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Synthesis and properties of bis(1,3-dithiole-2-thione-4,5-dithiolato)bismuthate(1-) salts, [Q][Bi(dmit)₂]. Crystal structure of [AsPh₄][Bi(dmit)₂]·1/2DMSO: comparison of the solid state structures of [Q][Bi(dmit)₂] and [Q][Sb(dmit)₂]

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Abstract

Ionic complexes, $[Q][Bi(dmit)_2]$ (5:Q=NEt₄, NBu₄, 1,4-Me₂-pyridinium and AsPh₄), have been obtained from BiBr₃ and $[Q]_2[Zn(dmit)_2]$ [H₂-dmit=4,5-dimercapto-1,3-dithiole-2-thione]. As established by the crystal structure determination of [(5:Q=AsPh₄)·1/2DMSO], the cations have near tetrahedral geometries and are well separated from the anions. The anions, containing chelating dmit ligands, are linked into chains via Bi-thiolato-S inter-anion bonds: Bi₂S₂ rings are formed within the chains, with Bi···Bi distances alternating between 3.7760(3) and 3.9092(3) Å. The bismuth atoms are six-coordinate, arising from two inter-anion Bi–S [Bi–S = 3.0391(13) and 3.1643(14) Å] and four intra-anion Bi–S bonds [between 2.6680(13) and 2.8370(13) Å], with stereochemistries, including the equatorial-sited stereochemically active lone pair, of distorted pentagonal bipyramids. There are no S···S contacts between the anions less than the sum of the van der Waals radii. Comparisons are made between the structure of [(5:Q=AsPh₄)·1/2DMSO] and those reported previously for (5:Q=NEt₄), [(5:Q=NEt₄)·1/2Et₂O] and [(5:Q=NBu₄) as well as those for [Q][Sb(dmit)₂] (4). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bismuth; Dmit; 1,3-Dithiole-2-thione-4,5-dithiolates; Crystal structures

1. Introduction

Metal-dmit complexes have attracted considerable attention in the recent past. Much of the interest has centred on transition metal compounds due, in the large part, to the conducting and super-conducting properties [1-5] of such compounds as $[NMe_4]_{0.5}[M(dmit)_2]$ (M =

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Ni [6]; M = Pd [7]. With main group compounds, the dominant concern has been the anion structures and packing arrangements. In complexes, $[Q]_2[Zn(dmit)_2 (1) [8-10], [Q]_2[Sn(dmit)_3], (2), [11,12] and [Q][Sb(dmit)_3] (3), [13] (Q = onium cation), the metal atoms are solely bonded to the dithiolate sulfur atoms within the <math>[M(d-mit)_n]^{m-}$ anions, and thus have distorted tetrahedral [Zn] or octahedral geometries [Sn or Sb]. There are, however, sulfur–sulfur intra-anion contacts, at distances less then the sum of the van der Waals radii for two sulfur atoms [3.70 Å] [14] in 1 and 3. In general, the packing of the anions is strongly dependent on $[Q]^+$.

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In contrast to 1-3, metal-S inter-anion bonds occur in solid [Q][Sb(dmit)₂] (4:Q=NEt₄, 1,4-dimethylpyridinium or PPh₄): these Sb-S inter-anion bonds involve thione S atoms [15,16]. Both the anion packing and the coordination number of the metal are strongly dependent on the cation: in (4:Q=NEt₄) the anions are arranged in a polymeric two-dimensional network with six-coordinate Sb, in (4:Q=1,4-dimethylpyridinium) the anions are arranged in dimeric units with five-coordinate Sb [15], while in (4:Q=PPh₄) the anions are arranged in centrosymmetric pairs of chains with six-coordinate Sb [16]. Recently we reported that the structure of [NBu₄][Bi(dmit)₂] (5:Q=NBu₄) was analogous to that of (4:Q=PPh₄) [17]. Also recently,

Table 1 Selected IR spectral data for 1, 4 and 5

				D.C.
Compound	v _{C=C}	v _{C=S}	v _{C-S}	Ref.
(5 :Q=NEt ₄)	1434	1053, 1019	873	This study
$(5:Q=C_7H_{10}N)$	1428	1054, 1021	879	This study
(5:Q=NBu ₄)	1409	1029	886	This study
(5:Q=AsPh ₄)	1435	1054, 1033	890	This study
(1:Q=NEt ₄)	1416	1056	887	This study
$(1:Q=C_7H_{10}N)$	1415	1053	876	This study
(1:Q=NBu ₄)	1411	1058	886	This study
(1:Q=AsPh ₄)	1437, 1417	1056	889	This study
$(4:Q=NEt_4)$	1433	1047, 1026	880	[15]
$(4:Q=C_7H_{10}N)$	1431	1049, 1026	880	[15]

Table 2

Selected bond lengths (Å) and bond angles (°) for [(5:Q=AsPh_4)·1/ 2DMSO $^{\rm a}$

Bond lengths			
Bi-S(1)	2.6680(13)	Bi-S(7)	2.8370(13)
Bi-S(6)	2.6777(13)	Bi−S(2) # 1	3.0391(13)
Bi–S(2)	2.8143(13)	Bi-S(7) # 2	3.1643(14)
Bond angles			
S(1)-Bi-S(6)	88.83(4)	S(1)-Bi-S(7) ⁱⁱ	155.88(4)
S(1)-Bi-S(7)	82.87(4)	S(6)-Bi-S(7) ⁱⁱ	69.90(4)
S(6)-Bi-S(7)	76.45(4)	S(2)-Bi-S(7) ⁱⁱ	89.65(3)
S(1)-Bi-S(2)	77.25(4)	S(7)-Bi-S(7) ⁱⁱ	102.23(3)
S(6)-Bi-S(2)	86.04(4)	S(2) ⁱ -Bi-(7) ⁱⁱ	127.83(3)
S(2)-Bi-S(7)	153.71(4)	C(1)-S(1)-Bi	99.34(17)
$S(1)-Bi-S(2)^i$	74.37(4)	C(2)-S(2)-Bi	96.73(18)
S(6)-Bi-S(2) ⁱ	162.00(4)	C(4)-S(6)-Bi	97.43(17)
S(2)-Bi-S(2) ⁱ	96.29(3)	C(5)-S(7)-Bi	95.08(18)
S(7)-Bi-S(2) ⁱ	94.71(4)	Bi-S(2)-Bi ⁱ	83.71(3)
C(5)–S(7)–Bi ⁱⁱ	98.49(18)	C(2)-S(2)-Bi ⁱ	100.04(17)
Bi–S(7)–Bi ⁱⁱ	77.77(3)		

^a Symmetry operations i: -x+1, -y, -z+1; ii: -x, -y, -z+1.



Fig. 1. Atom numbering scheme and arrangement of anions in $[(5:Q=AsPh_4)\cdot 1/2DMSO]$. Probability ellipsoids are drawn at 50%: symmetry operations i: -x + 1, -y, -z + 1; ii: -x, -y, -z + 1.

Sheng et al. [18] published the structures of $[NEt_4][Bi(dmit)_2]$ (5:Q=NEt₄) and $[NEt_4][Bi(dmit)_2]\cdot 1/2Et_2O$ [(5:Q=NEt₄)·1/2Et₂O], both of which contain six-coordinate Bi. While there are structural differences between (5:Q=NEt₄) and [(5:Q=NEt₄)·1/2Et₂O], both contain Bi-thiolato-S inter-anion bonds and thus are markedly different from the other Group 15 compounds. As all four compounds **5**, so far studied, have exhibited structural differences, we have carried out the structural analysis of a further compound, namely (5:Q=AsPh₄)·1/2DMSO. In this publication, we report a general synthesis of [Q][Bi(dmit)_2] (**5**), as well as the crystal structure of [(**5**:Q=AsPh₄)·1/2DMSO].

2. Results and discussion

The air-stable [Q][Bi(dmit)₂] compounds, [**5**:Q=NEt₄, NBu₄, 1,4-Me₂-pyridinium (C₇H₁₀N) and AsPh₄], were synthesized directly from BiBr₃ and [Q]₂[Zn(dmit)₂] (**1**). The compound, (**5**:Q=NEt₄), has been obtained previously from Na₂(dmit) and BiI₃ [18]: however, a higher yield was obtained by use of the [Zn(dmit)₂]²⁻ precursor. As also found for **1** and **4** [15], the C=C, C=S and C-S absorptions in **5** occur in the regions 1435–1409, 1054–1033 and 881–889cm⁻¹, respectively, see Table 1. All the salts, **5**, are dark red-brown in colour with λ_{max} , in the visible region, between 450 and 457 nm. The AsPh₄ salt used in the structure determination was obtained as a solvated material on crystallisation

was obtained as a solvated material on crystallisation from DMSO solution.

2.1. Crystal structure of $[(5:Q=AsPh_4)\cdot 1/2 \cdot DMSO]$

Selected bond angles and lengths for $[(5:Q=AsPh_4)\cdot 1/2 DMSO]$ are listed in Table 2. The atom arrangement

and numbering scheme in the anion is shown in Fig. 1. The [AsPh₄] cation has a near tetrahedral geometry: its structure is not further discussed here. The cations do not interact with the anions: however, as in other compounds **5**, there are inter-anion interactions in [(5:Q=AsPh₄)·1/2DMSO]: each Bi atom forms four strong intra-anion Bi–S bonds to the dithiolato S atoms, and 2 inter-anion and weaker bonds to sulfur atoms of adjacent anions. Each dmit unit is asymmetrically bound to Bi, with bite angles of 76.46(4) and 77.25(4)°, see Table 2. Each dmit ligand is essentially planar, with the Bi atom out of the dmit planes by 1.2585(19) and 1.488(2) Å.

The two Bi–S inter-anion bonds involve thiolato atoms of two adjacent U-shaped anions, thereby forming chains, Fig. 1. The spine of the chains, with Bi_2S_2 rings, can be considered to be a line of bismuth atoms with the Bi…Bi distances along the chain alternating in length between 3.7760(3) and 3.9092(3) Å. There are no S…S contacts between the chains at distances less than the sum of the van der Waals radii, 3.70 Å [14], for two S atoms. The six Bi–S bonds form a very distorted octahedral array about Bi, with the three largest S–Bi– S angles being 153.71(4) [S(2)-Bi-S(7)], 155.88(4) $[S(1)-B1-S(7)^{ii}]$ and 162.00(4)° $[S(6)-Bi-S(2)^{i}]$, [symmetry operations i: -x + 1, -y, -z + 1; ii: -x, -y, -z + 1]; however, the inclusion of a stereochemically active lone pair on Bi provides a more acceptable stereochemical designation. Inclusion of the lone pair in an equatorial site, between the inter-anion bonds to $S(2)^{i}$ and $S(7)^{ii}$, $[S(2)^{i}-Bi-S(7)^{ii} = 127.84(3)^{\circ}]$, produces a distorted pentagonal bipyramidal array about Bi, with the axial sites occupied by S(2) and S(7). The distortion from an ideal trans angle of 180° is accounted for, partially at least, by the small chelate bite angles of 76.45(4) and 77.25(4)°. The sum of the angles subtended by the equatorial S atoms $[S(1), S(6), S(2)^{i}$ and $S(7)^{ii}$] at Bi is 360.94°.

The anion-anion interactions in $[(5:Q=AsPh_4)\cdot 1/2DMSO]$ are analogous to those in $[(5:Q=NEt_4)\cdot Et_2O]$ [17] and $[AsPh_4][bis(1,2-dicyanoethene-1,2-dithio$ $lato)bismuthate], <math>[AsPh_4][Bi(S_2C_2(CN)_2]$ (6), reported by Hunter and Weakley [19]: comparative geometric data for the three species are provided in Table 3. The structure of $(4:Q=NEt_4)$ [15] was also considered to show some involvement of a stereochemically active

Table 3							
Selected	geometric	parameters	for	distorted	pentagonal	bipyramidal	4-6

thiolato M S						
	Primary bonds: M-dithiolate bonds ^a		Secondary bonds: inter-anion bonds	Geometry about M		
Compound [Ref]	d(M-S) (Å)	Chelate bite angle (°)	d(M-S) (Å)	Axial S atoms ∠S _{ax-} M-S _{ax} (°)	Equatorial S ¹ _{eq} & S ⁱⁱ _{eq} S ⁱ _{eq} -M-S ⁱⁱ _{eq} (°) Σ(S-M-S) _{eq} (°)	M—M Shortest distance
(4: Q=NEt ₄) [15]	2.672(3) & 2.496(3) 2.672(3) & 2.496(3)	83.2(1) 83.2(1)	3.27(3) [to thione-S] 3.27(3) [to thione-S]	thiolato-S:thiolato-S 158.8(2)	thione-S ^b :thione-S ^b 103.5(2) 369.9	
(4:Q=PPh ₄) [16]	2.724(3) & 2.504(4) 2.619(6) & 2.478(3)	80.3(3) 84.1(3)	3.54(1) [to thione-S] 3.40(1) [to thione-S]	thione-S ^b : thiolato-S 179.7(3)	thione-S ^b : thiolato-S 129.6(4) 355.9	
(5:Q=NBu ₄) [17]	2.8082(13) & 2.5872(14) 2.7299(11) & 2.6041(10)	78.74(4) 82.06(3)	3.4628(13) [to thione-S] 3.2548(11) [to thione-S]	thione-S ^b : thiolato-S 171.73(3)	thione-S ^b : thiolato-S 128.89(3) 355.46	4.180(3)
(5:Q=NEt ₄) ^c [18]	2.87(1) & 2.66(1) [2.80(1) & 2.66(1)]	73.6(4) -	3.11(1) [to thiolato S] 3.08(1) [to thiolato S]	thiolato-S ^b : thiolato-S 161.0(4)	thiolato-S ^b : thiolato-S 123.1(3) 360.3	4.20(1)
(5:Q=NEt ₄).1/2Et ₂ O [18] mol.1	2.834(4) & 2.660(3) 2.833(4) & 2.672(4)	76.66(10) 77.26(10)	3.138(4) [to thiolato S] 3.107(4) [to thiolato S]	thiolato-S: thiolato-S 152.51(10)	thiolato-S ^b : thiolato-S ^b 125.16(9) 361.0	3.83(1)
mol.2	2.841(3) & 2.659(4) 2.806(4) & 2.666(4)	76.88(11) 76.84(11)	3.094(4) [to thiolato S] 3.099(4) [to thiolato S]	thiolato-S: thiolato-S 152.30(10)	thiolato-S ^b : thiolato-S ^b 124.16(10)	3.79(2) 3.86(1)
(5:O=AsPh_),1/2DMSO	2.8143(13) & 2.6680(13)	77.25(4)	3.1643(14) [to thiolato S]	thiolato-S: thiolato-S	thiolato-S ^b : thiolato-S ^b	3.7760(3)
[this study]	2.8370 (13) & 2.6777(13)	76.45(4)	3.0391(14) [to thiolato S]	153.71(4)	127.83(3) 360.94	3.9092(3)
(6) ^d [19]	2.746(9) & 2.693(7) 2.836(8) & 2.664(7)	76.4(2) 75.0(2)	3.238(10) [to thiolato S] 3.182(10) [to thiolato S]	thiolato-S: thiolato-S 159.8(6)	thiolato-S ^b : thiolato-S ^b 132.8(3) 364 2	3.744(2) 3.816(2)

^a in all cases, except (5:Q=NEt₄), the primary bonds are to the chelating dithiolato ligands: ^b S^b atoms from adjacent anions: ^c Bi is bonded to a primarily chelating dithiolato ligand, and to two primarily bridging ligands: ^d ligand $[S_2C_2(CN)_2]$ only has thiolato S atoms.



Fig. 2. Idealised representations of the arrangements of anions in 5: (a) (5:Q=NEt₄)·1/2Et₂O] and [(5:Q=AsPh₄)·1/2DMSO]; (b) (5:Q=NEt₄); (c) (5:Q=NBu₄).

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lone pair, but the effect of the lone pair is very much less pronounced than in any of $[(5:Q=AsPh_4)\cdot 1/2DMSO]$, $[(5:Q=NEt_4)\cdot 1/2Et_2O]$ [18] or 6 [19].

The solvate molecules of DMSO, 0.5 molecules per molecule of $(5:Q=AsPh_4)$, are highly disordered over centrosymmetrically related pairs of sites in spaces left by the cations and anions.

2.2. Comparison of the anion arrangements in 4 and 5

The Bi centres in all four Bi compounds, [(5:Q=AsPh₄)·1/2DMSO], (5:Q=NBu₄), (5:Q=NEt₄) and [(5:Q=NEt₄)·1/2Et₂O], are six coordinate and, including the lone pairs, with pseudo pentagonal bipyramidal geometries. The lone pair on each bismuth in the chains is directed away from that on a neighbouring bismuth. Despite the gross similiarities about Bi in these compounds, and the formation of chains of anions and Bi_2S_2 rings, appreciable differences are exhibited in the anion arrangements. The three distinct anionic arrangements, found, so far, are:

- Single chains formed by inter-anion Bi-thiolato-S bonds, with a thiolato S atom of each dmit ligand involved in the inter-anion bonding, Figs. 1 and 2(a). This arrangement is found in the two solvates, [(5:Q=AsPh₄)·1/2DMSO] and [(5:Q=NEt₄)·1/2Et₂O]: the only difference being the weak S…S interactions, between the chains, detected in the latter.
- 2. Single chains also formed by inter-anion Bi-thio-lato-S bonds, but here there are different roles for the dmit ligands. One dmit type acts primarily as a chelate to one Bi centre-, with an additional, but weaker, interaction to a second Bi, while the other type of dmit group primarily bridges two Bi centres, with a weaker contact to one of these Bi atoms, see Fig. 2(b). This arrangement is found in (5:Q=NEt₄).
- 3. Centrosymmetric pairs of anion chains formed by inter-anion Bi-thione-S bonds, see Fig. 2(c). There are two types of chelating dmit ligands per anion: one is not involved in any inter-anion bonding, while in the other, the thione S acts as a μ_3 -bridging atom to Bi atoms in different chains within the chain pair. The Bi₂S₂ rings are formed between the chain pairs. The short separations between the parallel dmits in the two strands of the centrosymmetric chain pairs allows for $\pi-\pi$ interactions. This arrangement is present in (5:Q=NBu₄), as well as in (4:Q=PPh₄).

The chelating ligands are asymmetrically bound in all cases, with distinct ranges for the shorter [2.5872(14) - 2.677(13) Å] and the longer [2.7299(11) - 2.87(1) Å]Bi-S bonds of each chelate. The longer Bi-S bond to each chelating ligand results mainly from the proximity of the lone pair on the metal. As the ligand asymmetry is met in $(5:Q=NBu_4)$ and in 4, in which none of the thiolato S atoms are involved in bridging, bridging by a thiolato S can not be a prime cause of the asymmetry, as stated in reference [18]. The chelate bite angles and Bi–S primary bond lengths in **5** vary significantly from 73.6(4) in $(5:Q=NEt_4)$ to $82.06(3)^\circ$ in $(5:Q=NBu_4)$, see Table 3.

The secondary bonds to the thione S atoms in $(5:Q=NBu_4)$ [3.4628(13) and 3.2548(11) Å], are longer than those to thiolato-S atoms in $(5:Q=NEt_4)$, $[(5:Q=NEt_4)\cdot 1/2Et_2O]$ and $(5:Q=AsPh_4)\cdot 1/2DMSO]$, the range being 3.0391(14) to 3.1643(14) A, see Table 3. The longer Bi-thione-S bond, [3.4628(13) A], in (5:Q=NBu₄) is between the chain pairs: the equivalent value in $(4:Q=PPh_4)$ is 3.54(1) A. The minimum allowed perpendicular separation, ca. 3.5 Å, of parallel dmits places a lower limit on these M-thione-S bond lengths (M = Sb or Bi): both the M-thione-S bond lengths in $(5:Q=NBu_4)$ [3.4628(13) Å] and $(4:Q=PPh_4)$ [3.54(1) Å] appear close to this limit. The shorter Bi-thione-S bond in $(5:Q=NBu_4)$ [3.2548(11) Å], within a single chain, is still outside the range established for Bi-thiolato-S secondary bonds. This indicates that the Mthione-S secondary bonding (M = Sb or Bi) leads to weaker associations, which may be required for steric reasons. The bulkier the cation in 5, the greater will be the restrictions to the closeness of approach of the anions: hence, bulkier (5:Q=NB u_4), rather than smaller (5:Q=NEt₄), will prefer Bi-thione-S secondary bonding. All compounds, 4, possesses Sb-thione-S secondary bonding: the larger bite angles of Sb-dmit chelates and generally shorter Sb-S bonds, compared to the situation in Bi-dmit chelates, result in a more hindered approach to approach to the Sb centre and consequently there is a greater preference for Mthione-S secondary bonding in 4 compared with 5. Coupled to this will be the effect of the bulk of the cation, on both the aggregation and coordination number of Sb.

3. Experimental

NMR spectra were run on a Bruker 300 MHz instrument, IR spectra on a Nicolet Magna 760 FTIR instrument and UV–Vis spectra on a Varian-Cary 1E UV–Vis instrument. Melting points were measured on a Melt-TempII instrument. Elemental analyses were performed with a Perkin Elmer 2400 apparatus. The compounds, (1:[Q]₂[Zn(dmit)₂]) [Q=NEt₄, 1,4-Me₂-pyridinium (C₇H₁₀N), NBu₄ or AsPh₄] were prepared according to a published procedure [11].

3.1. Preparations of 5

3.1.1. Preparation of $(5:Q=NEt_4)$

A solution of $BiBr_3$ (0.313 g, 0.697 mmol) in acetone (30 ml) was added slowly to a solution of (1:Q=NEt₄)

Table 4

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Crystal data and structure refinement for [(5:Q=AsPh₄)·1/2DMSO]

Empirical formula	C ₃₁ H ₂₃ As Bi O _{0.5} S _{10.5}
Formula weight	1024.02
<i>T</i> (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\overline{1}$
Unit cell dimension	
a (Å)	7.54720(10)
b (Å)	14.4797(5)
<i>c</i> (Å)	17.6663(5)
α (°)	72.3992(13)
β (°)	89.3480(18)
γ (°)	82.3798(17)
V (Å ³)	1823.12(8)
Ζ	2
$D_{\text{calc}} (\text{mg m}^{-3})$	1.865
Absorption coefficient (mm ⁻¹)	6.362
F(000)	994
Crystal colour	red-brown
Crystal size (mm)	$0.25 \times 0.20 \times 0.15$
θ Range for data collection (°)	2.19-30.51
Index range	$-10 \le h \le 10, -20 \le k \le 20,$
	$-24 \le l \le 24$
Reflections collected/unique	$40012/10504 \ [R_{\rm int} = 0.0733]$
Completeness to 2θ (%)	30.51, 94.3
Absorption correction	semi-empirical from
	equivalents
Max. and min. transmission	0.855 and 0.742
Refinement method	Full-matrix least-squares on
	<i>F</i> ²
Data/restraints/parameters	10504/0/396
Goodness-of-fit on F^2	1.057
Final R indices $[I > 2\theta(I)]$	$R_1 = 0.0434, \ wR_2 = 0.0959$
R indices (all data)	$R_1 = 0.0632, \ wR_2 = 0.1038$
Largest difference peak and hole	2.423 and -2.291
$(e A^{-3})$	

(0.500 g, 0.697 mmol) in acetone (20 ml). Reaction occurred immediately as shown by the colour change. A dark red-brown solid precipitated on addition of propan-2-ol. Yield: 86%. The crude product was recrystallized from acetone-propan-2-ol; m.p. $160-162^{\circ}$ C. *Anal.* Calc. for C₁₄H₂₀NS₁₀Bi: C, 22.98; H, 2.73; N. 1.91. Found: C, 22.74; H, 3.17; N. 1.91%.

¹H NMR (acetone- d_6 , 300 MHz): δ 1.42 (tt, 12H, CH₃), 3.54 (q, 8H, CH₂N). ¹³C NMR (DMSO- d_6 , 75.5 MHz): δ 8.0 (CH₃), 52.0 (CH₂N), 135.1 (C=C), 213.5 (C=S). IR (KBr): 1434 cm⁻¹ (C=C), 1054, 1019 (C=S), 881 (C-S). UV–Vis (CH₃CN): 254, 291, 370, 453 nm.

3.1.2. Preparation of $(5:Q=C_7H_{10}N)$

This was prepared analogously to compound (5:Q=NEt₄), from $BiBr_3$ (0.697 mmol) and (1:Q=C₇H₁₀N) (0.697 mmol), and recrystallized from acetone as a dark brown solid; m.p. 203°C.

¹H NMR (acetone- d_6 , 300 MHz): δ 2.63 (s, 3H, H, C–CH₃), 4.34 (s, 3H, N–CH₃), 7.91 (d, 2H, H3), and 8.82 (d, 2H, H2). ¹³C NMR (DMSO- d_6 , 75.5 MHz): δ 21.3 (CH₃–C), 47.1 (CH₃–N), 127.93, 144.5 and 158.2

(aryl-C's), 135.5 (C=C), 213.7 (C=S). IR (KBr): 1428 cm⁻¹ (C = C), 1054, 1021 (C=S) and 879 (C-S). UV–Vis (CH₃CN): 241, 299, 358, 450 nm.

3.1.3. Preparation of $(5:Q=NBu_4)$

This was prepared analogously to compound (5:Q=NEt₄), from BiBr₃ (0.697 mmol) and (1:Q=NBu₄) (0.697 mmol), and was recrystallized from dimethyl sulfoxide as a dark brown crystalline solid; m.p. 191–192°C. ¹H NMR (300 MHz, acetone- d_6): δ 0.98 (t, 12H, CH₃), 1.41 (sext., 8H, CH₂), 1.81 (quint., 8H, CH₂), 3.43 (t, 8H, H₂C–N). ¹³C NMR (75.4 MHz, DMSO- d_6) δ 13.5 (CH₃), 19.2 (CH₂), 23.0 (CH₂), 57.0 (CH₂), 135.6 (C=C), 214.0 (C=S). IR (KBr) 1409 (C=C), 1029, 991 (C=S), 886 (C–S). UV–Vis (CH₃CN): 227, 366, 300, 456 nm.

3.1.4. Preparation of $(5:Q=AsPh_4)$

This was prepared analogously to compound (5:Q=NEt₄), from BiBr₃ (0.697 mmol) and (1:Q=AsPh₄) (0.697 mmol), and was recrystallized from DMSO to give a dark red crystalline solid; m.p. 193–195°C. *Anal.* Calc. for $C_{54}H_{40}As_2S_{10}Bi$: C, 36.58; H, 1.75. Found: C, 36.20; H, 2.03%.

¹H NMR (DMSO-d₆, 300MHz): δ 7.7–7.9 (m, aryl-H's). ¹³C NMR (DMSO-d₆, 75.5 MHz): δ 121.6, 131.5, 134.9 and 135.9 (aryl-C's), 133.7 (C=C), 213.8 (C=S). IR (KBr): 1435 cm⁻¹ (C=C), 1054, 1033 (C=S), 890 (C-S). UV–Vis (CH₃CN): 457, 295 nm.

3.2. Crystallography

Intensity data at 150 K were obtained with an Enraf Nonius KappaCCD diffractometer. The programs DENZO [20] and COLLECT [21] were used for data collection, cell refinement and data reduction. SORTAV was used to apply absorption correction by the multiscan technique [22]. The structure was solved by the heavy atom method with SHELXS-86 [23] and refined with SHELXL-97 [24]. All non-H atoms were refined anisotropically and H atoms were placed in calculated positions and refined with a riding model. The asymmetric unit contained one half of a DMSO solvate molecule: these molecules were highly disordered over centrosymmetrically related pairs of sites (Table 4).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147211. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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