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Reaction of thiones with dihalogens; comparison of the solid state structures of 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione–diiodine, –dibromine and –iodine monobromide

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Reaction of 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione **1** with diiodine or iodine monobromide in CH_2Cl_2 resulted in the formation of molecular charge-transfer complexes $\mathbf{1}\cdot I_2$ and $\mathbf{1}\cdot IBr$ respectively. Both complexes have been characterised crystallographically and contain a linear S–I–X (X = I or Br) moiety with the sulfur adopting a tetrahedral geometry taking into account the stereochemically active lone pairs. The S–I [2.716(3)] and I–I [2.808(3) Å] bond lengths in $\mathbf{1}\cdot I_2$ are similar to those reported for diiodine complexes of related thione donors. The adduct $\mathbf{1}\cdot IBr$ is the first crystallographically characterised thione–iodine monobromide charge-transfer complex. The S–I distance [2.589(2) Å] is shorter than that in $\mathbf{1}\cdot I_2$, consistent with IBr being a stronger acceptor than I_2. The I–Br distance [2.7138(11) Å] is lengthened with respect to that in unco-ordinated IBr, but within bonding distance when compared to the sum of the van der Waals radii for iodine and bromine (3.75 Å). Treatment of **1** with dibromine under identical conditions resulted in the formation of the adduct $\mathbf{1}\cdot Br_2$ and the dithiolylium salt $[C_5H_6S_4Br][Br_3]\cdot\frac{1}{2}Br_2$ **2**. Treatment of **1** with Br_2 in toluene led to the isolation of $\mathbf{1}\cdot Br_2$ only. The crystal structure of $\mathbf{1}\cdot Br_2$ shows the compound to contain a linear Br–S–Br moiety with the sulfur in a T-shaped or Ψ-trigonal bipyramidal environment (taking into account the stereochemically active lone pairs). The structure of **2** reveals a three component system consisting of the $[C_5H_6S_4Br]^+$ cation, the $[Br_3]^-$ anion and a molecule of Br_2 in a 2 : 2 : 1 ratio. These components are held in the lattice by a series of weak intermolecular interactions which link the tribromide ions and dibromine molecules into zigzag chains.

Introduction

The adducts formed through the interaction of dihalogens with triorgano Group 15[1,2] and diorgano Group 16[3–19] molecules play pivotal roles in a variety of chemical scenarios, ranging from organic and inorganic synthesis to biological processes and materials chemistry. Therefore, detailed knowledge of the structural nature of these adducts is essential if we are fully to understand their efficacy and the mechanisms by which they react.

The donor–dihalogen interaction can proceed *via* a number of pathways, resulting in the formation of a variety of products, for example: a simple molecular ‘donor–acceptor’ or ‘charge-transfer’ complex;[1–14] homolytic cleavage of the dihalogen bond with the concomitant formation of two donor–halide bonds;[1,15,16] the dihalogen may undergo heterolytic cleavage with the formation of halogen(I) salts;[17] in the presence of an excess of dihalogen, polyhalide salts may result;[3e,9,10] the adduct formed *in situ* may experience further spontaneous chemical reaction resulting in the formation of new products which are not simple adducts. The past decade has witnessed a massive increase in the quantity of available structural data on all the above types of product (led by seminal contributions from the group of McAuliffe[1] and others), which show that the pathway followed, and hence the product formed, is influenced not only by the donor and the dihalogen acceptor, but also by external factors such as the molar ratio of the reactants, the solvent and the reaction conditions.

Thiones (thiocarbonyls) present a large class of particularly useful donors, the dihalogen adducts of which have received attention in areas as diverse as the treatment of hyperthyroidism[18] and molecular electronics.[19] The structural nature of the diiodine adducts is, in general, well established.[3–11] However, there have been fewer studies into the interaction of thiones with the lighter dihalogens or interhalogens and only limited structural data are available.[15] Furthermore, few comparative studies have been carried out, in contrast to the situation for other classes of donor. Here we describe the structural nature of the adducts formed from the interaction of diiodine, iodine monobromide and dibromine with 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione **1**,[20] a heterocyclic sulfur rich thione which has been used as a building-block in tetrathiafulvalene-type materials chemistry.[21] This work represents the first comparative study of the interaction of a thione with these acceptors.

Results and discussion

The reactions of compound **1** with X_2 ($X_2 = I_2$, IBr or Br_2) are summarised in Scheme 1. Addition of I_2 or IBr to an equimolar quantity of **1** dissolved in refluxing dichloromethane resulted in the formation of an orange-red solution which deposited large brown crystals of $\mathbf{1}\cdot I_2$ (85% yield) or $\mathbf{1}\cdot IBr$, in quantitative yield, when cooled to −5 °C overnight. However, treatment of a solution of **1** in refluxing dichloromethane with Br_2 produced, after cooling, a brown microcrystalline powder, $\mathbf{1}\cdot Br_2$, in 50% yield. The brown solid was removed by filtration and the dichloromethane of the filtrate allowed to evaporate, yielding a purple oil, from which a small crop of purple crystals was

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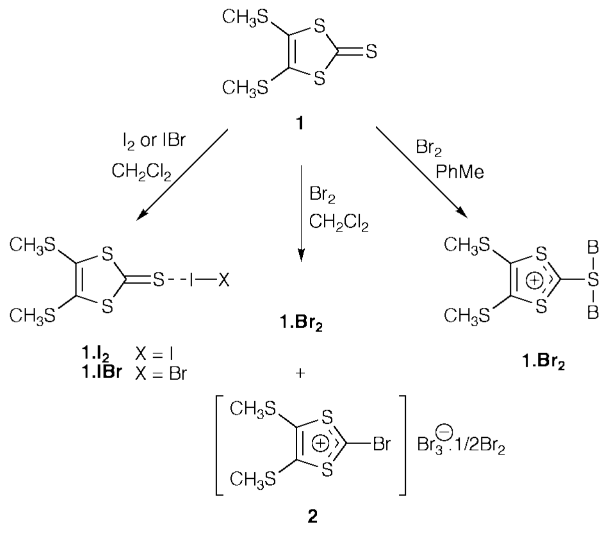


Scheme 1

deposited (10% yield). These purple crystals, which emitted pungent fumes of dibromine, were identified as dithiolylium salt **2** by X-ray crystallography. The salt **2** was found to be hygroscopic and decomposed slowly upon standing. The reaction of **1** and Br_2 was repeated using toluene as the solvent; on cooling, **1**·Br_2 was obtained as an orange-brown crystalline solid in 54% yield. It is worth noting that the presence of **2** was not detected in this reaction.

We have investigated the three dihalogen adducts of compound **1** using a combination of low frequency FT-Raman and FTIR spectroscopy. In particular, Raman spectroscopy provides a sensitive probe for the elucidation of charge-transfer interactions between donors and dihalogens, by means of a shift in the ν(X–X) vibrations in the complex, with respect to those in the free acceptors.[11] The Raman spectrum of **1**·I_2 contains a strong band at 135 cm^{-1} due to ν(I–I) in the charge-transfer complex. As expected, the value is shifted to a lower frequency from a value of 180 cm^{-1} seen for solid I_2, consistent with the decrease in the I–I bond order when diiodine interacts with a donor. The position of the ν(I–I) band of **1**·I_2, and the magnitude of the shift of ν(I–I) from free I_2 (45 cm^{-1}), concur with those for I_2 complexes of other thione donors.[6,7,11] Similarly, **1**·IBr exhibits a ν(IBr) band at 144 cm^{-1}, which is shifted considerably from the value of 262 cm^{-1} of solid IBr. The magnitude of the shift for **1**·IBr (118 cm^{-1}) is much greater than that for **1**·I_2 (45 cm^{-1}), since IBr is a better acceptor than I_2. The Raman spectrum of **1**·Br_2 contains a strong band at 162 cm^{-1}, attributable to symmetric Br–S–Br stretching.

The FTIR spectra of adducts **1**·I_2, **1**·IBr and **1**·Br_2 are very similar to that of the unco-ordinated donor **1**. The principal peak in the IR spectrum of **1** is a band at 1067 cm^{-1}, which can be attributed to an out-of-phase combination of the ν(C–S) and ν(SCS) stretching vibrations, coupled with the δ(CSS) deformation.[6,7] As expected, the co-ordination of a dihalogen to **1** results in a shift to a lower frequency for this band; thus, strong peaks are observed at 1017, 1030 and 991 cm^{-1} for **1**·I_2, **1**·IBr and **1**·Br_2, respectively.

The solid state structures of compounds **1**·I_2, **1**·IBr and **1**·Br_2 are shown in Figs. 1, 2 and 3 respectively. Selected geometry parameters for the three compounds are given in Table 1. The S···X and X–X distances for some related dihalogen complexes are collated in Table 2 for comparison. Compounds **1**·I_2 and **1**·IBr are molecular "charge-transfer" adducts containing linear S···I–X linkages. The S···I–I and S···I–Br angles are 177.46(7) and 175.63(5)° respectively. The molecular structure of "donor–acceptor" or "charge-transfer" complexes is relatively well understood; transfer of electron density from a lone pair of the donor to the σ^* antibonding orbital of the dihalogen leads to the formation of a donor–halogen bond with the concomitant elongation of the X–X bond. This is illustrated for thiones in Scheme 2. The sulfur atom of the thione (thiocarbonyl) donor is sp^2 hybridised with a double bond to the adjacent carbon atom and should be a reasonably good donor of electrons towards dihalogens. The ability of thiones to delocalise the positive charge onto the carbon atom of the C–S bond provides an additional factor which helps to stabilise the S–X–X interaction (Scheme 2). Thus, thiones should form stronger S–X bonds than, for example, the sp^3 hybridised sulfur in a thioether, which does not have the ability to delocalise the positive charge. Moreover, the complexes derived from the donor **1** are further stabilised by the resonance contribution of the 1,3-dithiole sulfur atoms (Scheme 2), such that the positive charge is delocalised over the S(1)–C(2)–S(3) fragment of the ring, forming a 6π pseudo-aromatic system. All three dihalogen adducts reported here provide good evidence for this. Ligand **1** contains sulfur atoms in three distinct environments; the thione sulfur (sp^2 hybridised), the two dithiole sulfurs and the two thioether sulfurs (all of which are sp^3 hybridised). In **1**·I_2, **1**·IBr and **1**·Br_2 the halogen atoms only interact with the thione sulfur. No interaction is observed between halogen atoms and the thioether or dithiole sulfurs. The thione C–S bonds in **1**·I_2 and **1**·IBr are longer than a typical carbon–sulfur double bond (1.60 Å)[22] but shorter than a carbon–sulfur single bond (1.82 Å)[22] consistent with the delocalisation of some positive charge on the C–S bond but retaining significant double bond character. The S···I distances in **1**·I_2 and **1**·IBr are 2.716(3) and 2.589(2) Å respectively; these values are longer than those expected on the basis of the sum of the covalent radii of sulfur

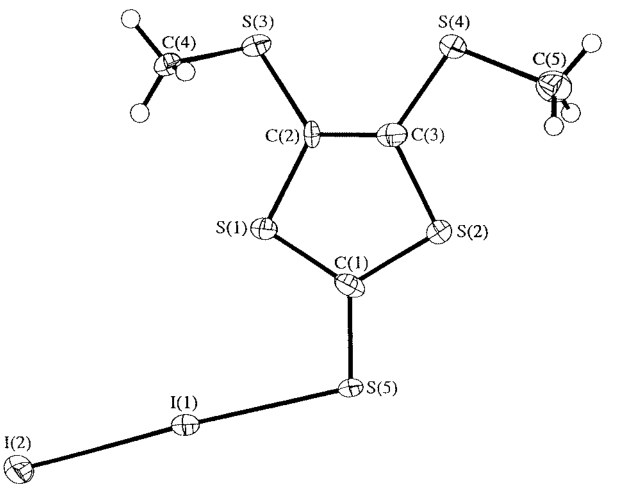
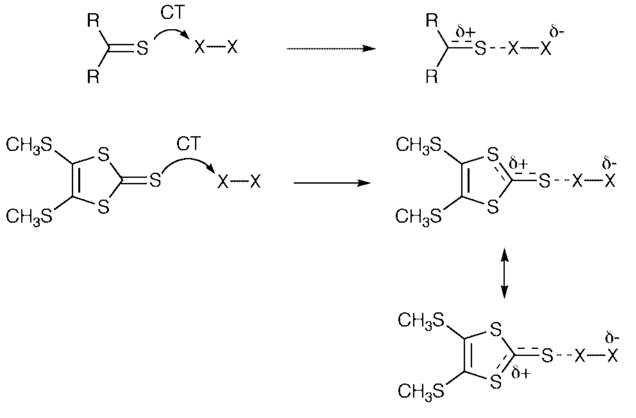


Fig. 1 Solid state structure of adduct **1**·I_2 showing the atom numbering scheme. The thermal ellipsoids are drawn at 50% probability level.



Scheme 2

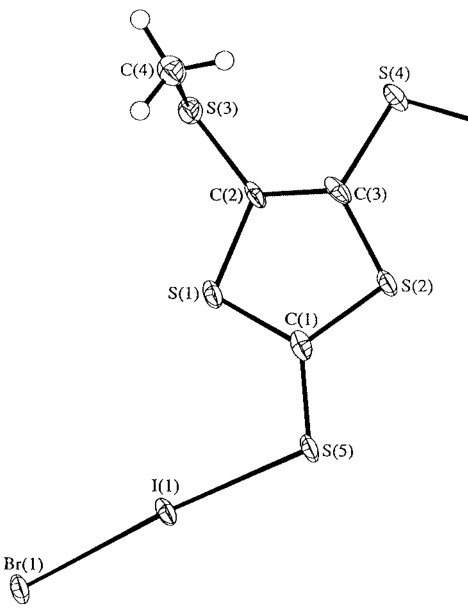


Fig. 2 Solid state structure of adduct **1**·IBr showing the atom numbering scheme. The thermal ellipsoids are drawn at 50% probability level.

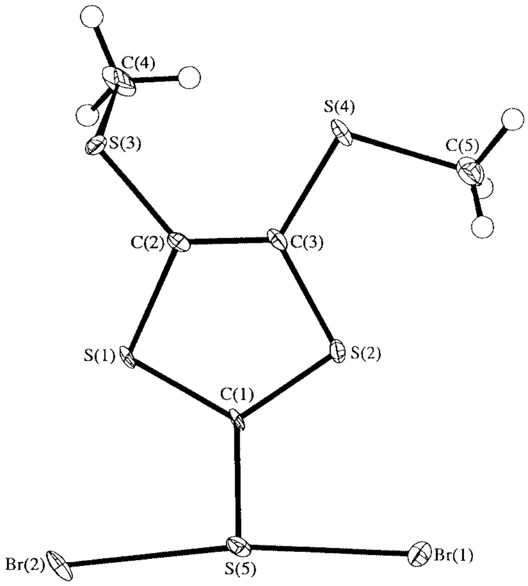


Fig. 3 Solid state structure of adduct **1**·Br_2 showing the atom numbering scheme. The thermal ellipsoids are drawn at 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) in adducts **1**·I_2, **1**·IBr and **1**·Br_2

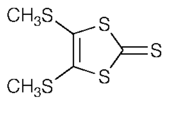
	1·I_2	**1**·IBr	**1**·Br_2
I(1)–I(2)/Br(1)	2.8083(14)	2.7138(11)	
S(5)–I(1)	2.716(3)	2.589(2)	
S(5)–Br(1)			2.496(4)
S(5)–Br(2)			2.437(4)
S(5)–C(1)	1.666(11)	1.688(8)	1.75(2)
S(1)–C(1)	1.663(13)	1.693(7)	1.71(2)
S(2)–C(1)	1.701(12)	1.712(8)	1.680(12)
S(1)–C(2)	1.703(11)	1.728(8)	1.739(14)
S(2)–C(3)	1.742(11)	1.730(8)	1.75(2)
C(2)–C(3)	1.31(2)	1.348(11)	1.34(2)
S(5)–I(1)–I(2)/Br(1)	177.46(7)	175.63(5)	
Br(1)–S(5)–Br(2)			171.6(2)
C(1)–S(5)–I(1)	101.9(4)	105.5(3)	
C(1)–S(5)–Br(1)			92.7(5)
C(1)–S(5)–Br(2)			95.7(5)
S(1)–C(1)–S(5)	125.0(7)	126.1(5)	120.7(7)
S(2)–C(1)–S(5)	119.9(7)	119.6(4)	123.9(9)
S(1)–C(1)–S(2)	115.1(7)	114.3(5)	115.4(8)

and iodine (1.02 + 1.33 = 2.35 Å),[22] but are also much shorter than the corresponding sum of the van der Waals radii (1.80 + 1.95 = 3.75 Å),[22] and are therefore indicative of definite S–I bonds. The S–I distance in **1**·IBr is shorter than that in **1**·I_2 reflecting the greater acceptor strength of IBr over I_2. No other structural data have been reported for a thione–IBr donor–acceptor complex, though data are available for IBr complexes of several other sulfur donors (Table 2). The S–I distance in **1**·IBr is shorter and the I–Br distance longer than the equivalent distances in IBr complexes of other sulfur donors.[12–14] This is not unexpected, since these complexes all contain sp^3 hybridised sulfurs or, in the case of Ph_3PS·IBr, an sp^2 hybridised sulfur atom bonded to a triphenylphosphine group, which is less effective at stabilising the accepted positive charge than is the heterocycle **1**. Consistent with this, the ν(I–Br) band in the Raman spectrum of **1**·IBr (144 cm^{-1}) occurs at a much lower frequency than the equivalent bands of [14]aneS_4·2IBr (184 cm^{-1}),[12] [16]aneS_4·4IBr (184, 164 cm^{-1}),[12] [18]aneS_6·2IBr (182 cm^{-1})[12] and Ph_3PS·IBr (206, 164 cm^{-1}).[13] The I–I and I–Br bonds in **1**·I_2 and **1**·IBr, respectively, are lengthened compared to the bonds in unco-ordinated I_2 [d_{I-I} = 2.715(6) Å[23] in the solid state, 2.667(2) Å[24] in the gas phase] and IBr [d_{I-Br} = 2.521(4) Å[25] in the solid state, 2.470(5) Å[26] in the gas phase], but are well within bonding distance when compared with the van der Waals radii of I_2 (3.40 Å)[22] and IBr (3.75 Å).[22] As can be seen from Figs. 1 and 2, the orientation of the S···I–X units in these two compounds is similar, whereas those of the S–CH_3 substituents are quite different.

The S–I distance in thione–diiodine complexes (Table 2) lies in the range 2.61 to 2.92 Å [shorter distances are observed in complexes where the diiodine is interacting with a second molecule of diiodine, *e.g.* ethylenethiourea–diiodine(1/2),[10] d_{S-I} 2.487(3) Å]. The S–I distance in **1**·I_2 falls within this range. Not surprisingly, the S–I distance in **1**·I_2 is virtually identical to those determined for the diiodine complexes of other sulfur-rich thiones, *i.e.* **3**·I_2, **4**·I_2 and **5**·I_2. Since there is usually a reciprocal relationship between the D–I and I–I bond lengths in D–I–I complexes one might expect the I–I distance in **1**·I_2 to be similar to those in **3**·I_2, **4**·I_2 and **5**·I_2. However, it is significantly shorter, indicating the absence of any secondary intermolecular interactions involving the S–I–I unit in **1**·I_2. In **1**·I_2 the molecules exist as discrete units within the crystal and pack parallel to (110) as shown in Fig. 4. The shortest contacts involving the neighbouring molecules are: 3.549 [S(3)···C(1) $(0.5 - x, 0.5 + y, -0.5 - z)$], 3.653 [S(3)···S(5) $(0.5 - x, 0.5 + y, -0.5 - z)$] and 3.660 Å [S(5)···I(2) $(0.5 + x, 0.5 - y, -0.5 - z)$], which indicate the absence of any significant stacking interactions. In **1**·IBr the molecules are packed parallel to (010) as shown in Fig. 5, but in this case several intermolecular contacts are identified which are significant and indicative of stacking interactions: 3.357 [S(3)···S(3) $(1 - x, 1 - y, 2 - z)$], 3.379 [S(2)···Br(1) $(x, -1 + y, z)$] and 3.445 Å [S(5)···Br(1) $(x, -1 + y, z)$].

The structure of adduct **1**·Br_2 is very different from those of **1**·I_2 and **1**·IBr, since the Br–Br bond of dibromine is completely broken and the compound has a three-co-ordinated sulfur atom and two terminal S–Br bonds. The geometry about the thione-sulfur atom is T-shaped or Ψ-trigonal bipyramidal taking into account the stereochemically active lone pairs (VSEPR model).[22] This contrasts neatly with **1**·I_2 and **1**·IBr in which the thione-sulfur has a bent or approximately tetrahedral geometry. The Br(1)–S(5)–Br(2) angle at 171.6(2)° is almost linear. The S(5)–Br distances, 2.437(4) and 2.496(4) Å, are of unequal length and considerably longer than the appropriate covalent radii sum (1.02 + 1.14 = 2.16 Å),[22] but well within bonding distance when compared with the sum of the van der Waals radii of bromine and sulfur (1.8 + 1.8 = 3.6 Å).[22] Similar asymmetry has been observed in the related compound **6**·Br_2 (Table 2) and

Table 2 Geometrical details for S–I–X and X–S–X moieties in dihalogen adducts of sulfur donor ligands



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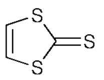

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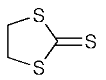

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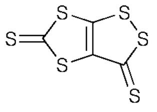

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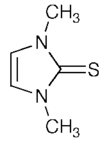

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Thione-diiodine complexes	S–I	I–I	S–I–I	Ref.
6·I_2	2.616(6)	2.967(12)	175.71(1)	9
	2.607(6)	2.984(12)	177.11(4)	
1,1′-Ethylene-bis(3-methyl-4-imidazoline-2-thione)·$2I_2$	2.642(3)	2.903(2)	177.0(1)	5(*a*)
1,5-Diphenylthiocarbazone·I_2	2.664(3)	2.918(1)	178.4(1)	10
1,1′-Methylene-bis(3-methyl-4-imidazoline-2-thione)·$2I_2$	2.683(2)	2.897(1)	175.71(3)	5(*a*)
N-Methylthiocaprolactam·I_2	2.688(2)	2.880(1)	176.21(4)	5(*d*)
4·I_2	2.715(4)	2.823(2)	176.5(1)	6
3·I_2	2.715(5)	2.843(2)	176.7(1)	7
1·I_2	2.716(3)	2.8083(14)		*a*
5·I_2	2.719(6)	2.841(2)		8
5,5-Dimethylimidazolidine-2,4-dithione·$2I_2$	2.737(1)	2.849(1)	177.94(4)	11
	2.844(1)	2.767(1)	173.74(4)	
5,5-Dimethylimidazolidine-2,4-dithione·I_2	2.748(1)	2.817(1)	176.89(2)	11
5,5-Dimethyl-2-thioxoimidazolidine-4-one·I_2	2.737(1)	2.802(1)	176.14(2)	11
4,5,6,7-Tetrathiocino[1,2,-*b*:3,4-*b*′]-diimidazolyl-1,3,8,10-tetraethyl-2,9-dithiole·$2I_2$	2.775(4)	2.822(2)	174.8(1)	5(*b*)
2(Morpholinothiocarbonyl)·$2I_2$	2.920(6)	2.751(2)	175.5(1)	5(*c*)
	2.789(6)	2.805(3)	174.7(1)	
	2.892(6)	2.738(2)	173.9(2)	
	2.801(6)	2.787(3)	176.5(2)	
Sulfur donor–iodine monobromide complexes	S–I	I–Br	S–I–Br	
1·IBr	2.589(2)	2.7138(11)		*a*
[14]aneS_4·2IBr	2.678(1)	2.654(2)	175.53(4)	12
[16]aneS_4·4IBr	2.618(2)	2.7049(11)	177.65(5)	12
	2.687(2)	2.6445(12)	177.57(5)	
[18]aneS_6·2IBr	2.619(3)	2.695(2)	175.00(6)	12
Ph_3PS·IBr	2.665(1)	2.668(1)	175.08(2)	13
Dithiacyclohexane·2IBr	2.687(2)	2.646(1)	178.2(4)	14
Thione-dibromine adducts	S–Br		Br–S–Br	–
1·Br_2	2.496(4)		171.6(2)	*a*
	2.437(4)			
6·Br_2	2.520			15
	2.477			

[a] This work.

in the dibromine complexes of several selenium donors.[16,27,28] In the latter cases the differences in the Se–Br bond lengths have been attributed to the existence of weak Se···Br[27] or Br···Br[28] interactions within the crystal lattice. The packing of molecules in **1**·Br_2 (Fig. 6) is similar to that of **1**·IBr, with interlayer distances of 3.675 [S(1)···Br(1) ($-x$, $1-y$, $-z$)], 3.685 [S(1)···Br(1) ($1-x$, $1-y$, $-z$)], 3.683 [S(2)···Br(2) ($-x$, $1-y$, $-z$)], 3.514 [S(5)···C(3) ($1-x$, $1-y$, $-z$)] and 3.357 Å [S(1)···C(5) ($-x$, $1-y$, $-z$)]. The thiocarbonyl bond in **1**·Br_2 is significantly longer than those in **1**·I_2 or **1**·IBr and is closer to that expected for a single C–S bond. We have calculated the C–S bond orders in the three complexes (using the method of Husebye *et al.*);[4] the values are 1.515, 1.366 and 1.05 for **1**·I_2, **1**·IBr and **1**·Br_2 respectively. Thus, both **1**·I_2 and **1**·IBr retain significant multiple bond character whereas **1**·Br_2 shows very little.

The C_3S_2 heterocycles in all three complexes are planar, the maximum deviations of any atom from the respective mean planes being 0.019(5), 0.005(5) and 0.019(5) Å for **1**·I_2, **1**·IBr and **1**·Br_2, respectively. The S(5) atom is coplanar with the ring plane in **1**·I_2 [deviation = 0.001(10) Å] but is significantly out of the respective planes in **1**·IBr [0.093(15)Å] and **1**·Br_2 [0.051(15) Å]. The S(5)–I(1)–X (X = I or Br) moieties in **1**·I_2 and **1**·IBr are coplanar with their respective C_3S_2 heterocycles as shown by the I(1)–S(5)–C(1)–S(1) torsion angles of −1.5(9)° in **1**·I_2 and 6.5(6)° in **1**·IBr. The Br(2)–S(5)–C(1)–S(1) torsion angle in **1**·Br_2 is 1.5(7)°, which shows that the SBr_2 moiety in this molecule is also coplanar with the associated C_3S_2 ring.

The formation of dithiolylium salt **2**, together with **1**·Br_2, on addition of Br_2 to compound **1** in dichloromethane was totally unexpected, although the analogous bromine salt **7** has been prepared by the reaction of dibromine with *N*-methyl-1,3-thiazolidine-2(3*H*)-selone.[16,27] Additionally, previous workers[29] have reported the isolation of the 2-chloro-1,3-dithiolylium salt **8**, which was obtained *via* the reaction of **1** and phosphorus pentachloride. The formation of **2** proceeds in dichloromethane

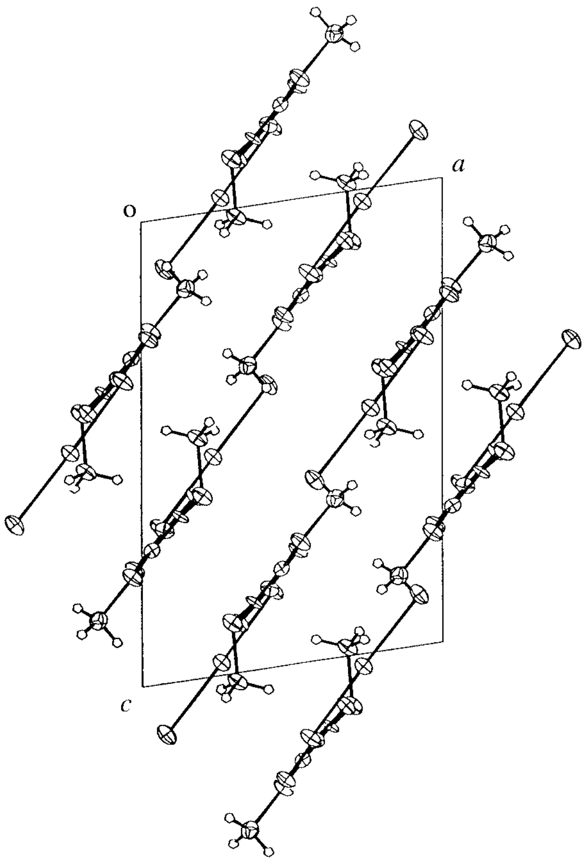


Fig. 4 Unit-cell contents of adduct **1**·I_2 viewed along the *b* axis.

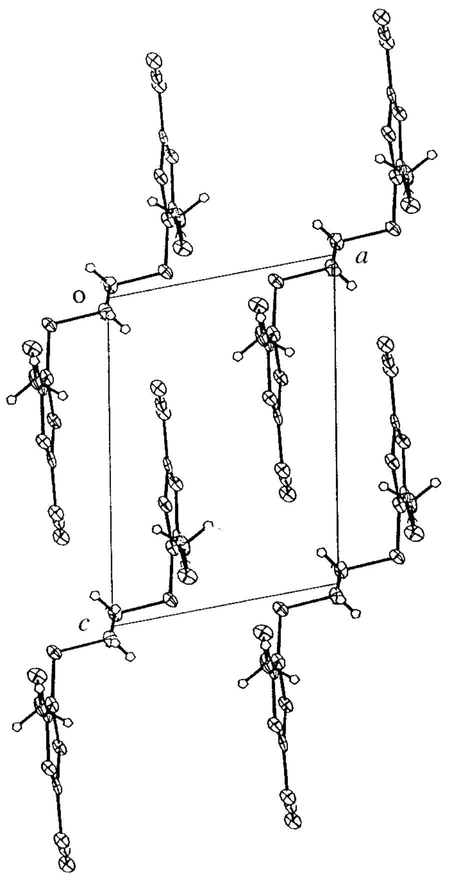


Fig. 5 Unit-cell contents of adduct **1**·IBr viewed along the *b* axis.

but not in toluene, suggesting that the polarity of the solvent and hence the polarisation of the intermediates/reagents is an important factor in the reaction mechanism.

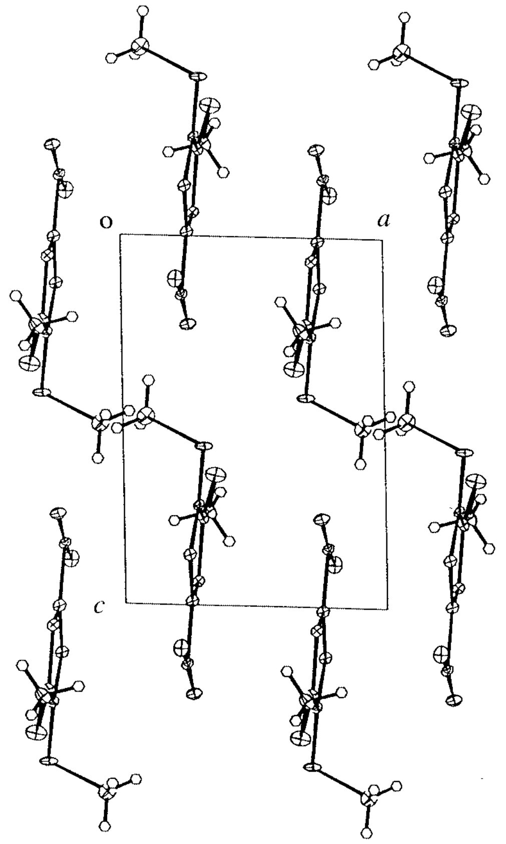


Fig. 6 Unit-cell contents of adduct **1**·Br_2 viewed along the *b* axis.

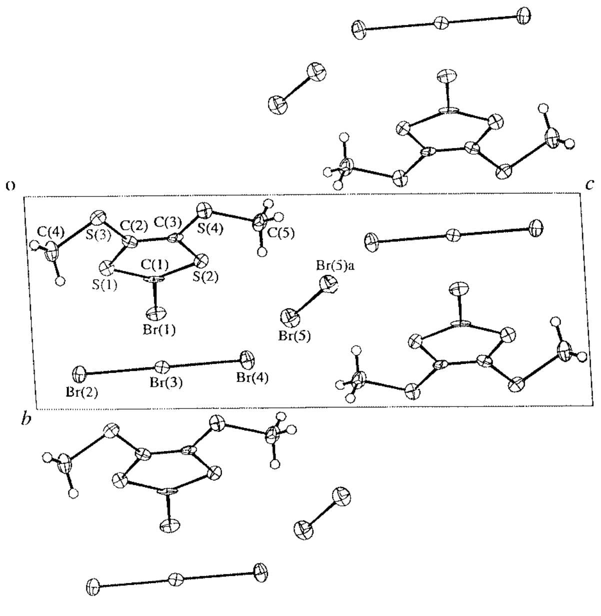


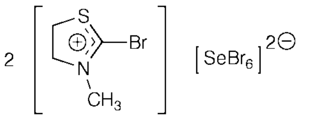
Fig. 7 Unit-cell contents of compound **2** viewed along the *a* axis. The thermal ellipsoids are drawn at 50% probability level. The atom numbering is shown for the asymmetric unit.

The structure of compound **2** is shown in Fig. 7. Selected bond lengths and angles are listed in Table 3. The compound consists of a dithiolylium cation and a tribromide anion together with a molecule of dibromine occluded in the lattice, akin to a solvent of crystallisation. The ratio of the above species in this compound is 2:2:1. The tribromide anion is virtually linear [178.14(5)°], as expected for a trihalide anion,[30] and lies sandwiched between two dithiolylium cations. The Br–Br bond lengths are unsymmetrical, Br(3)–Br(4) [2.555(2) Å], Br(2)–Br(3) [2.512(2) Å], but are similar to those reported in other salts containing this ion.[30] The Br–Br bond of the

Table 3 Selected bond lengths (Å) and angles (°) in compound **2**

Br(2)–Br(3)	2.512(2)	S(2)–C(3)	1.711(10)
Br(3)–Br(4)	2.555(2)	S(3)–C(2)	1.743(10)
Br(5)–Br(5)[a]	2.329(2)	S(3)–C(4)	1.776(10)
Br(1)–C((1)	1.865(9)	S(4)–C(3)	1.739(10)
S(1)–C(1)	1.648(11)	S(4)–C(5)	1.773(10)
S(1)–C((2)	1.719(10)	C(2)–C(3)	1.36(2)
S(2)–C(1)	1.668(11)		
Br(4)···Br(5)	3.214	Br(2)···Br(2)[b]	3.439
Br(2)–Br(3)–Br(4)	178.14(5)	C(3)–S(4)–C(5)	100.8(5)
C(1)–S(1)–C(2)	95.9(5)	S((1)–C(1)–S(2)	117.7(6)
C(1)–S(2)–C(3)	95.4(5)	S(1)–C(1)–Br(1)	121.5(6)
C(2)–S(3)–C(4)	102.0(5)	S(2)–C(1)–Br(1)	120.7(6)
Br(3)–Br(4)–Br(5)	117.69	Br(4)–Br(5)–Br(5a)	172.37

Symmetry operator: [a] $1-x, 1-y, 1-z$. [b] $-x, 2-y, -z$.



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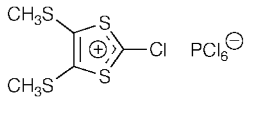

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occluded Br_2 molecule [2.329(2) Å] is considerably shorter than the Br–Br distances in the $[Br_3]^-$ ion, but somewhat longer than that in crystalline Br_2 [2.27 Å].[31] There are several short contacts involving the $[Br_3]^-$ ion and of the Br_2 molecule with the dithiolylium cation, the most important of which are: 3.525 [Br(3)···C(1)], 3.196 [Br(1)···Br(3) $(-1+x, y, z)$], 3.643 [Br(2)···S(1) $(x, 1+y, z)$], 3.506 Å [Br(2)···S(3) $(-1+x, 1+y, z)$], 3.627 [Br(3)···C(2) $(x, 1+y, z)$], 3.557 [Br(3)···C(3) $(x, 1+y, z)$], 3.668 [Br(4)···S(4) $(-1+x, 1+y, z)$] and 3.501 Å [Br(4)···C(5) $(-x, 1-y, 1-z)$]. All these weak interactions hold the three different chemical species in the crystal. However, the most important are weak interactions between the $[Br_3]^-$ ions and the Br_2 molecule [Br(4)···Br(5) 3.214 Å] and between two adjacent $[Br_3]^-$ anions [Br(2)···Br(2) 3.439 Å], which link the tribromide ions and the dibromine molecules into 'zigzag' chains. Polybromide ions, other than the tribromide ion, are rare[30,32] and can generally be considered as an assemblage of tribromide ions and dibromine molecules linked by weak interactions, as is observed here for **2**; for example, the $[Br_{10}]^{2-}$ ion consists of two tribromide ions and two dibromine molecules.[32] Similarly, the inclusion of a molecule of dibromine within the lattice of **2** is also rare, but not unknown: the salts $[Me_4N][Sb_2Br_9]\cdot Br_2$[33] and $[TeBr_3][AuBr_4]\cdot\frac{1}{2}Br_2$[34] have been characterised crystallographically. The dibromine molecule in $[Me_4N][Sb_2Br_9]\cdot Br_2$ acts as a bridge between two $[Sb_2Br_9]^-$ anions. The Br–Br bond distance [2.31(3) Å] is similar to that in **2** [2.329 (2) Å], and both are significantly longer than the Br–Br distance in dibromine [2.27 Å]; the elongation in the Br–Br distance is probably due to intermolecular interactions. The dibromine molecule in $[TeBr_3][AuBr_4]\cdot\frac{1}{2}Br_2$ has a Br–Br distance of 2.294(8) Å, much shorter than those in **2** or $[Me_4N][Sb_2Br_9]\cdot Br_2$, indicative of the absence of any significant intermolecular interactions.

In the structure of compound **2** the cationic heterocycle is planar within 0.015(4) Å and the Br(1) atom shows a displacement of 0.170(13) Å from this plane with a concomitant C(2)–S(1)–C(1)–Br(1) torsion angle of 174.0(6)°. Replacement of the thione-sulfur atom with a bromine atom and the associated positive charge do not have any appreciable effect on the bond lengths and angles of the ring, other than a slight increase in the C(1)–S(1)/(2) bond distances and an increase in the S(1)–C(1)–S(2) bond angle. As observed for **1**·I_2, **1**·IBr and **1**·Br_2, the two $S–CH_3$ groups on the ring are oriented differently as shown by the torsion angles C(4)–S(3)–C(2)–C(3) 154.5(8) and C(5)–S(4)–C(3)–C(2) 172.9(8)°.

Conclusion

We have demonstrated that the solid-state structures adopted by thione–dihalogen adducts, $R_2C{=}S\cdot X_2$, are dependent upon the nature of the halogen X_2. When $X_2 = I_2$ or IBr the molecular 'charge-transfer' adducts are obtained, containing linear S···I–X (X = I or Br) moieties in which the sulfur atom is in a Ψ-tetrahedral environment (taking into account the stereochemically active lone pairs). However, when $X_2 = Br_2$ homolytic cleavage of dibromine occurs, with concomitant formation of two S–Br bonds. The Br–S–Br moiety is linear and the sulfur atom adopts a T-shaped (or Ψ-trigonal bipyramidal) geometry. The geometric dependence of the thionyl sulfur atom in $R_2C{=}S\cdot X_2$ upon X (X = I or Br) is clearly established.

The FT-Raman spectra of the three adducts confirm the observed structural features. Although thione–diiodine complexes have been widely investigated, there is a paucity of comparative data on adducts of the lighter halogens and interhalogens which is readdressed to some extent in this study. The solvent dependency of the reactions of Group 15 or 16 donors with dihalogens or interhalogens is illustrated by the reaction of **1** with Br_2: when the reaction is carried out in toluene, the adduct of **1**·Br_2 is the sole product; however, in dichloromethane **1**·Br_2 is obtained, together with the dithiolylium salt **2** which contains an unusual dibromine of crystallisation.

Experimental

4,5-Bis(methylsulfanyl)-1,3-dithiole-2-thione **1** was prepared as described.[20] Iodine, iodine monobromide and bromine were purchased from Aldrich and used as received.

Melting points were taken using an Electrothermal Melting Point apparatus and are uncorrected. Infrared spectra were recorded on a Mattson Genesis Series FTIR spectrometer. Elemental analyses were carried out by MEDAC Ltd. Raman spectra were obtained from a Renishaw Ramascope 1000 Raman Microscope. The laser used was a 780 nm near IR laser. All spectra were recorded using a 200 exposure 'extended' scan between 3400 and 300 cm^{-1} and a 0.5 s static scan at lower wavenumbers.

Preparations

4,5-Bis(methylsulfanyl)-1,3-dithiole-2-thione–diiodine 1·I_2. To a solution of compound **1** (260 mg, 1.15 mmol) in dichloromethane (50 ml) was added iodine (290 mg, 1.14 mmol) in one portion. The mixture was stirred at room temperature for 2 h, followed by cooling at −5 °C over 16 h. The reaction contents were filtered and the solids washed with diethyl ether (2 × 25 ml) to give **1**·I_2 as a brown crystalline material (470 mg, 85% yield); mp 62–64 °C (Found: C, 12.77; H, 1.32; S, 33.77. $C_5H_6I_2S_5$ requires C, 12.51; H, 1.26; S, 33.38%); $\tilde{\nu}_{max}/cm^{-1}$ 1443, 1308, 1017 (C–S), 532 and 458.

4,5-Bis(methylsulfanyl)-1,3-dithiole-2-thione–iodine monobromide 1·IBr. To a solution of compound **1** (400 mg, 1.77 mmol) in dichloromethane (100 ml) was added iodine monobromide (400 mg, 1.93 mmol) in one portion. The reaction mixture was refluxed for 5 min, followed by cooling at −5 °C over 16 h. The product was filtered off and washed with diethyl ether (2 × 25 ml) to give **1**·IBr as an orange-brown crystalline solid (760 mg, 99% yield); mp 98–100 °C (Found: C, 13.74; H, 1.46; S, 37.74. $C_5H_6BrIS_5$ requires C, 13.86; H, 1.40; S, 37.00%); $\tilde{\nu}_{max}/cm^{-1}$ 1435, 1302, 1030 (C–S), 973 and 463.

4,5-Bis(methylsulfanyl)-1,3-dithiole-2-thione–dibromine 1·Br_2 (Method A) and 2-bromo-4,5-bis(methylsulfanyl)-1,3-dithiolylium tribromide–bromine [2/1] 2. To a solution of compound **1** (400 mg, 1.77 mmol) in dichloromethane (100 ml) was added bromine (0.1 ml, 1.94 mmol) dropwise. The reaction mixture was refluxed for 5 min, followed by cooling at −5 °C

Table 4 Crystal data and details of data collection and structure refinement for adducts $\mathbf{1}\cdot I_2$, $\mathbf{1}\cdot IBr$, $\mathbf{1}\cdot Br_2$ and **2**

	$\mathbf{1}\cdot I_2$	$\mathbf{1}\cdot IBr$	$\mathbf{1}\cdot Br_2$	**2**
Chemical formula	$C_5H_6I_2S_5$	$C_5H_6BrIS_5$	$C_5H_6Br_2S_5$	$C_5H_6Br_4S_4\cdot\frac{1}{2}Br_2$
Formula weight	480.21	433.21	386.22	593.89
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	9.037(3)	7.5933(12)	6.9403(9)	6.4872(6)
b/Å	9.606(2)	8.601(2)	8.3128(14)	7.0403(9)
c/Å	13.906(5)	10.8848(14)	10.554(4)	17.166(4)
α/°	—	110.710(8)	69.042(13)	84.060(10)
β/°	98.57(2)	91.227(9)	87.146(11)	80.958(9)
γ/°	—	111.989(13)	87.880(8)	69.198(9)
V/Å^3	1193.7(6)	606.8(2)	567.8(2)	722.8(2)
Z	4	2	2	2
μ(Mo-Kα)/cm^{-1}	60.92	67.41	80.03	144.40
Reflections collected	3811	2681	1981	3011
Unique reflections	1729	1694	1181	1973
R_{int}	0.0646	0.0672	0.0778	0.0615
Final $R1$, $wR2$	0.0675 (0.0514)[a] 0.1258 (0.1187)[a]	0.0418 (0.0382), 0.1042 (0.1031)	0.0590 (0.0492), 0.1346 (0.1325)	0.0534 (0.0450), 0.1136 (0.1116)

[a] Values for all unique data; those calculated for data with $I > 2\sigma(I)$ are given in parentheses.

over 16 h. The solution was filtered and the solid washed with diethyl ether (2 × 25 ml) to give $\mathbf{1}\cdot Br_2$ as a brown powder (340 mg, 50% yield). After slow evaporation of the filtrate a purple oil was obtained, from which dark red crystals of **2** were obtained after 16 h under ambient conditions (120 mg, 10% yield). $\mathbf{1}\cdot Br_2$: mp 72 °C (decomp.) (Found: C, 16.00; H, 1.70; S, 41.09. $C_5H_6Br_2S_5$ requires C, 15.55; H, 1.57; S, 41.51%); $\tilde{\nu}_{max}$/cm^{-1} 1434s, 1312, 1058, 1043, 991 (C–S), 964 and 465. **2**: $\tilde{\nu}_{max}$/cm^{-1} 1262, 1096, 1024 and 803.

Method B. To a solution of compound **1** (400 mg, 1.77 mmol) in toluene (50 ml) was added bromine (0.1 ml, 1.94 mmol) dropwise. The reaction mixture was refluxed for 5 min, followed by cooling at −5 °C for 2 h. After filtering and washing with diethyl ether (2 × 25 ml) the product was isolated as an orange-brown crystalline solid (370 mg, 54% yield); all spectroscopic data were identical to those of $\mathbf{1}\cdot Br_2$ obtained *via* Method A.

X-Ray crystallography

All crystallographic measurements for complexes $\mathbf{1}\cdot I_2$, $\mathbf{1}\cdot IBr$, $\mathbf{1}\cdot Br_2$ and **2** were made at 150 K on a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator, using Mo-Kα radiation (λ = 0.71069 Å) in a manner described previously.[35] All data sets were corrected for absorption using DIFABS.[36] The structures were solved by direct methods (SHELXS 86),[37] developed *via* difference syntheses, and refined on F^2 by full-matrix least squares (SHELXL 93)[38] using all unique data with intensities greater than 0. In all cases the non-hydrogen atoms were anisotropic, and the hydrogen atoms included in calculated positions (riding model). The crystallographic data and refinement details are presented in Table 4.

CCDC reference number 186/1543.

See http://www.rsc.org/suppdata/dt/1999/3007/ for crystallographic files in .cif format.

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