **5**, showing the atom labels and 40% probability thermal vibration ellipsoids.

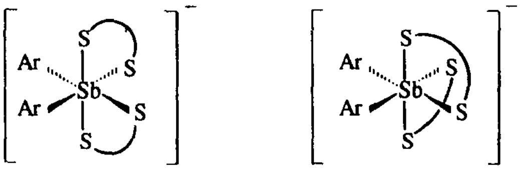

Fig. 3. Stereoisomeric anions of **4** and **5**.

contacts which are likely to bring this about. The AA′ anion pairs will in any case produce some small element of disorder in either of the non-centrosymmetric space groups. It is concluded that despite the evident disorder, the representation of the structure in the space group $P2_1/n$ is probably the best that can be achieved.

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