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Syntheses and structures of diorgano(halo- or pseudohalo-) (1,3-dithiole-2-thione-4,5-dithiolato)stannates (1-), [Q] [R₂SnX(dmit)] (Q=onium cation; X=halide or pseudohalide)

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Abstract—Ionic compounds, [Q] [R_2 SnX(dmit)] [dmit=1,3-dithiole-2-thione-dithiolate; Q=1,4-dimethylpyridinium or tetraalkylammonium; R=Ph or alkyl; X=Cl, Br, I, NCS, NCSe, or N₃] have been obtained by (a) from R_2 SnX₂ and [Q]₂[Zn(dmit)₂] in the presence of excess QX, (b) from halide exchange reactions in acetone solution between [Q] [R_2 SnCl(dmit)] and a halide or pseudohalide source, or (c) by addition of QX to [R_2 Sn(dmit)]. Crystal structure determinations of [NEt₄] [Ph₂SnI(dmit)] and [1,4-Me₂pyridinium] [Ph₂SnBr(dmit)] as well as of the mixed halides, [1,4-Me₂pyridinium] [Ph₂SnCl_nI₁₋*n*(dmit)] (*n*=0.57, 0.42 or 0.22), indicated that the tin atoms have distorted trigonal bipyramidal geometries in the anions, with the X ligand and a dithiolato atom in the axial sites. The [R_2 SnX(dmit)]⁻ anions remain essentially intact in organic solvents, but lose X⁻ on extraction with H₂O to give the neutral species, R_2 Sn(dmit). © 1998 Elsevier Science Ltd. All rights reserved

Keywords: stannates; crystal structures; organotin; dithiolates.

INTRODUCTION

Complexes of the 1,3-dithiole-2-thione-4,5-dithiolato ligand, (1, dmit, $C_3S_5^{2-}$) attracted considerable attention in recent years [1]. While much of the interest has centred on transition metal compounds, main group metal complexes have not been neglected and indeed have featured in a number of synthetic and structural studies [2–5].



While bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate salts, $[Q]_2[Zn(dmit)_2]$, as precursors of other metal dmit complexes, are clearly of general importance [2], tin dmit complexes have arguably enticed more structural study than those of any other main group metal [3]. *Mono-*, *bis-* and *tris-*dmit complexes, e.g [R₂Sn(dmit)]. (2: R = alkyl or aryl) [3], [Q] [RSn(dmit)_2] (3) [3], [Q]_2[SnX_2(dmit)_2] (4: X = I or Br) [3] and [Q]_2[Sn(dmit)_3] (5) [3], can be obtained, with the synthesis and

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structural details for 2–4 being fully reported. Some limited information on the ionic species, [Q] $[R_2SnX(dmit)]$ (6: Q=onium cation; X=halide), [3] has been provided in earlier communications; we now wish to report more fully on 6.

RESULTS AND DISCUSSION

Synthesis

The syntheses of [Q] $[R_2SnX(dmit)]$ (6: R = unfunctionalised alkyl or aryl group) have been achieved $in three ways: (a) from a reaction between <math>R_2SnX_2$ and [Q] $[Zn(dmit)_2]$ in the presence of an excess QX, (b) from halide exchange reactions in acetone solution between [Q] [R_2 SnCl(dmit)] and either NaX or QX, or (c) by addition of QX to [R_2 Sn(dmit)], see Scheme 1.

Tables 1 and 2 list the compounds, **6**, with analytical, melting point and selected IR and NMR spectral data. The work-up of all products involved the minimum use of aqueous extractions to reduce the risks of loss of QX from [Q] [$R_2SnX(dmit)$] to give polymeric [$R_2Sn(dmit)$], (reaction d in Scheme 1 [3a]. The use of R_2SnX_2 with functionalised R groups able to complex intramolecularly to tin, such as $R'O_2CCH_2CH_2$, led directly to [$R_2Sn(dmit)$] species on reactions with [Q]₂[$Zn(dmit)_2$] [3a].

The halide (or pseudohalide) exchange reactions

	Preparative			Analysis. %, (calcd/(found)(%))		
Compound	(Yield, %)	m.p. (°C), recryst. solvent	Colour	С	Н	Ν
[NBu ₄] [Me ₂ Sn(dmit)Cl]	a; (71)	115 Pr ⁱ OH/CHCl ₃	deep- orange	40.5 (40.3)	6.8 (6.8)	2.3 (2.2)
[NBu ₄] [Me ₂ Sn(dmit)I]	b	109–111 MeOH	red-brown	. ,	. ,	, í
[NEt ₄] [Bu ₂ Sn(dmit)Br]	c		orange			
[NEt ₄] [Ph ₂ Sn(dmit)Cl]	a; (79)	157–158 MeOH	orange	43.5 (43.6)	4.5 (4.6)	2.2 (2.3)
[NBu ₄] [Ph ₂ Sn(dmit)Cl]	a, (61)	101–103 Me ₂ CO/EtOH	orange	49.8 (49.3)	6.2 (6.5)	
[1,4-Me ₂ pyr] [Ph ₂ Sn(dmit)Cl]	a; (78)	140-142 MeOH	orange	43.1 (43.0)	3.3 (3.2)	2.3 (2.2)
[FcCH ₂ NMe ₃] [Ph ₂ Sn(dmit)Cl]	a; (78)	197–200	orange-red	()	()	
[methylviologen] [Ph ₂ Sn(dmit)Cl] ₂	c; (54)	125–127 CH ₂ Cl ₂ /Me ₂ CO	black	42.2 (42.1)	2.9 (2.8)	2.3 (2.2)
[PPh ₃ Et] [Ph ₂ SnCl(dmit)]	a;	114–116 MeOH/Pr ⁱ OH	red-orange	. ,		, í
[NEt ₄] [Ph ₂ Sn(dmit)Br]	b; (83)	74–77 MeOH	yellow-orange	40.7 (41.1)	4.5 (4.6)	2.1 (2.2)
	c; (40)	77–9		(40.5)	(4.3)	(1.9)
[NBu₄] [Ph₂Sn(dmit)Br]	c; (78)	119–122 CHCl ₃ /petrol	orange	()		
[1,4-Me ₂ pyr] [Ph ₂ Sn(dmit)Br]	b; (79)	139-140 MeOH/Me ₂ CO	orange	40.2 (40.2)	3.1 (3.0)	2.1 (2.1)
[NEt ₄] [Ph ₂ Sn(dmit)I]	c; (79)	134–136 MeOH	orange	38.0	4.2 (4.2)	1.9
[NBu ₄] [Ph ₂ Sn(dmit)]]	b	115–117 CHCl ₂ /EtOH	vellow/ orange	(2010)	()	(110)
$[1,4-Me_2pyr] [Ph_2Sn(dmit)I]$	c	134–136 MeOH/petrol	orange	38.1 (37.5)	2.7 (2.9)	2.0 (2.0)
[NEt ₄] [Ph ₂ Sn(dmit)NCS]	b; (84)	129–30 MeOH	orange	43.8 (43.7)	4.6	4.3 (4.2)
[1,4-Me ₂ pyr] [Ph ₂ Sn(dmit)NCS]	b; (77)	134–135 MeOH/Me ₂ CO	orange	43.5 (43.0)	3.2 (3.1)	(4.2)
[NEt ₄] [Ph ₂ Sn(dmit)NCSe]	b; (78)	109–10 MeOH/Me ₂ CO	orange	40.9	(3.1) 4.3 (4.3)	(1.2) 3.7 (4.0)
[1,4-Me ₂ pyr] [Ph ₂ Sn(dmit)NCSe]	b; (87)	137–138 Me ₂ CO/petrol	orange	40.5	(3.0)	(3.8)
[1,4-Me ₂ pyr] [Ph ₂ SnCl _{0.22} I _{0.78} (dmit)]	b	130–134 MeOH/petrol	orange	(39.7) 39.9 (38.7)	(2.5) 3.0 (2.7)	(3.0) 2.1^{b} (2.0)

Table 1. Analytical and physical data for [Q][R₂SnX(dmit)]

^aFor preparative methods a, b and c, see Section 2.1

^bI found 14.3%, calc. 14.5%.

Syntheses and structures of diorgano(halo- or pseudohalo-)



Compound	$IR(KBr, cm^{-1})$	δ^{13} C(CD ₃ COCD ₃)		δ^{119} Sn(CD ₃ COCD ₃)	
	C=S	C=C	C=S	-	
[NBu ₄] [Me ₂ SnCl(dmit)] ^a	1057, 1032	131.7 [125.3, 138.7] ^b	207.9 [208.6] ^b	$-24.7(\text{CDCl}_3)[-33.2]^{b}$	
[NBu ₄] [Me ₂ SnI(dmit)]	1055,1034		208.6	-7.8	
[NEt ₄] [Bu ₂ SnBr(dmit)]				-36.1	
[NEt ₄] [Ph ₂ SnCl(dmit)]	1063,1036			-143.2	
[NBu ₄] [Ph ₂ SnCl(dmit)]	1055,1036		207.7	-135.5	
[1,4-Me ₂ pyr] [Ph ₂ SnCl(dmit)]	1055		208.1	-145.1	
[FcCH ₂ NMe ₃] [Ph ₂ SnCl(dmit)]	1055	129.7	208.6	-145.8, -146.3	
				(CDCl ₃)	
[methylviologen] [Ph2SnCl(dmit)]	1055, 1036		208.1	-144.2	
[PPh ₃ Et] [Ph ₂ SnCl(dmit)]	1053, 1032				
[NEt ₄] [Ph ₂ SnBr(dmit)]	1061, 1036	131.2	208.3	-149.6	
[NBu ₄] [Ph ₂ SnBr(dmit)]	1057, 1036	131.5	206.2	-150.4	
[1,4-Me ₂ pyr] [Ph ₂ SnBr(dmit)]	1055			-149.8	
[NEt ₄] [Ph ₂ SnI(dmit)]	1061, 1035	130.7	207.9	-158.2	
[NBu ₄] [Ph ₂ SnI(dmit)]			207.2	-136.8	
[1,4-Me ₂ pyr] [Ph ₂ SnIdmit)]	1053, 1032	131.2	207.8	-160.3	
$[1,4-Me_2pyr]$ [Ph ₂ SnI _{0.58} Cl _{0.42} (dmit)]	1055			-152.6	
[NEt ₄] [Ph ₂ Sn(NCS)(dmit)]	1055, 1036, 2047		208.5	-162.9	
[1,4-Me ₂ pyr] [Ph ₂ Sn(NCS)(dmit)]	1055, 2046 (NCS)	129.7	208.5	-163.3	
[NEt ₄] [Ph ₂ Sn(NCSe)(dmit)]	1055, 1035, 2051 (NCSe)			-148.4	
[1,4-Me ₂ pyr] [Ph ₂ Sn(NCSe)(dmit)]	1065, 2051 (NCSe)			-149.1	
$[1,4-Me_2pyr] [Ph_2SnN_3(dmit)]$	1062,1037, 2104 (N ₃)				

Table 2. spectral data for $[Q] [R_2Sn(dmit)X]$

^a δ^{1} H(Me 1.16 (J^{119,117}Sn⁻¹H = 74.2, 71.0 Hz); δ^{13} C(Me) 13.1 (J^{119,117}Sn⁻¹³C = 569, 547 Hz). ^b solid state values.

(reaction b in Scheme) proceeded readily in Me₂CO solution for most [Q] [R2SnCl(dmit)] complexes, using NaX or QX (X = Br, I, NCS or NCSe) in moderate excess (i.e. 2 to 4 mole equivalents): with these excesses, halide exchanges were generally complete. However, for the NaI/[1,4-Me₂pyridinium] [Ph₂SnCl (dmit)] exchange reaction, a larger excess of NaI was required to drive the exchange to near completion. Products with mixed chloride/iodide contents, [1,4-Me₂pyridinium] [Ph₂SnCl_n I_{1-n} (dmit)], could be isolated from incomplete exchanges. Examples of such mixed halide products had I:Cl mol ratios of 0.43: 0.57; 0.58: 0.42 and 0.78: 0.22, as deduced from X-ray and elemental analyses, e.g. iodine analysis in the three mixed chloride/iodide complexes were 8.2, 11.4 and 14.3%, compared to calculated values of 8.4, 11.1 and 14.5%, for [1,4-Me₂pyridinium] [Ph₂SnCl_nI_{1-n}(dmit)] with n = 0.43, 0.57 and 0.78, respectively.

A simple exchange reaction was not obtained between $[NEt_4]$ $[Ph_2SnCl(dmit)]$ and a large excess of NH₄F (mol ratio 1:22) in MeOH; the product isolated analysed for the fluorine bridged dinuclear species, $[NEt_4]$ $[Ph_2(dmit)SnFSn(dmit)Ph_2]$.

Organotin-dmit complexes undergo ready disproportionation reactions in solution, with products showing suitable losses and gains of organic and dmit groups. Tris(dmit)stannate salts, [Q]₂[Sn(dmit)₃], are ubiquitous materials, appearing as unwanted coproducts in various tin-dmit preparations and solutions, e.g. crystals of [NEt₄]₂[Sn(dmit)₃] were deposited, albeit in a low yield, from a dilute solution of analytically pure [NEt₄] [Ph₂Sn(NCSe)(dmit)] in MeOH. The isolation of a product bearing a greater number of organic groups than the original organotin compound is a strong indication of a disproportionation reaction; such an example is [NEt₄] [Ph₃Sn(NCS)₂], isolated [6] as a minor product, from a reaction mixture containing $Na_2(dmit)$, $Ph_2Sn(NCS)_2$ and [NEt₄]Br. Disproportionations of diorganotin compounds, R₃SnX, to di- and tetra-organotin species, are also well-established processes, especially for compounds with chelating X groups [7].

Holmes et al. reported the isolation of [NEt₄]₂[Sn(o- $SC_6H_4O_3$], (7), from solutions of [NEt₄, SnF(o- $SC_6H_4O_2$ in organic solvents [8]; rather than disproportionation, Holmes et al. suspected hydrolysis was responsible for the formation of 7 and suggested the intermediacy of $[NEt_4]_2[Sn(HO)_2(o-SC_6H_4O)_2]$ [8]. Hydrolysis of carbon-tin bonds was also invoked for the formation of [NEt₄] [Na] [Sn(mnt)₃], from PhSnCl₃, Na₂(mnt) and NEt₄Cl in Me₂CO solution (mnt = 1, 2-dicyanoethylene-1, 2-dithiolate)] [9] and for the preparation of $[Sn(catecholato_3)^{2-}]$ in the reaction of [PhSn(O)OH] with catechol in the presence [8] of NEt₃ and Me₂C(OMe)₂. However, our experience with the dmit complexes suggests that disproportionations are more probable causes of the unexpected products than are hydrolyses. The mobility of dmit group between tin centres has been additionally shown in exchange reactions between R_2SnX_2 and $R'_2Sn(dmit)$ [3a].

A limited number of other [Q] $[R_2SnX(dithiolate)]$ complexes have been previously reported; these include $[NEt_4]$ $[Ph_2SnCl(3,4-toluenedithiolate)]$, prepared by addition of NEt₄Cl to Ph₂Sn(3,4-toluenedithiolate) [10a, 10b] and [Ph₄As] [Me₂SnX(mnt)], from¹¹ Me₂SnX₂ (X=Cl, Br or I), Na₂(mnt) and [Ph₄As]NO₃ [11].

Crystal structure determinations

In addition to the previously reported structures of $[NBu_4]$ [Me₂SnCl(dmit)] [3f] and [1,4-Me₂pyridinium] [Ph₂Sn(NCS)(dmit)] [3g], the crystal structures of the single halide species, [NEt₄] [Ph₂SnI(dmit)] and [1,4-Me₂pyridinium] [Ph₂SnBr(dmit)] have been determined.

Unfortunately, suitable crystals of the bridged fluoride complex, [NEt₄] [(dmit)Ph₂SnFSnPh₂(dmit)] could not be obtained for an X-ray diffraction study.

As well as those of the single halide species, the structures of the mixed halide species, [1,4-Me₂ pyridinium] [Ph₂SnCl_nI_{1-n}(dmit)] (n = 0.57, 0.42 and 0.22) have been determined. The structure of [1,4-Me₂pyridinium] [Ph₂SnC_{0.57}I_{0.43}(dmit)] was solved with a R factor of 0.049; although much less satisfactory R values (ca. 0.10) were obtained for the other mixed I/Cl species, the data is sufficient to allow useful comparisons to be made with those of the other compounds. The mixed halide species can be considered to be solid solutions, obtained by crystallisation from solutions containing both halides, with structures in which an axial site in the trigonal bipyramidal array is randomly occupied by either of the different halide ligands. In the cases of the [1,4-Me₂pyridinium] [Ph₂SnCl_nI_{1-n}(dmit)] (n=0.57 and0.42), the positions of both ligands, as well as their occupancy factors, could be resolved. However. only a single site could be determined for the halides in $[1,4-Me_2pyridinium]$ [Ph₂SnCl_{0.22}I_{0.78}(dmit)].

Selected bond lengths and angles in these ionic compounds, including data for the previously published [NBu₄] [Me₂SnCl(dmit)] [3f] and [1,4-Me₂pyridinium] [Ph₂Sn(NCS)(dmit)] [3g] are listed in Table 3. Figs 1– provide the atom arrangements in [1,4-Me₂ pyridinium] [Ph₂SnBr(dmit)], [NEt₄] [Ph₂SnI(dmit)], [1,4-Me₂pyridinium] [Ph₂SnCl_{0.57}I_{0.43}(dmit)] and [1,4-Me₂pyridinium] [Ph₂SnCl_{0.42}I_{0.58}(dMit)], respectively. The atom numbering system used for [1,4-Me₂ pyridinium] [Ph₂SnCl_{0.22}I_{0.78}(dmit)] is the same as that used for [1,4-Me₂pyridinium] [Ph₂SnCl_{0.42}I_{0.58}(dmit)] although for the latter only a single halide site was determined.

There are no interactions between the cations and anions of the [Q] [$R_2SnX(dmit)$] species, however, in general there are S–S contacts between anions just within the sum of the van der Waals radii (3.67 Å) [8]. In all cases, the structures of the anions are basically



Fig. 1. The atom arrangement in the anion of [1,4-Me₂pyridinium] [Ph₂SnBr(dmit)]. Displacement ellipsoids are shown at the 50% probability level.

trigonal bipyramidal with some distortions towards rectangular pyramidal structures. In the distorted trigonal bipyramidal anions of each compound, a thiolato sulfur and the halide or thiocyanate ligand occupy the axial sites, with the S_{ax} -Sn-X angle in the narrow range of 162.1(1) to 167.9(7)°; the equatorial atoms in each case being the other thiolato sulfur and the two carbon atoms of the organic groups. There is a particularly narrow range of values for the equatorial Sn-S_{eq} bond lengths [2.439(7) to 2.454(5) Å]; a much greater variation is found for the Sn-S_{ax} bond lengths [2.551(4) to 2.662(3)Å]. The dithiolato bite angles, S_{ax} -Sn- S_{eq} , vary over the range 84.5(1) to 86.37(3)°. The bond angles and lengths within the dmit moiety vary little in the various ionic complexes; the average geometric parameters of the dmit units are provided in Fig. 5.

The Sn-Cl, Sn-Br, Sn-I and Sn-N(CS) bond lengths in [1,4-Me₂pyridinium] [Ph₂Sn(NCS)(dmit)], $[NBu_4]$ [Me₂SnCl(dmit)], [1,4-Me₂pyridinium, Ph₂SnBr(dmit)] and [NEt₄] [Ph₂SnI(dmit)] are 2.261(3), 2.556(3), 2.7139(10) and 2.985(2) Å, respectively; these values are ca. 5, 7, 7 and 9% longer, respectively, than the appropriate sums of the covalent bond radii [12] of 2.15, 2.39, 2.54 and 2.73 Å. Very few compounds of a similar nature have been reported. The Sn-Cl bond length in [NBu₄] [Me₂SnCl(dmit)] is similar to that determined of 2.556(3) Å in the trigonal bipyramidal anion of [NEt₄] [Ph₂SnCl(3,4-toluenedithiolate] [10a]. The Sn–I bond length, 3.225(1)Å, in [PPh₄, Me₂SnI(o-OC₆H₄S)] is considerably longer than the Sn-I bond length in [NEt₄] [Ph₂SnI(dmit)], however the anions in [PPh₄] $[Me_2SnI(o-SC_6H_4O)]$ are linked via Sn–O bridges into centrosymmetric dimers¹³ to give six coordinate tin centres [13].

The Sn–Cl and Sn–I bond lengths, determined for the mixed halide complexes, $[1,4-Me_2pyridinium]$ [Ph₂SnCl_nI_{1-n}(dmit)], are 2.62(2) and 2.873(9)Å for

Q	Bu ₄ N [3f]	$C_7H_{10}N$	Et_4N	C ₇ H ₁₀ N [3g]	$C_7H_{10}N$	$C_7H_{10}N$	$\mathrm{C_7H_{10}N}$
R	Me	Ph	Ph	Ph	Ph	Ph	Ph
Х	Cl	Br	Ι	NCS	Cl(0.57) ^g	Cl(0.42)	Cl(0.22)
					I(0.43)	I(0.58)	I(0.72)
S(eq)	S2	S 1	S 1	S2	S9	S1	S 1
S(ax)	S1	S4	S 5	S1	S 3	S2	S2
C(A)	C5	C4	C11	C7	C17	C9	C9
C(B)	C4	C10	C21	C1	C11	C15	C15
Х	Cl	Br	Ι	Ν	Cl or I	Cl or I	Cl/I
Sn–X	2.556(3)	2.7139(10)	2.985(2)	2.261(3)	2.873(8) ^a , 2.62(2) ^b	2.859(13) ^a , 2.724(3) ^b	2.926(3)
Sn-C(A)	2.131(10)	2.153(5)	2.14(1)	2.137(4)	2.142(5)	2.16(2)	2.12(2)
Sn-C(B)	2.132(11)	2.168(5)	2.18(1)	2.139(4)	2.147(6)	2.20(3)	2.18(3)
Sn-S(eq)	2.451(3)	2.453(2)	2.454(5)	2.4399(10)	2.448(2)	2.439(7)	2.444(7)
Sn-S(ax)	2.662(3)	2.596(2)	2.551(4)	2.5917(10)	2.590(2)	2.592(8)	2.593(8)
X-Sn-S(ax)	167.3(1)	165.79(4)	162.1(1)	164.58(8)	164.9(1) ^a , 167.8(4) ^b	1643(3) ^a , 167.9(7) ^b	165.0(2)
X–Sn–C(A)	91.2(4)	92.34(13)	89.6(3)	88.75(12)	92.8(2) ^a , 91.3(4) ^b	92.9(8) ^a , 97.3(10) ^b	92.0(6)
X-Sn-C(B)	92.5(4)	95.3(2)	95.7(3)	91.45(13)	95.9(2) ^a , 94.3(4) ^b	98.0(10) ^a , 90.6(11) ^b	94.7(8)
X-Sn-S(eq)	83.1(1)	80.24(4)	78.4(1)	78.53(8)	79.5(1) ^a , 82.5(4) ^b	79.7(3) ^a , 82.3(7) ^b	80.1(2)
C(A)-Sn-C(B)	120.9(6)	116.6(2)	110.5(3)	119.36(13)	116.3(2)	115.0(9)	117.1(9)
C(A)–Sn–S(eq)	120.8(4)	123.79(13)	127.0(3)	121.91(10)	123.7(1)	124.1(7)	123.2(6)
C(B)–Sn–S(eq)	118.2(4)	119.50(14)	121.9(3)	117.42(10)	120.0(1)	120.9(7)	119.5(7)
C(A)–Sn–S(ax)	93.0(4)	92.20(13)	93.7(3)	96.71(10)	92.3(2)	90.9(7)	92.8(6)
C(B)–Sn–S(ax)	95.6(4)	94.7(2)	99.5(4)	98.33(10)	94.5(2)	94.1(10)	95.8(9)
S(eq)-Sn-S(ax)	84.5(1)	86.04(5)	85.6(2)	86.37(3)	85.83(6)	85.7(2)	85.4(2)

Table 3. Selected bond lengths (Å) and angles (°) for [Q] [$R_2SnX(dmit)$]

 ${}^{a}X = I.$



Fig. 2. The atom arrangement in the anion of [NEt₄] [Ph₂SnI(dmit)]. Displacement ellipsoids are shown at the 50% probability level.

n = 0.57 and 2.724(3) and 2.859(13) Å for n = 0.42, i.e. the Sn-Cl and Sn-I bond lengths are longer and shorter respectively, than values determined for single halide complexes. As already indicated, only an average tin-halide bond length [2.926(3) Å] could be extracted from the X-ray data for [1,4-Me₂pyridinium] [Ph₂SnCl_{0.22}I_{0.78}(dmit)]. Yoon and Parkin have clearly demonstrated that bond lengths obtained from disordered structures can be incorrect, when judged against values in pure compounds [14]. Our results are in agreement with the conclusion of Yoon and Parkin, that while satisfactory refinement of a disordered structure be taken as evidence for the nature of the disorder and therefore a good indication of the molecular structure, attempts to extract the true bond lengths from such a structure must be treated with caution.

Spectra

All isolated compounds are orange to red–brown in colour: λ_{max} in Me₂CO solution for [Q] [R₂SnX(dmit)] (e.g. Q=NEt₄, NBu₄or PPh₃Et; R=Me or Ph; X=Cl or Br) is 455±5 m μ , compared to values of 433±5 m μ for the corresponding iodides. The asymmetry of the C=C unit in the dmit group, as established by X-ray crystallography, is observed in the solid state ¹³C NMR spectra, $\delta^{13}C(C=C)$ values for [1,4-Me₂ pyridinium] [Ph₂SnI(dmit)] being 127.7 and 136.4 ppm and for [NBu₄] [Me₂SnCl(dmit)] 125.3 and 138.7 ppm. In solution, the ethylenic carbons of each anion are equivalent, with $\delta^{13}C$ values in the range 130.5±0.8 ppm. The $\delta^{13}C(C=S)$ values are grouped around 207 ppm; the solid state $\delta^{13}C(C=S)$ value for [1,4-Me₂pyridinium] [Ph₂SnI(dmit)] is 205.2 ppm. In the IR spectra in KBr discs, the v(C=S) values are in the ranges 1055–1065 and 1032–1035 cm⁻¹.

Acetone was generally used as the NMR solvent in order to obtain reasonable concentrations. Such a coordinating solvent could influence the structure of the anions; however, essentially the same δ^{119} Sn values for [FcCH₂NMe₃] [Ph₂SnCl(dmit)] were obtained in Me₂CO and CDCl₃ solutions suggest that this is not the case, at least not for this complex. The δ^{119} Sn values could also be effected by dissociation, as shown in eq. (1) a process readily realised in aqueous systems (cf. step d in Scheme).

$$[Q]^{+}[R_{2}SnX(dmit)]^{-} = [Q]^{+}X^{-} + R_{2}Sn(dmit).$$
(1)

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Fig. 3. The atom arrangement in the anion of $[1,4-Me_2$ -pyridinium] [Ph₂SnCl_{0.57}I_{0.43}(dmit)]. Displacement ellipsoids are shown at the 50% probability level.



Fig. 4. The atom arrangement in the anion of $[1,4-Me_2-pyridinium]$ [Ph₂SnCl_{0.42}I_{0.58}(dmit)]. Displacement ellipsoids are shown at the 40% probability level.

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Bond lengths (Å)

Bond angles (°)

Fig. 5. The average geometric parameters within the dmit units in [Q] [R₂SnX(dmit)].

The δ^{119} Sn values in Me₂CO solution for [Q] [R₂SnX(dmit)] and R₂Sn(dmit) show considerable differences; e.g. δ^{119} Sn for Ph₂Sn(dmit) is -25 ppm, compared to the values for [Q] [Ph₂SnCl(dmit)] of -143.2, -145.1, -146.3, -144.2 and -135.5 for Q=NEt₄, 1,4-Me₂-pyridinium, FcCH₂NMe₃, methylviologen (2[Q]) and NBu₄, respectively. Significant differences in δ^{119} Sn values are also realised between the pairs Me₂Sn(dmit)/[Q] [Me₂SnX(dmit)] and Bu₂Sn(dmit)/[Q] [Bu₂SnX(dmit)]; δ^{119} Sn for Me₂Sn(dmit) and Bu₂Sn(dmit) Me₂CO-d₆ are 135.2 and 161.5 ppm, respectively [3a].

Only a single δ^{119} Sn value was observed for each solution of [Q] [R₂SnX(dmit)] suggesting either a single tin species was present in solution, or a rapid equilibrium process was at hand. The δ^{119} Sn values for [Q] [R₂SnX(dmit)] do not vary with changes in concentration or Q. This suggests that dissociations, as shown in eq. (1), can be generally ignored; furthermore, the cations and anions must be essentially independent in solution. Exception could be some NBu₄ salts, e.g. of [Ph₂SnX(dmit)]⁻ (X = Cl or I) which do show lower field values than do salts of other cations, Q⁺. Of interest, the mixed halide compounds, [1,4-Me₂pyridinium] [Ph₂SnCl_nI_{1-n}(dmit)], exhibit a single δ^{119} Sn value between those expected for the simple chloride and iodide. The similarity in the solid

state and CDCl₃ solution δ^{119} Sn values for [NBu₄] [Me₂SnCl(dmit)], -33.2 and -24.7 ppm, respectively, also points to no change in structure on dissolution.

The average δ^{119} Sn values for [Ph₂SnX(dmit)]⁻ vary slightly in the sequence Cl, NCSe, Br, I and NCS; -144.6, -148.3, -149.9, -159.3 and -163.3 ppm, respectively. These values indicate that the X group has little influence on the tin centres in the [Ph₂SnX(dmit)]⁻ anions. The J(^{119,117}Sn-¹³C) values for the *ipso* aryl carbon in the [Ph₂SnX(dmit)]⁻ anions also show little variation with X, being *ca.* 800 Hz.

Reactions

The complexes, [Q, $R_2SnX(dmit)$] can act as dmit sources, as shown by the reactions with iodine, to give the dmit dimer, C_6S_{10} and with 2-O₂NC₆H₄SCl (see equations 2 and 3).

EXPERIMENTAL

Melting points were measured using a Kofler hotstage microscope and are uncorrected. NMR spectra were obtained on a Bruker 250 MHz instrument. Ten second pulse delays were utilised in the acquisition of



the ¹³C NMR spectra of the dmit compounds. IR spectra were recorded on Phillips Analytical PU900 and Nicolet 205 Fourier-transform instruments. Solid state NMR spectra were obtained by the EPSRC service at the University of Durham.

Zincate salts, $[Q]_2[Zn(dmit)_2]$, $[Q = NEt_4, NBu_4, 1, 4-dimethylpyridinium or ferrocenylmethyl(trimethyl) ammonium] [15] and R₂Sn(dmit) (R = Me or Ph) were prepared by published routes [3a]. Onium salts were commercial samples, except 1,4-dimethylpyridinium iodide, which was obtained from 4-methylpyridine and methyl iodide.$

Preparation of [Q] [R₂SnX(dmit)] complexes

The [Q] [R_2 SnX(dmit)] complexes were produced by three reactions: (a) from reaction between R_2 SnX₂ and [Q]₂[Zn(dmit)₂] in the presence of excess QX; (b) from halide exchange reactions in acetone solution between [Q, R_2 SnCl(dmit)] and either NaX, KX or QX; or (c) by addition of QX to [R_2 Sn(dmit)]. Each of these routes is illustrated below. Melting points, solvents used for recrystallisation, colours, yields, analyses and selected spectral data for [Q] [R_2 SnX(dmit)] complexes are listed in Tables 1 and 2.

Reaction (a); preparation of [NEt₄] [Ph₂SnCl(dmit)]

A solution of Ph_2SnCl_2 (5.0 g, 14.5 mmol) in MeOH (10 ml) was added to a solution of $[NEt_4] [Zn(dmit)_2]$ (5.22 g, 7.27 mmol) in Me₂CO (50 ml). After stirring the reaction mixture for 30 min, it was filtered and the volume of the filtrate was reduced to *ca*. 25 ml. Orange coloured crystals were formed. These were collected and washed successively with a little water and petrol (40–60°C). The title compound was recrystallised from MeOH.

Reaction (*b*); *preparation of* [1,4-Me₂-pyridinium] [Ph₂Sn(NCSe)(dmit)]

A solution of KSeCN (0.72 g, 5.0 mmol) in MeOH (10 ml) was added to a solution of $[1,4-Me_2$ pyridinium] [Ph₂SnCl(dmit)] (1.53 g, 2.5 mmol) in Me₂CO (50 ml). The reaction mixture darkened in colour on reaction and a precipitate of KCl formed. The reaction mixture was filtered and the filtrate was rotary evaporated to leave an orange coloured solid residue. This was washed successively with a little water, propan-2-ol and petrol (40–60°C) and was recrystallised from Me₂CO/petrol (40–60°C).

Reaction (c); preparation of [NEt₄] [Ph₂SnNCS(dmit)]

The compound $[Ph_2Sn(dmit)]$ (0.47 g, 1 mmol) was mixed with NEt₄Br (0.21 g, 1 mmol) and an excess of NaSCN.2H₂O (0.46 g, 4 mmol) in MeOH (20 ml) and agitated on an ultrasonic bath for 2 h. The reaction mixture was filtered and the solid recrystallised from MeOH/Me₂CO to give orange needles.

Preparation of [methylviologen, Ph₂SnCl(dmit)]₂

A solution of Ph₂Sn(dmit) (0.75 g, 1.6 mmol) and methylviologen dichloridehydrate (0.45 g, 1.8 mmol) in Me₂CO (75 ml) was agitated in an ultrasonic bath for 15 min. The reaction mixture was filtered and the filtrate evaporated under vacuum. The solid residue was recrystallised from CH_2Cl_2/Me_2CO as black crystals.

General NMR spectral data for [Q] [$Ph_2SnX(dmit)$] complexes in Me₂CO- d_6 solutions are as follows:

[NBu₄]⁺: ¹H NMR (Me₂CO- d_6 , 250 MHz): δ : 0.93±0.02 [12H, t, J 7.3 Hz], 1.31±0.03 [8H, m, CH₂CH₂Sn], 1.56±0.03 [8H, m, CH₂CH₂CH₂Sn], 3.16±0.03 [8H, t, J 7.3 Hz, CH₂N] ¹³C NMR(Me₂CO- d_6 , 63 MHz): δ : 13.5, 19.2, 23.1 and 57.5.

[1,4-Me₂pyridinium]⁺: ¹H NMR (Me₂CO- d_6 , 250 MHz): δ : 2.69 ±0.02 [3H, s, Me–C], 4.51 ±0.03 [3H, s, Me–N], 7.41 ±0.03 [2H, d, J 7 Hz] and 8.02±0.055 [2H, d, J 8 Hz] (aryl). ¹³C NMR (Me₂CO- d_6 , 63 MHz): δ : 21.9 [Me–C], 48.3 [Me–N], 129.3 [C₃+C₅], 145.3 [C₂+C₆], 160.2 [C₄].

 $\begin{array}{l} [\mathrm{Ph}_{2}\mathrm{SnX}(\mathrm{dmit})]^{-:} \, ^{1}\mathrm{H} \ \mathrm{NMR} \ (\mathrm{Me}_{2}\mathrm{CO}\text{-}d_{6}, 250 \ \mathrm{MHz}):\\ \delta: \ 7.42 \pm 0.04 \ [6\mathrm{H}, \ \mathrm{m}, \ \mathrm{m}\text{-}+p\text{-}\mathrm{H}], \ 8.06 \pm 0.06 \ [4\mathrm{H}, \ \mathrm{m}, \ o\text{-}\mathrm{H}] \, ^{13}\mathrm{C} \ \mathrm{NMR} \ (\mathrm{Me}_{2}\mathrm{CO}\text{-}d_{6}, 63 \ \mathrm{MHz}): \ \delta: \ 129.3 \pm 0.03 \ \mathrm{J} \mathrm{J} \, ^{119}\mathrm{Sn}\text{-}^{13}\mathrm{C} \ 83 \ \mathrm{Hz}, \ \mathrm{Cm}], \ 130.0 \pm 0.3 \ [\mathrm{J}^{119}\mathrm{Sn}\text{-}^{13}\mathrm{C} \ 17 \ \mathrm{Hz}, \ \mathrm{C}_{p}], \ 136.9 \pm 0.5 \ \mathrm{J}^{119}\mathrm{Sn}\text{-}^{13}\mathrm{C} \ 61 \pm 1 \ \mathrm{Hz}, \ \mathrm{C}_{o}], \ 148.0 \pm 0.5 \ \mathrm{[J}^{119}\mathrm{Sn}\text{-}^{13}\mathrm{C} \ 800 \pm 10 \ \mathrm{Hz}, \ \mathrm{C}_{i}], \ \ 130\text{-}131 \ \ [\mathrm{C=Cl}, \ 208.2 \pm 0.5 \ [\mathrm{C=S}]. \end{array}$

Reaction between $[NEt_4]$ $[Ph_2SnCl(dmit)]$ and animonium fluoride; formation of $[NEt_4, {Ph_2Sn (dmit)}_2F]$

A solution of $[NEt_4, Ph_2SnCl(dmit)]$ (0.634 g, 1.00 mmol) and NH₄F (0.80 g, 22 mmol) in MeOH (75 ml) was stirred for 10 min. The solution was concentrated under vacuum and cooled to yield an orange coloured solid, which was recrystallised from MeOH/Me₂CO; m.p. 195°C (dec.).

IR (KBr, cm⁻¹); 3045, 2984, 2982, 1478, 1431, 1425, 1390, 1061, 1046, 1029, 997, 893, 727, 694.

¹H NMR (250 MHz, Me₂CO-*d*₆): δ : 1.41 (12H, tt, J 7.2 and 1.9 Hz, Me), 3.51 (8H, q, J 7.2 Hz, CH₂), 7.41 (12H, m, *m*-H+*p*-H), 7.82 (8H, m, *o*-H).

Found: C, 42.0; H, 3.7; N, 1.5. $C_{38}H_{40}FNS_{10}Sn_2$ requires: C, 42.0; H, 3.7; N, 1.3%.

Reaction of [NEt₄] [Ph₂SnCl(dmit)] *with o-nitrobenzenesulfenyl chloride; preparation of* 4,5-*bis(o-nitrobenzenethiolato)*-1,3-*dithiole*-2-*thione*

benzenesulfenyl chloride (0.190 g, 1.00 mmol) in MeOH (10 ml) were mixed and stirred for 10 min. A yellow precipitate formed, which was collected, washed with MeOH and recrystallised from EtOH; yield 0.097 g, 66%, m.p. 158–160°C.

IR (KBr, cm⁻¹): 3094, 1590, 1568, 1510, 1451, 1334, 1307, 1105, 1065, 1040, 1022, 853, 785, 737.

UV–VIS (Me₂CO, $m\mu$): 367.

Found: C, 35.1; H, 1.7; N, 5.4. $C_{15}H_8N_2O_4S_7$ requires: C, 35.7; H, 1.6; N, 5.6%.

Reaction of [NEt₄] [Ph₂SnCl(dmit)] *with iodine; preparation of* (dmit)₂MeOH

To a stirred suspension of $[NEt_4]$ [Ph₂SnCl(dmit)] (0.317 g, 0.500 mmol) in MeOH (10 ml) was added a solution of I₂ (0.127 g, 0.500 mmol) in MeOH (10 ml). The solution was filtered and the solid was collected and dried under vacuum; m.p. 155–158°C.

IR (KBr, cm^{-1}): 1061.

Found: C, 19.5; H, 0.6; S, 75.3. C₇H₄OS₁₀ requires: C, 19.8; H, 1.0; S, 75.5%.

Treatment of [NEt₄] [Ph₂SnCl(dmit)] *with water; preparation of* [Ph₂Sn(dmit)]

A solution of $[NEt_4]$ $[Ph_2SnCl(dmit)]$ (0.513 g, 0.809 mmol) in Me₂CO (10 ml) was shaken with H₂O (30 ml). Addition of petrol (b.p. 40–60°C, 20 ml) led to the formation of an orange solid. This was collected, refluxed for 1 h in H₂O/MeOH (2:1), filtered and dried under vacuum at 100°C; m.p. 204–206°C (Ref.[3a]; value 206–207°C). NMR and IR spectra were identical with those of an authentic sample.

Crystal structure determinations

[1,4-Me₂pyridinium] [Ph₂SnBr(dmit)]. The unit cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines ENDEX, REFINE and MADONL in the madness programme [16] and processed using ABSMAD [17]; detailed procedures have been described [18]. Absence of crystal decay in the X-ray beam was confirmed by checking equivalent reflections at the beginning and end of data collection, which lasted ca. 8 h. The structure was solved with SIR92 [19] and refined with SHELXL97 [20]. Attempts to solve the structure in the super group C222₁ with a = 15.395, b = 34.746 and c = 9.479 Å were unsuccessful. Crystal data and structure refinement details are listed in Table 4. The Sn, Br, S and C atoms were refined with anisotropic thermal displacement parameters. The hydrogen atoms were allowed to ride on their attached atoms with common isotropic temperature factors which converged at 0.010 Å². Molecular diagrams were obtained by the program ZORTEP [21].

The cation is disordered with an inversion centre in

the middle of the ring. The asymmetric unit of the monoclinic cell contains the anion and two half cations, C(16)-C(19) and C(20)-C(23). See Fig. 1; the remaining atom positions in the cation are generated by the inversion centre. The positions 17 and 21 are each shared by a carbon and nitrogen atom constrained to have identical population parameters (0.5) and identical thermal parameters.

[NEt₄] [Ph₂SnI(dmit)]. The data were collected on a CAD-4 instrument. The structure was refined by full matrix least squares. All nonhydrogen atoms, except the phenyl and ethyl carbons, were refined anisotropicially. Restraints were applied to the refinement of the phenyl and tetraethylammonium groups. The hydrogen atoms were placed in calculated positions with C–H=1.00 Å. The first phasing model was obtained and the structure completed using SIR92 [19]. Structure refinement used CRYSTALS-PC [22]. Computations were performed on a Viglen Genie P590 Pentium PC with CRYSTALS-PC running under the Salford Software Services memory manager DBROS. Crystal data and structure refinement details are listed in Table 4.

[1,4-Me₂pyridinium] [Ph₂SnCl_{0.57}I_{0.43}(dmit)]. The structure was solved using direct methods, SIR92 [19], followed by CRYSTALS-PC [22] for Fourier and least squares refinement. A difference Fourier synthesis yielded a peak, which was identified as Cl. This was added to the cell contents and the I and Cl occupancies refined as a limited pair. The hydrogen atoms were placed in calculated positions with C–H=1.00 Å.

Restraints were applied to the refinement of the cation, which were on two inversion centres and the phenyl groups which were regulised before refinement. Computations were performed on a Viglen Genie P590 Pentium PC with CRYSTALS-PC running under the Salford Software Services memory manager DBROS. Crystal data and structure refinement details are listed in Table 4.

[1,4-Me₂pyridinium] [Ph₂SnI_{0.78}Cl_{0.22}(dmit)] and [1,4-Me₂pyridinium] [Ph₂SnI_{0.58}Cl_{0.42}(dmit)]. Cell dimensions were determined using 14 reflections at 8.5–8.7° in θ for [1,4-Me₂pyridinium] [Ph₂SnI_{0.78} Cl_{0.22}(dmit)] and at 8.6–9.1° in θ for [1,4-Me₂ pyridinium] [Ph₂SnI_{0.58}Cl_{0.42}(dmit)].

Data collection and cell refinement employed Nicolet P3 software [23]. Data collection used 2θ scan rates of 5.33 ($I_p < 150$) to 58.6 ($I_p > 2500$)°min⁻¹, where I_p was the prescan intensity. Scan widths were 2.4 to $2.7^{\circ} 2\theta$. Refinement was by full matrix least squares. The asymmetric unit consists of a single anion in one of the 4*e* general positions of P2₁/c and half of each of the two independent cations in the centrosymmetric 2b and 2c sites respectively. The cations are therefore disordered in terms of the position of the nitrogen atoms and all their constituent atoms were treated as C. In the final stages of refinement, the site occupancy factors of I and Cl were refined to give the best values of *R*.

The disorder of the cations and the partial occu-

0	1.4-Me ₂ pvr	Et.N	1.4-Me ₂ pyr	1.4-Me ₂ pyr	1.4-Me ₂ pvr
Ř	Ph	Ph	Ph	Ph	Ph
X	Br	I	Cl _{0.57} /I _{0.43}	Cl _{0.42} /I _{0.58}	Cl _{0.22} /I _{0.78}
Empirical formula	$C_{22}H_{20}BrNS_5Sn$	C ₂₃ H ₃₀ INS ₅ Sn	$C_{22}H_{20}Cl_{0.57}I_{0.43}NS_5Sn$	$C_{22}H_{20}Cl_{0.42}I_{0.58}NS_5Sn$	$C_{22}H_{20}Cl_{0.22}I_{0.78}NS_5Sn$
Formula wt	657.29	726.40	652.00	665.71	684.00
Temperature (K)	293(2)	298(2)	293	298	298
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions					
a (Å)	19.002(5)	16.614(5)	15.362(6)	15.354(11)	15.49(2)
b (Å)	9.479(5)	9.6722(12)	9.497(2)	9.504(5)	9.620(10)
<i>c</i> (Å)	15.395(5)	18.8005(6)	18.917(7)	19.960(12)	19.10(2)
β (°)	113.90(5)	97.64(4)	113.60(3)	113.79(6)	114.03(10)
Volume (Å ³)	2535.2(17)	2994.3	2524.5	2532(3)	2598(6)
Ζ	4	4	4	4	4
Density (calc.) (mg/m ³)	1.722	1.611	1.72	1.727	1.800
Absorption coefficient (mm ⁻¹)	3.007	2.223	2.01	2.08	2.56
F(000)	1296	1428	1285.9	1307.5	1336.3
Crystal size (mm)	$0.215 \times 0.072 \times 0.11$			$0.44 \times 0.42 \times 0.06$	$0.6 \times 0.2 \times 0.1$
Colour	orange	orange	orange	orange	orange
Theta range for data coll ⁿ (°)	2.20-25.02	0 to 23.7	1. 17 to 23.99	max. 25	max 25
Index ranges					
h	$-20 \le h \le 19$	$-22 \le h \le 21$	$-16 \le h \le 16$	$-16 \le h \le 16$	$-15 \le h \le 15$
k	$-10 \le k \le 10$	$0 \le k \le 13$	$0 \leq k \leq 10$	$0 \le k \le 11$	$0 \le k \le 10$
l	$0 \le l \le 17$	$0 \le l \le 25$	$0 \le l \le 21$	$0 \le l \le 22$	$0 \le l \le 21$
Reflections collected	7116	15349	4410	4966	5056
Independent reflections	4032	7529	3958	3528	3739
Observed reflections	2857 $[I > 2\sigma(I)]$	$1237 [I > 3\sigma(I)]$	2906 $[I > 3\sigma(I)]$	$1854 [F > 4\sigma(F)]$	2110 $[F > 4\sigma(F)]$
R _{int}	0.0745	0.10	0.034	0.059	0.086
Refinement method	Full-matrix l.s.	Full-matrix l.s.	Full-matrix l.s.	Full-matrix l.s.	Full-matrix l.s.
Number of parameters	273	180	281	276	272
Goodness-of-fit (S)	1.025	1.126	1.147		
Final <i>R</i> indices	$R1 = 0.0471; [I > 2\sigma(I)] wR2 = 0.1043$	R = 0.047, wR = 0.048	R = 0.049, wR = 0.054	R = 0.100, Rw = 0.107	R = 0.101, Rw = 0.107
R indices (all data)	R1 = 0.0668, wR2 = 0.1109		-		
Final weighting scheme	a	b	с	$w = 1[\sigma^2(F) + 0.011072 F^2)$	$w = 1/\sigma^2(F) + 0.005119 F^2$
Residual diffraction	1.289 (at Sn), -0.469	1.25, -0.92	0.95, -0.72	2.02, -1.78	1.71, -1.47

Table 4. Crystal data and structure refinement for [Q, R₂SnX(dmit)]

 ${}^{a}w = 1/[\sigma^{2}(F_{0}^{2}) + (0.0713 P)^{2}]$ where $P = (F_{0}^{2} + 2F_{c}^{2})/3$. ${}^{b}W = w[1 - \Delta F/6\sigma(F)^{2}]^{2}$ where w is calculated using a three term Chebychev series with coefficients: 12.7, -7.63 and 8.76 [28]. ${}^{c}W = w[1 - \Delta F/6\sigma(F)^{2}]^{2}$ where w is calculated using a three term Chebychev series with coefficients: 5.94, -1.39 and 4.57 [28].

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pancy of the halide sites, taken with the marginal quality of the crystals as evidenced by the poorly determined unit cells are all considered to be contributory factors to the relatively high *R* values for both compounds. No attempt was made to position or refine H. All computations were performed on the SUN SpARCserver (UNIX operating system) of the Computing Centre of Aberdeen University, SHELXS86 [24] and SHELX76 [25] were used for structure solution and refinement, respectively. Molecular graphics used are: PLOTAID [26] and ORTEX [27]. Crystal data and structure refinement details are listed in Table 4.

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