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The reactions of sulfur and selenium donor molecules with dihalogens and interhalogens

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Abstract

The structural diversity of 1:1 addition products between sulfur and selenium donor molecules and dihalogens and interhalogens has become of particular interest during the last 10 years, with a wealth of structural publications debating the factors that determine the precise structural motif of a given system. In this article, we review the main crystallographic reports, discuss the structural factors affecting these systems and describe some potential applications for the future.

Keywords: Charge-transfer; Sulfur; Selenium; Dihalogen; Interhalogen

1. Introduction

The ability of organo-Group 16 compounds to form addition complexes with dihalogen and interhalogen acceptors has long been recognised. However, it is only relatively recently that the solid-state structures of these compounds have been elucidated. The subtlety of variation in the structural motifs exhibited has led to a considerable renewal of interest in these systems. For compounds of the type R_2E, $R_2C{=}E$, $(R_2N)_2C{=}E$ and $R_3P{=}E$ ($E = S$, Se), the precise nature of the solid-state structures formed upon reaction with X_2 ($X_2 = I_2$, Br_2, Cl_2, F_2, IBr and ICl), and thus the geometry of the Group 16 atom, appears to depend on several factors: the identity of the Group 16 atom (i.e. S or Se); the identity of the dihalogen or interhalogen; the stoichiometry of the reactants; the nature of the R group(s) bound to the donor atom and, in some cases, the relative permittivity of the solvent employed for the reaction. Of course, it must be remembered that changing these variables does not automatically involve a change in the structure of the dihalogen complex, but changing even one of the above variables is likely to (at least) result in a subtle variation of solid-state structure and may result in a change in geometry at the sulfur or selenium atom.

In this overview, an attempt is made to draw together all of the knowledge concerning the dihalogen and interhalogen addition products of diorganosulfides, diorganoselenides, thiones, selones, thioamides, selenoamides and tertiary phosphine sulfides and selenides, and to review variations in the structures exhibited. Additionally, aspects of bonding will be discussed together with, where possible, explanations as to why certain geometries for the Group 16 atoms prevail. Finally, 'gaps' in current knowledge will be highlighted.

From a purely academic point of view, the structural diversity of organo-Group 16 dihalogen and interhalogen compounds has led to considerable interest. For example, to date materials synthesised have exhibited charge-transfer (CT) spoke and extended spoke adduct, polyiodide, see-saw, ionic, T-shaped, bent, mixed-valence, dication-bridged and dimeric structural motifs. However, in addition to purely academic interest, there are numerous potential applications for these materials, which embrace fields as diverse as medicine and electronics and as novel synthetic reagents in both organic and inorganic chemistry.

1.1. Charge-transfer complexes

Many of the addition products described herein are CT adducts[1] between a Group 16 donor molecule with (usually) diiodine or sometimes other dihalogens or interhalogens. Therefore, we shall briefly review the concept of CT to allow a greater understanding of concepts discussed later in the article. In a simplistic sense, CT can be said to occur whenever there is a weak coordination involving a transfer of charge. An example of this is phenoquinone, where the phenol and quinone moieties are associated with CT between the two molecules' aromatic ring systems [1]. A better view, however, is that CT arises from the movement of an electron from an orbital that is mainly ligand to one that is mainly metal in character (ligand-to-metal CT) or vice versa (metal-to-ligand CT). These transitions are allowed (unlike d–d transitions) and often result in very intense absorptions,

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[1] The use of the term 'adduct' to describe the kind of complex under discussion here is variable amongst different groups of researchers. For the purpose of this review, we have only described as adducts those compounds containing an intact X–X bond upon product formation. This includes all 1:1 CT spoke adducts. It could be argued that compounds in which X–X bond cleavage and oxidative addition to form T-shaped or see-saw products could also be considered adducts. We do not disagree with this assertion; however, they are not described as such here. Rather, we have described them as the dibromine or dichlorine addition products of the parent compounds, to reflect the manner in which they are prepared. Additionally, one might envisage some controversy about when an X–X CT bond should really be considered an $X^{+}\cdots X^{-}$ ionic interaction. Most researchers in this field take the sum of the van der Waals radii of the two halogen atoms as their criterion. Species in which d(X–X) is less than this sum are generally considered CT, with an intact (albeit sometimes greatly lengthened) X–X bond. Values greater than this sum indicate ionic complexes.

detectable by electronic spectroscopy, and typically giving rise to brightly coloured compounds [2]. More information about CT in the context of the compounds under discussion here can be obtained from detailed accounts in the literature [3].

Hassel and Rømming reviewed the direct structural evidence for CT bonds in solids containing chemically saturated molecules [3a]; at that time (1962) this was largely limited to electron density maps such as those of the addition products of iodoform [4]. However, this work gave a valuable insight into systems that, although well known to chemists (such as the 1:1 benzene–diiodine complex [5]), were not structurally well understood. It became clear that single crystal X-ray diffraction experiments were vital when elucidating the exact nature of CT adducts; hence much of the work presented here discusses crystallographic reports in preference to spectroscopic investigations.

2. Diorganosulfur dihalogen and interhalogen compounds, R_2SX_2 and R_2SIX' ($X = I, Br, Cl, F$; $X' = Br, Cl$)

In total, there have been 13 structural reports featuring the 1:1 CT adducts R_2SI_2, R_2SIBr, R_2SBr_2 and the non-CT compounds R_2SCl_2, two-thirds of which describe adducts of stoichiometry R_2SI_2. It is interesting that (to date) there has been little structural diversity noted for these compounds.

2.1. Diorganosulfur diiodine CT adducts, R_2SI_2

These are the most well-known type of adduct of diorganosulfur compounds and from crystallographic investigations they appear to exclusively exhibit CT spoke structures. Rømming and McCullough reported the structures of benzyl sulfide diiodine [6] and 1,4-dithiane-bis(diiodine) [7], respectively, Fig. 1. Both compounds have nearly linear S–I–I arrangements. A comparison of bond distances might suggest that benzyl sulfide is a slightly better donor than 1,4-dithiane (c.f. benzyl sulfide diiodine d(I–I) 2.819(9), d(S–I) 2.78(2) Å; 1,4-dithiane-bis(diiodine) d(I–I) 2.787(2), d(S–I) 2.867(6) Å); however, it should be borne in mind that in 1,4-dithiane diiodine the donation by one donor sulfur atom to a diiodine acceptor may well alter the electronic properties of the second donor sulfur atom. Therefore, these molecules should perhaps not be compared too closely.

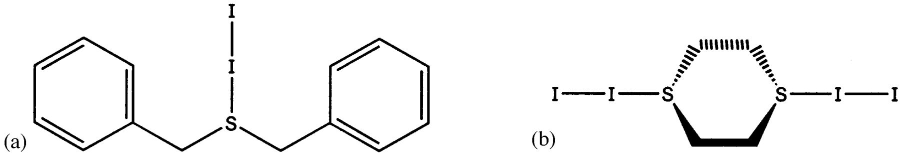


Fig. 1. The molecular CT spoke structures of: (a) benzyl sulfide diiodine and (b) 1,4-dithiane (bis) diiodine.

Two further crystallographic reports feature more complicated donor molecules, although the CT linear S–I–I arrangement is essentially the same as in Fig. 1. These are the (bis)diiodine adducts of dithia[3.3.1]propellane and dithia[3.3.2]propellane [8] and of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane [9]. S–I and I–I distances are in keeping with those observed by Rømming [6] and McCullough [7].

More recently, Devillanova and Schröder have described the synthesis and single crystal X-ray studies of diiodine adducts of a large number of thioether crowns: viz. (1,4,7-trithiacyclononane)$_2$(I$_2$)$_4$ [10], 1,4,7-trithiacyclononane · 3I$_2$ [11], 1,4,7,10-tetrathia-cyclododecane · I$_2$, 1,4,8,11-tetrathiacyclotetradecane · I$_2$, 1,4,8,11-tetrathia-cyclo-tetradecane · 2I$_2$, 1,5,9,13-tetrathiacyclohexadecane · I$_2$, 1,5,9,13-tetrathia-cyclohexa-decane · 4I$_2$ [12], 1,4,7,10,13-pentathiacyclopenta-decane · 7I$_2$, 1,4,7,10,13,16-hexathia-cyclooctadecane · I$_2$, 1,4,7,10,13,16-hexathiacyclooctadecane · 4I$_2$, 1,4,7,10,13,16,19,22-octathiacyclotetra-cosane · I$_2$ and 1,4,7,10,13,16,19,22-octathia-cyclotetra-cosane · 4I$_2$ [13]. Examples of these are shown in Fig. 2.

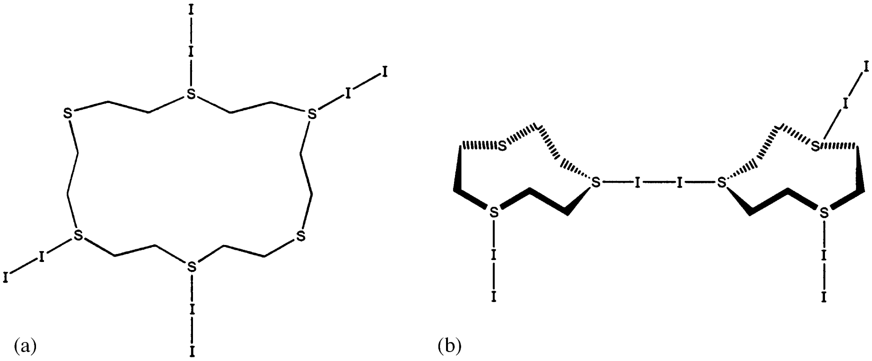


Fig. 2. Thioether crown–diiodine CT complexes: (a) 1,4,7,10,13,16-hexathiacyclooctadecane · 4I$_2$ and (b) (1,4,7-trithiacyclononane)$_2$(I$_2$)$_4$.

These molecules are similar to those previously mentioned [6–9], although (1,4,7-trithiacyclononane)$_2$(I$_2$)$_4$ is particularly interesting as it additionally contains a bridging diiodine molecule linking sulfur atoms of two donor molecules. This bridging I$_2$ molecule has the shortest *d*(I–I) for this structure (2.754(2) as compared to 2.816(2) Å for the longest 'spoke' I–I distance in the structure) which means the interactions with both sulfur atoms are weak.

In addition to crystallographic studies, there have been a few reports based on spectrophotometric [14], ^{1}H- and ^{13}C-NMR [15], Raman and IR [16] spectroscopic investigations that have all come to the same general conclusion that compounds of the form R$_2$SI$_2$ are always CT.

2.2. Diorganosulfur interhalogen CT adducts, R_2SIX ($X = Br$, Cl)

There are very few structural reports indeed that concern interhalogen adducts of diorganosulfur donor molecules. Fig. 3 illustrates the molecular crystal structure of 1,4-dithiane · 2IBr as reported by McCullough et al. [17]. It is isostructural with the

CT adduct 1,4-dithiane · $2I_2$ [7], previously mentioned, which enables a useful comparison to be made: d(S–I) for the I_2 adduct is 2.867(6) Å which is significantly longer than that for the IBr adduct, 2.687(2) Å. This exemplifies the superior acceptor ability of IBr with respect to I_2. That is, one expects Group 16 donor CT adducts of interhalogens to be stronger complexes (i.e. to have a stronger sulfur–acceptor interaction) than those of diiodine.

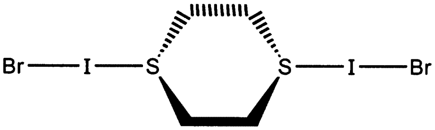


Fig. 3. The 1,4-dithiane · 2IBr molecule.

The only other known report describing interhalogen adducts of diorganosulfur donor molecules is a crystallographic study of the CT thioether crown–IBr complexes 1,4,8,11-tetrathiacyclotetradecane · 2IBr, 1,5,9,13-tetrathiacyclohexa-decane · 4IBr and 1,4,7,10,13,16-hexathiacycloocta-decane · 2IBr [18]. These adducts are extremely similar to those described in Section 2.1 and illustrated in Fig. 2 and contain an isostructural linear S–I–Br arrangement. The distances d(S–I) range from 2.618(2) to 2.687(2) Å and d(I–Br) from 2.6445(12) to 2.7049(11) Å which are in keeping with those observed by McCullough for 1,4-dithiane · 2IBr [17].

Surprisingly, there have been *no* crystallographic reports featuring a diorganosulfur CT adduct of iodine monochloride. However, one would expect the structure of a hypothetical R_2SICl complex to be in keeping with those of R_2S with diiodine and iodine monobromide (i.e. CT linear 'spoke') but with an even shorter d(S–I) reflecting the acceptor ability series $ICl > IBr > I_2$.

2.3. Diorganosulfur dibromine CT compunds, R_2SBr_2

Until recently, the 1:1 dibromine adduct of thiophane was the only compound of stoichiometry R_2SBr_2 to have been characterised using single crystal X-ray diffraction and was found to have the molecular CT structure illustrated in Fig. 4 [19]. The exact structural nature of dimethylsulfide dibromine has been a subject of some controversy, however, with different groups alternately proposing an ionic $[Me_2SBr]^+Br^-$ structure [20] or a CT arrangement Me_2S–Br–Br [21] in the solid state. Recently, a single crystal X-ray diffraction and a high resolution powder X-ray diffraction study [22] revealed the structure to be CT, in keeping with that of

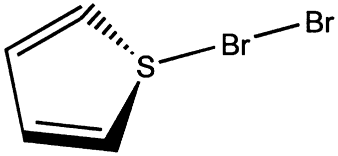


Fig. 4. The molecular CT structure of thiophane · Br_2.

tetrahydrothiophene · Br_2. This is of some importance, as Me_2SBr_2 has found considerable utility as a brominating agent in organic synthesis [23], the mechanisms for which previously have been based on ionic models.

2.4. *Diorganosulfur dichloride compounds, R_2SCl_2*

Dimethylsulfide dichloride, Me_2SCl_2 is known to be extremely unstable [24] and spontaneously decomposes at − 40 °C. However, the crystal structure of bis(*p*-chlorophenyl) sulfide dichloride is known [20] and is a see-saw shaped molecule consisting of a linear Cl–Se–Cl arrangement (174.5(1)°) with the chlorine atoms occupying axial positions to an equatorial plane consisting of the two *p*-chlorophenyl groups, Fig. 5. The fact that the molecule adopts this geometry is almost certainly a consequence of the oxidising power/acceptor ability of dichlorine: so much charge is accepted into the dichlorine molecular antibonding orbital that the Cl–Cl bond cleaves and oxidation of the sulfur atom occurs to form a see-saw shaped molecule. (NB see-saw geometry is also sometimes referred to as ψ-trigonal bipyramidal by some workers.) An additional feature of this structure is a significant asymmetry of 0.064(3) Å between the two S–Cl bond distances (*d*(S–Cl) 2.259(3) and 2.323(3) Å); this appears to arise due to short (3.307(3) Å) intermolecular interactions between Cl atoms of aligned molecules.

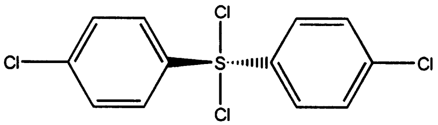


Fig. 5. The see-saw molecular structure of bis(4-chlorophenyl) sulfide dichloride (projection of (4-$ClC_6H_4)_2SCl_2$.

2.5. *Diorganosulfur difluoride compounds, R_2SF_2*

There are no known crystallographic reports concerning 1:1 difluoride adducts of diorganosulfides. This is perhaps not surprising, considering the pronounced instability of diorganosulfur di*chloride* compounds; one might expect difluoride adducts to be even less stable. However, $(CF_3)_2S$ reacts with difluorine at − 78 °C to form $(CF_3)_2SF_2$ [25] and there are several reports that claim the isolation of various diorganosulfur difluoride products obtained using F_2 [26], XeF_2 [27], CF_3OF [28] or ClF_3 [29] as fluorinating agents.

3. Diorganoselenium dihalogen and interhalogen compounds, R_2SeX_2 and R_2SeIX' ($X = I$, Br, Cl, F; $X' = Br$, Cl)

The 1:1 dihalogen and interhalogen adducts of diorganoselenides have received marginally more attention than those of diorganosulfides, but there are few crystallographic reports available. Interestingly, there are fewer structural accounts of the diiodine adducts than of those of the lighter dihalogens, i.e. dibromine and dichlorine (the reverse of the case for diorganosulfide dihalides).

3.1. Diorganoselenium diiodine CT adducts, R_2SeI_2

There are five crystallographic reports of compounds of the form R_2SeI_2, all of which exhibit a CT structure with an almost linear Se–I–I arrangement. Described to date are the 'spoke' structures of 1,4-diselenane · $2I_2$ [30], 1,4-selenothiane · $2I_2$ [31], tetra-hydroselenophene · I_2 [32], 1-oxa-4-selenacyclohexane · I_2 [33] and dimethylselenide · I_2 [34]. One example is illustrated in Fig. 6.

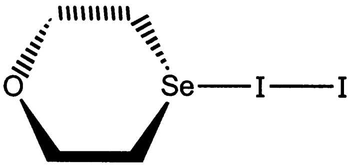


Fig. 6. 1-Oxa-4-selenacyclohexane · I_2.

Examination of *d*(I–I) and *d*(Se–I) reveals two trends. First, the donor power of the diorganoselenium molecules can be considered to be in the series 1-oxa-4-selenacyclohexane (*d*(I–I) 2.956(3) Å) > dimethylsulfide (2.916(3) Å) ca. tetrahydroselenophene (2.914(4) Å); clearly the presence of the electronegative oxygen atom in the heterocycle has an effect on the donor ability of the selenium atom. Second, the change in *d*(I–I) from that in free diiodine (2.66 Å [35]) on coordination to a diorganoselenide is on average nearly *double* that for a diorganosulfide. This means diorganoselenides are far better donor molecules than diorganosulfides.

3.2. Diorganoselenium interhalogen CT adducts, R_2SeIX ($X = Br$, Cl)

Interhalogen addition products of diorganoselenium donor molecules have received very little attention. The iodine monochloride 1:1 adduct with 1-oxa-4-selenacyclohexane was shown by a crystallographic study [36] to adopt a nearly linear (175.8°) CT spoke arrangement with a very short *d*(S–I) of 2.630(5) Å, reflecting the superior acceptor ability of ICl with respect to IBr and I_2. A crystallographic study of four interhalogen adducts of 1,4-selenothiane, C_4H_8SSe, was attempted [37] (viz. C_4H_8SSe · IBr, C_4H_8SSe · 2IBr, C_4H_8SSe · ICl and C_4H_8SSe · 2ICl) but unfortunately none were resolved sufficiently to allow structural assignment with any certainty. However, the authors thought it likely that all adopted CT 'spoke' arrangements at the donor atoms (i.e. Se and S), which seems reasonable in view of the known structures of organosulfur interhalogen adducts [17,18]. In addition, a CT structure was assigned to Me_2SeIBr from a vibrational spectroscopic study [21].

3.3. Diorganoselenium dibromide 1:1 compounds, R_2SeBr_2

Five dibromine addition products of diorganoselenides have been crystallographically characterised and they all exhibit see-saw geometry with a virtually linear Br–Se–Br arrangement, one example is illustrated in Fig. 7. That is, upon the addition of one equivalent of dibromine the Br–Br bond is cleaved and oxidation of the selenium atom occurs to give the dibromide products diphenylselenium dibromide [38], bis(4-methylphenyl)selenium dibromide [39], selenocyclopentane dibromide [40], 1-thia-4-selenacyclohexane dibromide [41] and dimethylselenium dibromide [34]. The Se–Br bond distances are similar in each case at ca. 2.55 Å; however, much of the original crystallographic work was conducted up to 60 years ago so it is hard to make comparisons between donor molecules due to especially large standard deviations for the geometrical parameters.

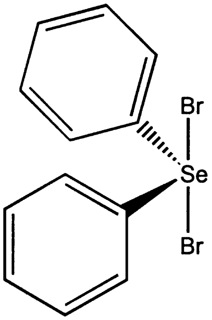


Fig. 7. Diphenylselenium · Br_2.

It is interesting, therefore, that (from crystallographic data alone) it appears dibromine products of diorganoselenium donor molecules adopt exclusively see-saw geometries whereas those of diorganosulfur molecules adopt a CT 'spoke' arrangement. This is likely to be a consequence of the superior donor power of selenium as compared to sulfur donors; the effect becomes important when strong acceptors such as dibromine are present and the combined strong donor–strong acceptor system is sufficient to cleave the Br–Br bond.

However, there is some spectroscopic evidence [42,43] that suggests, for certain organo-groups, diorganoselenium dibromide compounds can indeed be CT in nature, viz. $(4\text{-}NCC_6H_4)_2SeBr_2$, $(4\text{-}O_2NC_6H_4)_2SeBr_2$, $(3,5\text{-}Cl_2C_6H_3)_2SeBr_2$, $(2\text{-}ClC_6H_4)_2SeBr_2$ and $(2,6\text{-}Cl_2C_6H_3Ph)_2SeBr_2$. This is probably because the strongly electron-withdrawing R-groups reduce the electron density on the selenium atom, making the molecule a sufficiently poor donor to prevent Br–Br cleavage on coordination.

3.4. Diorganoselenium dichloride 1:1 compounds, R_2SeCl_2

Adducts of the form R_2SeCl_2 have been the subject of more crystallographic reports than any material of formula R_2EX_2 (E = S, Se; X = I, Br, Cl, F) except perhaps R_2SI_2. To date, diphenylselenium dichloride [44], bis(4-methylphenyl) selenium dichloride [38], 1,4-diselenane bis(dichloride) [45], 2-chloropropyl-1,4′-tolyl selenium dichloride [46], 2,5-bis(*N*-chlorothioimino)-3,4-dicyanoselenophene dichloride [47], bis(2-chloroethyl) selenium dichloride [34] and dimethylselenium dichloride [61] have all been examined using single crystal X-ray diffraction and were found to exhibit a molecular see-saw geometry. Fig. 8 illustrates one of these molecules.

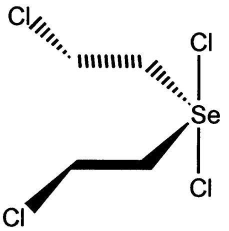


Fig. 8. Bis(2-chloroethyl) selenium · Cl_2.

It can be seen that in each case the linear Cl–Se–Cl moiety lies axial to the equatorial plane consisting of the two organo-groups and a lone pair on the selenium atom. Se–Cl bond distances vary from 2.30(5) to 2.40(1) Å and sometimes exhibit a degree of asymmetry [34,47]; this is similar behaviour to diorganosulfur dichloride compounds, Section 2.4. An IR and Raman study [49] assigned bands at 293 and 270 cm^{-1} for Me_2SeCl_2 to Se–Cl stretching modes; the crystallographic study [34] showed this to be the correct interpretation.

3.5. Diorganoselenium difluoride 1:1 compounds, R_2SeF_2

There are notably few reports that concern difluoride adducts of diorganoselenium molecules. Me_2SeF_2 is a liquid and is postulated from ^1H- and ^{19}F-NMR studies [50] to have see-saw geometry. This seems reasonable, as one would expect the extremely high acceptor ability of F_2 to lead to oxidation of the selenium atom and the formation of a linear F–Se–F moiety. $(CF_3)_2SeF_2$ and $(C_2F_5)_2SeF_2$ have also been described [51].

4. Tertiary phosphine sulfide and selenide dihalogen and interhalogen compounds, R_3PEX_2 and R_3PEIX' ($E = S, Se; X = I, Br; X' = Br, Cl$)

Tertiary phosphine sulfides and selenides have the general structures illustrated in Fig. 9 and consist of a phosphine group linked to a chalcogen atom by a P=S or P=Se double bond. There have been few crystallographic reports regarding their addition products with dihalogens or interhalogens until recently and even now there are only a handful of crystallographic descriptions of these structurally diverse systems.

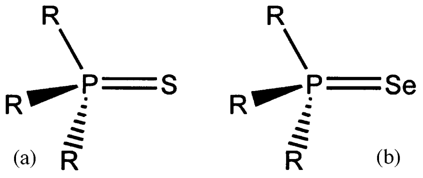


Fig. 9. The structures of: (a) tertiary phosphine sulfides and (b) tertiary phosphine selenides (R = aryl, alkyl group).

4.1. Tertiary phosphine sulfide diiodine and iodine monobromide adducts, R_3PSI_2 and R_3PSIBr

There are only three crystallographic reports known to us that concern tertiary phosphine sulfide dihalide or interhalide adducts. It was initially believed that triphenylphosphine sulfide diiodine could not be isolated, although the CT compound $(Ph_3PS)_2(I_2)_3$ was structurally characterised and found to consist of two CT $Ph_3P{=}S{-}I{-}I$ moieties linked by a diiodine molecule to form an I_6 polyiodide chain [52]. It was 30 years after this discovery that the molecular crystal structure of Ph_3PSI_2 was reported [53] and found to be a molecular CT 'spoke' arrangement, in agreement with previous IR and UV–vis spectroscopic studies concerning that molecule and other adducts of stoichiometry R_3PSI_2 [54]. These two structures are illustrated in Fig. 10.

Very recently, the CT adducts $(Me_2N)_3PSI_2$ and Ph_3PSIBr have been described [55] and were found to be isostructural with Ph_3PSI_2. As with other CT systems, examination of bond distances yields information about the strength (or stability) of the complex. However, for tertiary phosphine chalcogenides one expects *three* important changes on coordination, i.e. in *d*(I–X) (where X = I, Br), *d*(E–I) and *d*(P–E). Table 1 compares these selected geometrical parameters for the four so far crystallographically characterised tertiary phosphine sulfide adducts [51,52,54].

The complexes' stability can be said to increase across the table, i.e. the 2:3 adduct of Ph_3PS and I_2 can be considered a stronger donor–acceptor system than the 1:1 adduct due to the shorter (and therefore stronger) *d*(S–I) and the longer (and therefore weaker) *d*(I–I) in $(Ph_3PS)_2(I_2)_3$ with respect to Ph_3PSI_2. From this it

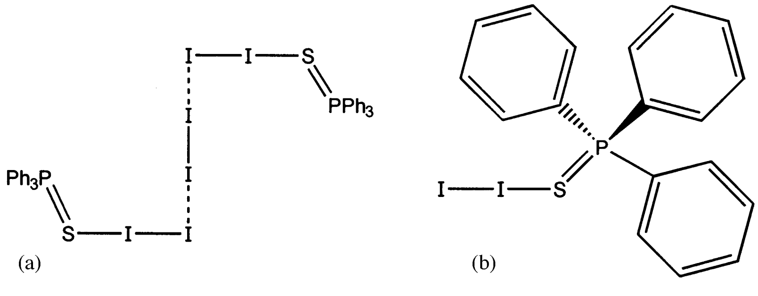


Fig. 10. The molecular CT structures of: (a) $(Ph_3PS)_2(I_2)_3$ and (b) Ph_3PSI_2.

Table 1
A comparison of selected geometrical parameters for crystallographically characterised tertiary phosphine sulfide diiodide and iodine monobromide adducts

Geometrical parameter (Å or °)	Ph_3PS	Ph_3PSI_2	$(Ph_3PS)_2(I_2)_3$	$(Me_2N)_3PSI_2$	Ph_3PSIBr
d(P–S)	1.950(3)	1.998(2)	2.007(3)	2.014(4)	2.007(1)
d(S–I)	–	2.753(2)	2.729(2)	2.705(3)	2.656(1)
d(I–I)	–	2.8230(11)	2.838(1)	2.856(1)	–
d(I–Br)	–	–	–	–	2.6832(6)
S–I–X (X = I, Br)	–	175.51(3)	175.23(5)	177.98(6)	175.13(2)

can also be seen that $(Me_2N)_3PS$ is a better donor molecule than Ph_3PS and that the IBr complex is stronger than the other three adducts, as shown by its short *d*(S–I). The P–S bond distance lengthens (with respect to the parent molecule) upon coordination to I_2 or IBr, which is indicative of a partial positive charge being located on the phosphine moiety as negative charge is donated into the LUMO of the acceptor.

There have been no crystallographic reports of an iodine monochloride, dichloride or difluoride compound of a tertiary phosphine sulfide. However, it has been found [54] that when Ph_3PS is reacted with dibromine, cleavage of the P–S bond occurs to give the phosphorus donor–dibromide acceptor species, Ph_3PBr_2, and elemental sulfur as products; this phenomenon was also noted in solution (using ^{31}P-NMR) for the product of the reaction of $(C_6H_{11})_3PS$ with dibromine, but interestingly not in the solid state for which there is evidence that $(C_6H_{11})_3PSBr_2$ forms. Intriguingly, the reaction of $(Me_2N)_3PS$ with dibromine produced the minor product $[\{(Me_2N)_3PS\}_2S][Br_3]_2$, Fig. 11, the mechanism of formation of which is unclear.

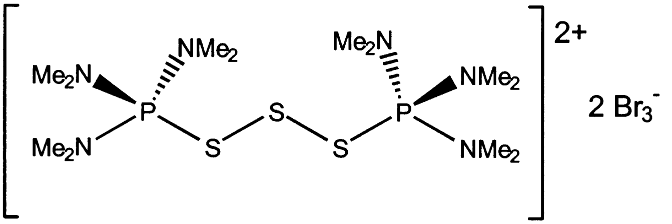


Fig. 11. The structure of $[\{(Me_2N)_3PS\}_2S][Br_3]_2$.

4.2. Tertiary phosphine selenide dihalogen compounds, R_3PSeX_2 (X = I, Br)

Until very recently there had been no crystallographic reports concerning tertiary phosphine selenide dihalogen or interhalogen addition products, although the reaction of Ph_3PSe and $(C_6H_{11})_3PSe$ with diiodine, iodine monobromide and iodine monochloride to produce stable 1:1 adducts was spectroscopically shown to occur [53]. However, two reports have now shown that R_3PSeI_2 (R = Ph, Me_2N, Et_2N) compounds adopt a CT molecular spoke structure [56] analogous to Ph_3PSI_2 [52] and $(Me_2N)_3PSI_2$ [54]. In addition, $(Me_2N)_3PSeBr_2$ and $(C_6H_{11})_3PSeBr_2$ were shown to adopt a T-shaped geometry [57]. Fig. 12 contrasts these two structural types.

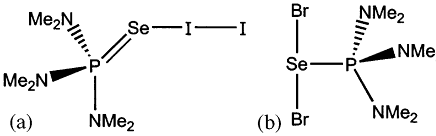


Fig. 12. (a) The 'spoke' structure of $(Me_2N)_3PSeI_2$ and (b) the T-shaped structure of $(Me_2N)_3PSeBr_2$.

The diiodine adducts increase in stability in the order $Ph_3PSeI_2 < (Me_2N)_3PSeI_2 < (Et_2N)_3PSeI_2$, with d(I–I) of 2.881(2), 2.959(2) and 2.985(2) Å, respectively, reflecting increasing CT to the I_2 acceptor. If these are compared to the d(I–I) of corresponding tertiary phosphine sulfide diiodine adducts (Table 1) it can clearly be seen that compounds of the form R_3PSe are superior donors to R_3PS; this is analogous to the superior donor ability of diorganoselenides (Section 3) with respect to diorganosulfides (Section 2).

There is a fascinating structural difference between diiodide and dibromide tertiary phosphine selenide compounds. If one takes $(Me_2N)_3PSe$ as a case in point, then a comparison of d(P–Se) reveals the distance to be that of a slightly longer double bond in $(Me_2N)_3PSeI_2$ (2.175(8) Å) but that of a single bond in $(Me_2N)_3PSeBr_2$ (2.262(2) Å). That is, on oxidation by dibromine, the selenium atom expands its valence shell from eight (as in the diiodine adduct) to ten electrons. This change in electronic distribution necessitates a positive charge to be located on the now tetravalent phosphorus atom and a negative charge on the $SeBr_2$ moiety, i.e. the dibromide adducts of tertiary phosphine selenides can be considered zwitterionic molecules.

Also of interest are the ionic and polyiodide arrangements exhibited by the compounds (triiodo)[tris{dimethylamino)phosphaneselenide] iodine and bis{(triiodo)[tri(*N*-morpholyl)phosphaneselenide] iodine diiodine molecular complexes described by Rudd [3b] and the (iodoseleno)phosphonium ions in polyiodide matrices described by Seppälä et al. [58].

There are no crystallographic reports that feature dichloride or difluoride adducts of tertiary phosphine selenides (although Skowronska provides good evidence for their occurrence in solution when R = R′O [59]). However, one might expect the lengthening of the P–Se bond to be so severe on oxidation by either of these dihalogens that cleavage of the bond may well occur, perhaps preventing adduct formation taking place at all.

5. The reaction of thioamides with dihalogens and interhalogens to form RR′C = SX_2 and RR′C = SIX′ (R = alkyl, aryl, amino; R′ = amino group; X = I, Br, Cl, F; X′ = Br, Cl)

Thioamides differ from diorganosulfides in that they contain a sulfur atom with a double bond to a carbon atom rather than single bonds to two carbon atoms. This, in some ways, makes them analogous to tertiary phosphine sulfides, $R_3P{=}S$ (Section 4.1). However, thioamides also contain at least one nitrogen atom on the carbon to which the C=S group is located. This leads to a certain amount of resonance about the N–C–S system.

The interaction of thioamides with dihalogens and interhalogens has received renewed interest in recent years, with several groups from around the world engaged in research into their fascinating structural nature and potential applications.

5.1. The reaction of thioamides with diiodine

Several groups have attempted to elucidate the array of possible structural motifs available for thioamide diiodine addition complexes using purely spectroscopic methods. There have been reports of UV–vis [60], IR [61] and FT-Raman investigations [62–64], but unfortunately it appears to be very difficult to assign a particular structural type to a particular adduct without the aid of single crystal X-ray diffraction. This is in keeping with other systems, such as dihalogen and interhalogen adducts of diorganosulfides (Section 2) and tertiary phosphine sulfides (Section 4.1); however, the array of structural motifs exhibited by thioamide diiodide adducts is significantly greater and more subtle than for those systems, as proved by a series of crystallographic reports during the last ten years.

The principle structural type favoured by 1:1 diiodine adducts of thioamides is perhaps not surprisingly the molecular CT spoke, and this has been crystallographically observed for: (i) 1,3-dimethylimidazole-2-thione diiodine [65]; (ii) bis(morpholinothiocarbonyl) bis(diiodine) [66]; (iii) 4,5,6,7-tetrathiocinodiimidazolyl-1,3,8,10-tetraethyl-2,9-dithione diiodine [67]; (iv) 5,5-dimethylimidazolidine-2,4-dithione diiodine, 5,5-dimethylimidazolidine-2,4-dithione bis(diiodine) and 5,5-dimethyl-2-thioxoimidazolidin-4-one diiodine [68]; (v) 4,5,6,7-tetrathiocinodiimidazolyl-1,3,8,10-tetrabutyl-2,9-dithione bis(diiodine) [69]; and (vi) 1,1′-methylenebis(3-methyl-4-imidazoline-2-thione) bis(diiodine) and 1,1′-ethylenebis(3-methyl-4-imidazoline-2-thione) bis(diiodine) [70]. Two examples are shown in Fig. 13. The *d*(I–I) varies from 2.75 to 2.98 Å, the latter value (for the molecule in Fig. 13a) represents a very large degree of CT indeed. In certain cases, therefore, thioamides seem to be especially good donors compared to diorganosulfur and tertiary phosphine sulfide molecules.

In addition, there has been a crystallographic report concerning the ‘extended spoke’ structural motif of benzoxazole-2-thione bis(diiodine), which features a 1:1 CT thioamide moiety interacting with an additional diiodine molecule to form a 1:2 adduct [71]. Other structural types include non-stoichiometric ionic forms contain-

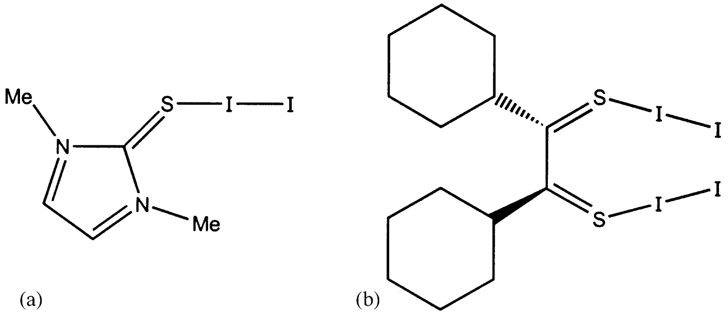


Fig. 13. (a) 1,3-dimethylimidazole-2-thione diiodine and (b) bis(morpholinothiocarbonyl)bis(diiodine).

ing a linear S–I$^+$–S moiety, as exemplified by the 2:1 adduct (thiourea)$_2$I$_2$ [72], the 1:1 adduct 1,3-dimethyl-2-thiourea · I$_2$ (Fig. 14) [64], the 1:2 adduct (3-methylbenzothiazole-2-thione)$_2$(I$_2$)$_4$ [73] the 2:3 adduct (ethylenethiourea)$_2$(I$_2$)$_3$ [74] and the 2:7 adduct (dithizone)$_2$(I$_2$)$_7$ [73,75]. In fact, it has recently been shown from FT-Raman and crystallographic data how complicated mixtures of intriguing polyiodide species can be produced from a single reaction, such as with thiourea and diiodine [64]. Fig. 15 illustrates just two arrangements crystallographically shown to occur from that reaction. There is also some evidence that suggests 1:1 T-shaped diiodide adducts exist for thioamides [76], analogous to phosphine selenide dibromide adducts [57] (Section 4.2). The four basic structural motifs known are schematically illustrated in Fig. 16.

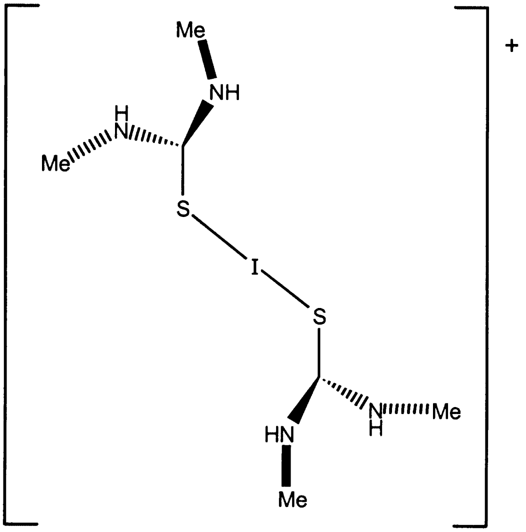


Fig. 14. The ionic structure of 1,3-dimethyl-2-thiourea · I$_2$.

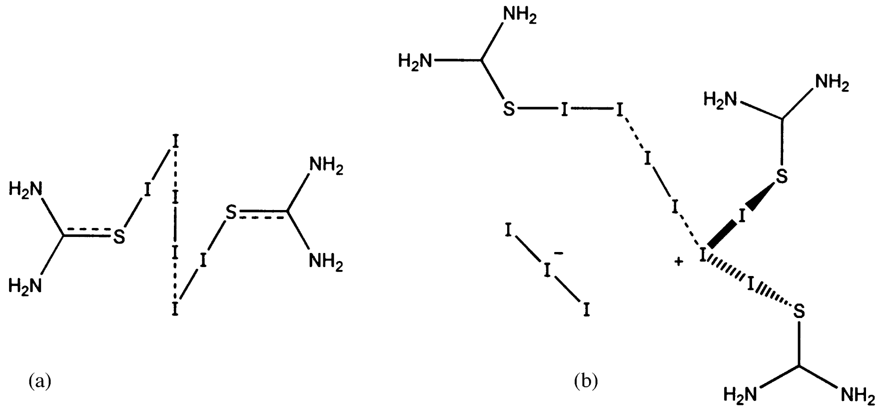


Fig. 15. Polyiodide arrangements of thiourea (tu) and diiodine: (a) $(tu)_2(I_2)_3$ and (b) $(tu)_3(I_2)_5$.

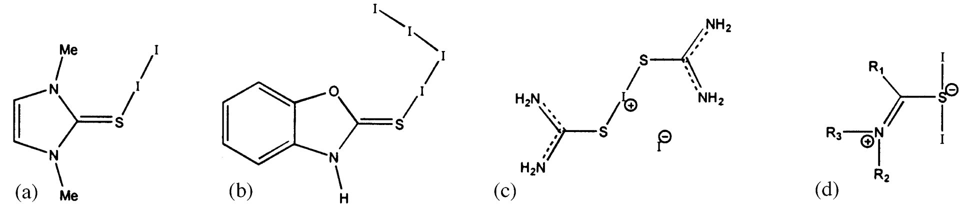


Fig. 16. The structural diversity of thioamide diiodine compounds: (a) the molecular CT spoke arrangement of 1,3-dimethylimidazole-2-thione diiodine; (b) the molecular CT ‘extended’ spoke arrangement of benzoxazole-2-thione bis(diiodine); (c) the ionic $(thiourea)_2I_2$; and (d) an (as yet) unproven thioamide diiodide zwitterionic T-shaped arrangement.

Which motif is favoured for a particular thioamide is not easily predicted, but it is thought that it depends in part on the molecule’s donor strength: one might expect very strong donors to cause a large increase in d(I–I) such that the bond cleaves, oxidation to give tetravalent sulfur occurs and a T-shaped molecule may form. Also of importance is the non-donating part of the molecule; on coordination to diiodine the C=S bond lengthens, imparting a partial positive charge on the rest of the molecule. This helps explain why thioamides are particularly good donors: the positive charge is easily supported by nitrogen atoms, especially if they contain *N*-alkyl groups. Generally, the greater the stabilisation ability of the *N*-aryl or -alkyl groups, the stronger one might expect the resulting diiodine complex to be. In addition, this ability to support a positive charge may well be the reason why the ionic structural motif is favoured over CT in certain cases.

5.2. The reaction of thioamides with interhalogens, dibromine and chlorinating and fluorinating agents

There have been no crystallographic reports of interhalogen adducts of thioamides, although the synthesis of a series of 1:1 TA · IX adducts (TA = thioamide, X = Br, Cl) has been recently reported [64], as has the synthesis of the thermally unstable 1:1 IBr adduct of 1,3-dimethylimidazolthione [76]. Reported in the same work, however, was the molecular crystal structure of the dibromide compound for the same molecule; this was found to be a T-shaped zwitterionic molecule. A similar arrangement is exhibited by the dichloride addition product of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, although that molecule exhibits significantly asymmetric *d*(S–Cl) (i.e. 2.365(1) and 2.295(1) Å) [77]. These two isostructural compounds are illustrated in Fig. 17. However, we have recently found that a further structural motif is exhibited by 1:1 products of thioamides and dibromine, namely that of 1,3-diethyl-2-thiourea · Br_2 (Fig. 18) [78]. This species contains an S–S dicationic bridge balanced by Br_3^- and Br^- anions to preserve the overall 1:1 stoichiometry. Additionally, we have found that the reaction of *N*-methylbenzothiazole-2-thione (mbtt), with one equivalent of dibromine yields a bulk material of stoichiometry $(mbtt)_2Br_6$ and the minor product $[(C_8H_7NSBr)_2Br]Br_3$, Fig. 19. The

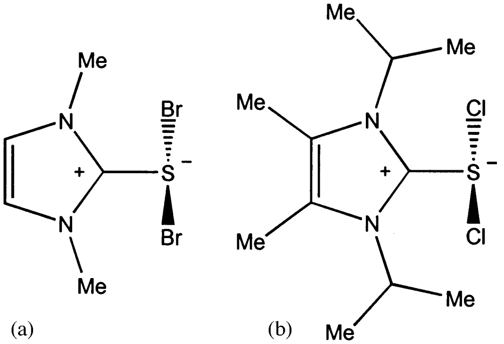


Fig. 17. The zwitterionic T-shaped species: (a) 1,3-dimethylimidazol-2-ylidene dibromide and (b) 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene dichloride.

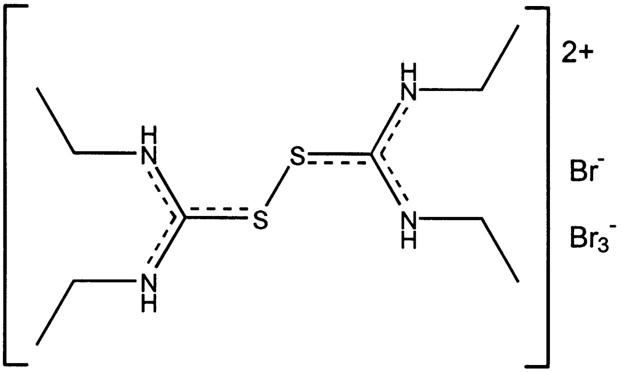


Fig. 18. The ionic structure of the 1:1 dibromine addition product of 1,3-diethyl-2-thiourea.

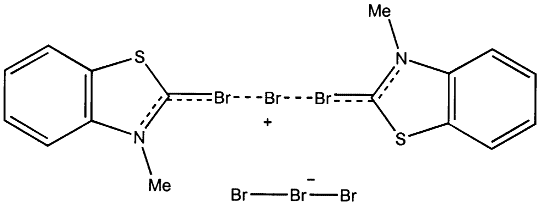


Fig. 19. The ionic structure of $[(C_8H_7NSBr)_2Br]Br_3$.

latter species exhibits cleavage of the C=S double bond to form an organic cation with interactions to a bromide anion and balanced by a discrete Br_3^- anion.

No difluoride compounds of thioamides have been described. These would be expected to be highly unstable and to spontaneously decompose at room temperature.

6. The reaction of selenoamides with dihalogens and interhalogens to form RR′C = SeX$_2$ and RR′C = SeIX′ (R = alkyl, aryl, amino; R′ = amino group; X = I, Br, Cl, F; X′ = Br, Cl)

Although there are fewer reports concerning the interaction of selenoamides (the selenium analogue of thioamides) with dihalogens than thioamides, the structural diversity exhibited by selenoamide products appears to be even more striking. This has made these systems receive attention from main group chemists from several countries in recent years.

6.1. The reaction of selenoamides with diiodine

Spectroscopic studies of diiodine complexes of selenoamides did not appear until the 1980s; these include UV–vis [60,79,61], IR [61] and NMR [80] investigations, all of which were inconclusive regarding the exact structural nature of these type of materials, although a T-shaped system was indicted as one possibility.

During the 1990s, there were seven crystallographic reports describing a total of six different arrangements exhibited by diiodide adducts of selenoamides. There appeared to be little predilection for CT molecular spoke structures, although these were found to exist, such as those of 5,5-dimethyl-2-selenoxoimidazolin-4-one diiodine [68] and 1,1′-bis(3-methyl-4-imidazolin-2-selone) methane bis(diiodine) [81]. This latter molecule is a prime example of the structural sensitivity of these systems: if the number of carbons linking the two nitrogen atoms is increased from one to two atoms then a T-shaped compound instead of a CT adduct forms, Fig. 20. Other crystallographically characterised T-shaped structures are the 1:1 [82] and the 2:3 [83] diiodide compounds of 2-selenoxoimidazolines; the latter being of especial interest as it consists of two T-shaped molecules linked via a diiodine molecule. Again, asymmetry of nearly 0.1 Å between the two d(Se–I) is observed. For the CT

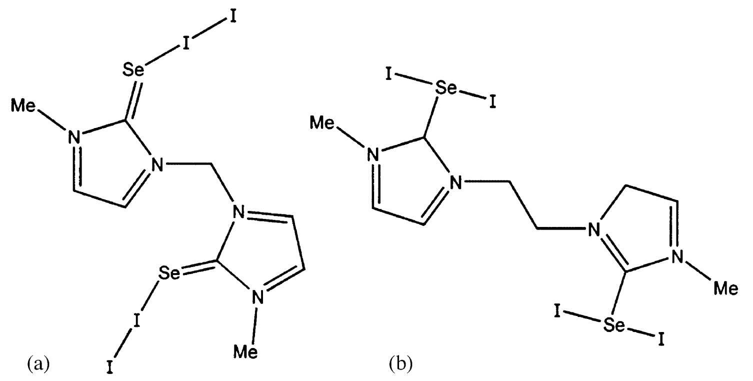


Fig. 20. Subtle changes in the donor molecule can lead to surprising structural differences in the diiodide species: (a) the CT molecular spoke structure of 1,1′-bis(3-methyl-4-imidazolin-2-selone) methane bis(diiodine) and (b) the T-shaped structure of 1,2-bis(3-methyl-4-imidazolin-2-ylium diiodo selenanide) ethane.

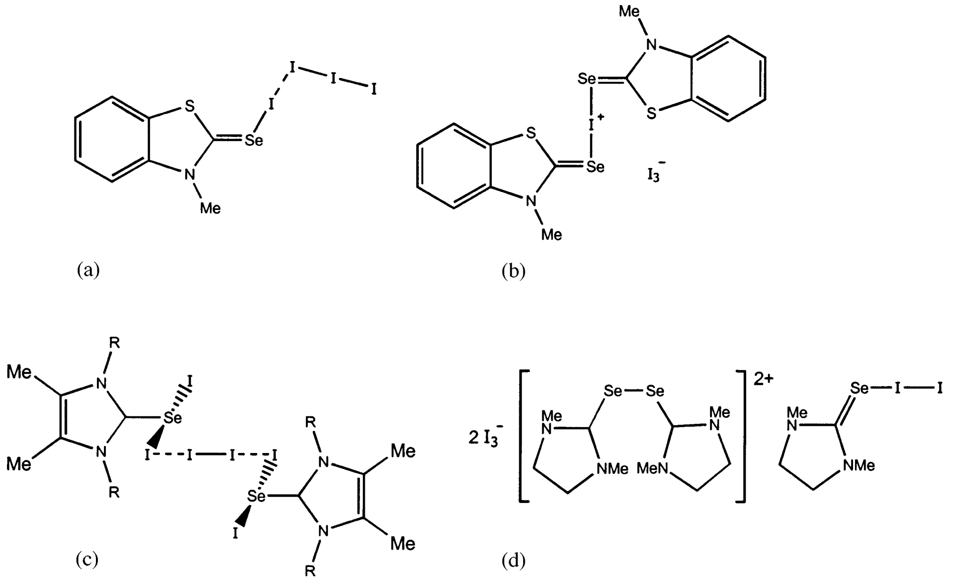


Fig. 21. Structural motifs of selenoamide diiodide compounds: (a) the 'extended spoke' of mbts · $2I_2$; (b) the ionic $[(mbts)_2I]^+I_3^-$; (c) two T-shaped 2-selenoimidazolines (R = Me, Et, ^{i}Pr) linked by a neutral diiodine molecule; and (d) the mixed valence $[(L \cdot I_2)(L_2)]^{2+}2I_3^-$ compound (L = 1,3-dimethylimidazolidine-2-selone).

adducts [68,81,84], *d*(I–I) ranges from 2.912(1) to 3.071(1) Å, meaning selenoamides have the greatest donor ability of all the Group 16 molecules described in this review. This fact helps explain why I_2 bond fission to form T-shaped species can occur: donation into the molecular antibonding orbital of the acceptor molecule is of a sufficient magnitude to cleave the I–I bond. The largest change in *d*(I–I) with respect to uncoordinated diiodine is seen for the 1:2 CT adduct of 3-methylbenzothiazole-2-selone (mbts) [84]. This 'extended spoke' structure consists of an mbts · I_2 moiety interacting with a second diiodine molecule (analogous to benzoxazole-2-thione bis(diiodine) [71], Fig. 16b).

It is interesting that, although mbts · $2I_2$ exists as an extended spoke CT system, the 1:1 compound mbts · I_2 is an ionic arrangement of two mbts molecules linked by an I^+ moiety balanced by an I_3^- anion [73]. A sixth structural motif is that of the mixed valence $[(L \cdot I_2)(L_2)]^{2+} 2I_3^-$ compound (L = 1,3-dimethylimidazolidine-2-selone) [85], which consists of a neutral CT spoke adduct, L · I_2, an Se–Se dicationic molecule and two triiodide anions. Examples of the structural diversity of selenoamide diiodine compounds are illustrated in Fig. 21.

6.2. The reaction of selenoamides with the interhalogens iodine monobromide and iodine monochloride

Considerably less attention has been devoted to the interaction of selenoamides with interhalogens than with diiodine. However, CT spoke and extended spoke structures have crystallographically been shown to occur for the 1:1 adduct *N*-methyl-1,3-thiazolidine-2-selone iodine monobromide and the 1:2 adduct mbts · 2IBr, respectively [84]. It is interesting that the C=Se double bond lengthens on CT from the selenium atom to the IBr acceptor molecule (by ca. 0.6 Å for mbts · 2IBr [84]), indicating a partial positive charge becomes located on the nitrogen atom of the molecule and a partial negative charge is imparted onto the acceptor molecule. Very recently, the CT structure of mbts · ICl has been reported [86]. This is isostructural with mbts · IBr, reported in the same work, and *N*-methyl-1,3-thiazolidine-2-selone iodine monobromide [84] and is the only selenoamide–iodine monochloride adduct so far described in the literature.

The only further report known concerns the reaction of certain selenoamides with IBr and ICl to produce dicationic molecules containing an –Se–Se– bridge [87]. The organic part of the molecule is shown again to be of importance; the exact nature of products formed appears to be significantly affected by slight changes in the donor molecule. For example, the reaction of 1,3-dimethyl-4-imidazolidine-2-selone (dmis), with IBr produces a dication balanced by two Br^- anions; the equivalent reaction with ICl produces the same dication balanced by a single Cl^- anion and an I_3^- anion. Also, when one examines the crystalline product from the reaction of IBr with 1,3-dimethylimidazolidine-2-selone, a selenoamide only subtly different to dmis, this dication is balanced not by two Br^- anions but by a Br^- and an IBr_2^- anion. The three known selenoamide–interhalogen structural types are shown in Fig. 22. A further curiosity, illustrated in Fig. 23, is the product of stoichiometry $C_8H_7Cl_3INS$, which reveals that the reaction of mbts with two equivalents of ICl does not lead to a 1:2 addition product (as is the case for mbts with two equivalents of IBr) [86]. Rather, CSe bond cleavage occurs and the Se atom is substituted by a Cl atom to form an organic cation balanced by an inorganic anion.

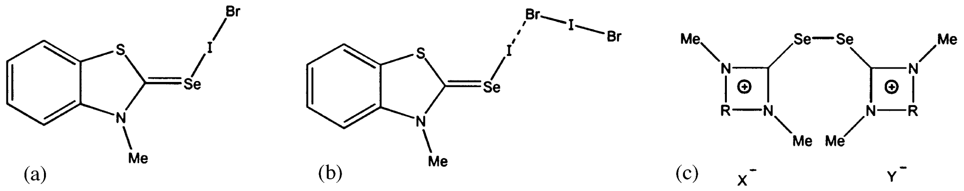


Fig. 22. (a) The CT spoke structure of mbts · IBr; (b) the extended spoke structure of mbts · 2IBr; and (c) schematic diagram illustrating three products containing a dicationic Se–Se bridge ((i) $R = HC{=}CH$; X, Y = Br; (ii) $R = HC{=}CH$; X = Cl, Y = I; (iii) $R = CH_2CH_2$; X = Br; Y = IBr_2).

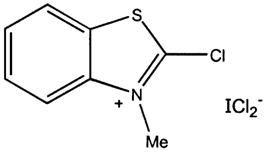


Fig. 23. The ionic structure of $[C_8H_7NSCl]ICl_2$.

6.3. The reaction of selenoamides with dibromine

Addition reactions between dibromine and selenoamides have, until recently, received similarly scant attention. In 1997, the first crystallographic report of a 1:1 selenoamide dibromide product described the T-shaped structure of 1,3-dimethyl-2-(Se,Se-dibromoseleno)-2(3*H*)-imidazolylidene [88]; shortly afterwards the structures of *N*-methylthiazolidine-2(3*H*)-selone dibromide and mbts · Br_2 [89] and 1,2-bis(3-methyl-4-imidazolin-2-ylium dibromoselenanide)ethane [90] were reported. Two of these T-shaped adducts are illustrated in Fig. 24. The structure of mbts · Br_2 was later crystallographically re-examined at low temperature [91] causing some controversy about the assignment of bond length data to the molecule [92]. One group described the C=Se double bond as remaining essentially intact on coordination, implying considerable back donation in a carbene–acceptor system [89,93], and another described mbts · Br_2 as being a zwitterionic molecule with a positive charge on the nitrogen atom, a negative charge on the $SeBr_2$ moiety and a CSe single bond [91,92].

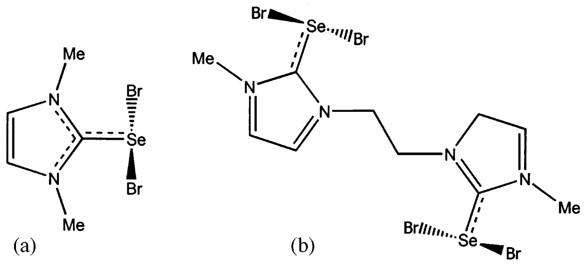


Fig. 24. The T-shaped structures of: (a) 1,3-dimethyl-2-(Se,Se-dibromoseleno)-2(3*H*)-imidazolylidene and (b) 1,2-bis(3-methyl-4-imidazolin-2-ylium dibromoselenanide)ethane.

The effect does appear to be that *d*(C–Se) lengthens to that of a single bond upon coordination of dibromine (analogous to that seen for tertiary phosphine selenide dibromide complexes, Section 4.2), e.g. from 1.815 in mbts [94] to 1.916(10) Å in mbts · Br_2 [89]. This effect was also noted by Williams et al., who illustrated their molecule as a zwitterionic arrangement with a C–Se single bond, a positive charge delocalised around the organic part of the molecule and a negative charge on the $SeBr_2$ moiety (Fig. 24a) [88]. However, Devillanova et al. illustrated mbts · Br_2 as having a C=Se double bond (Fig. 25a) [89,93]. Both workers described the species as a carbene donor–$SeBr_2$ acceptor system. Our interpretation [91,92] of a purely zwitterionic molecule is shown in Fig. 25b. Clearly, there is still some controversy about the bonding in the mbts · Br_2 molecule.

Also described [91] are two crystal structures of dmsu · Br_2, one containing CH_2Cl_2 solvent of crystallisation and one not. Although the bond lengths about the molecule are changed little by the solvent's presence, an interesting comparison between packing in the two structures is made.

It has also been reported [89] that when *N*-methylthiazolidine-2(3*H*)-selone is reacted with two equivalents of dibromine the C=Se double bond cleaves, the Se atom is oxidised to an $SeBr_6^{2-}$ anion and a *N*-methyl-2-bromothiazolidinium cation forms, Scheme 1. However, this was not found to occur for the reaction of mbts with two equivalents of dibromine. There is no evidence to date that suggests 1:2 addition products may form between selenoamides and dibromine in an analogous manner to diiodine or iodine monobromide [84]. Certainly, when dmsu is reacted with two equivalents of dibromine, CSe bond cleavage occurs and a range of inorganic anions (Br_3^-, $Se_2Br_9^-$ and $SeBr_6^{2-}$) form to counter the bromo-substituted organic cations [91].

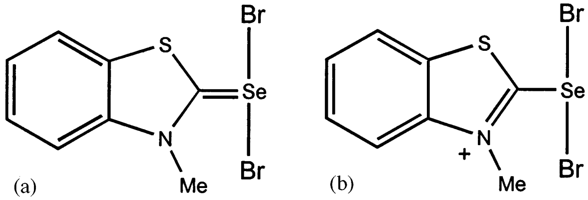
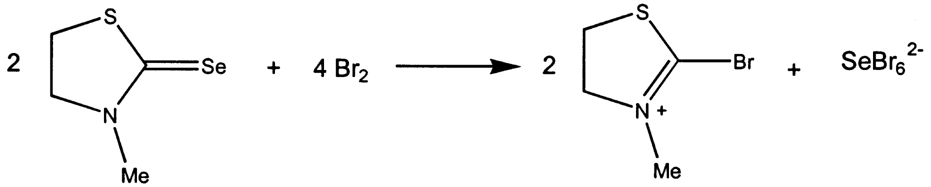


Fig. 25. Two ways of representing mbts · Br_2: (a) carbene-stabilised acceptor system and (b) zwitterionic molecule.



Scheme 1. The reaction of *N*-methylthiazolidine-2(3*H*)-selone with two equivalents of dibromine.

6.4. The reaction of selenoamides with chlorinating and fluorinating agents

There are no spectroscopic or crystallographic reports of 1:1 dichloride or difluoride compounds of selenoamides in the literature. This may be due to severe instability. It was mentioned in Section 6.3 that the C–Se bond lengthens considerably on coordination to dibromine; one might envisage such a pronounced change in *d*(C–Se) on reaction with the more strongly oxidising/accepting dihalogens would actually lead to cleavage of the bond, as seen for various reactions with mbts and dmsu with sulfuryl chloride and dichlorine [95]. However, very recently we have observed that the 1:1 adduct mbts · Cl_2 can indeed form [96], Fig. 26, and it is isostructural with mbts · Br_2, Fig. 25. However, it is still not certain whether 1:1 difluoride adducts can exist; we would expect their instability to be pronounced.

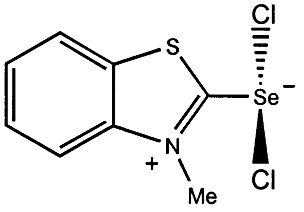


Fig. 26. mbts · Cl_2.

7. CT adducts of 'thiones' with dihalogens and interhalogens

Although the bulk of the research into the interaction of dihalogens and interhalogens with Group 16 donor molecules containing a C=S double bond (i.e. a thione group) has concerned thioamides (Section 5), it is worth pointing out that these are not the only types of C=S group-containing molecule that have been found to form 1:1 adducts with diiodine.

Thioamides are generally considered more stable than simple thiones, due to the resonance possibilities provided by the N–C=S system. However, stability is maintained if the nitrogen heteroatom in a heterocycle is replaced by a sulfur atom. Reaction of such molecules with diiodine yields 1:1 CT adducts that exhibit an S–I–I 'spoke' moiety, several examples of which have been crystallographically

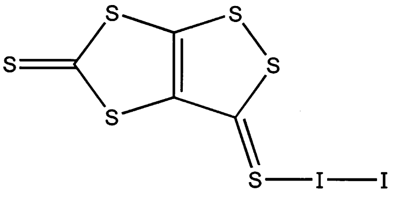


Fig. 27. 1,3,6,7-Tetrathiopentalene-2,5-bisthione · I_2.

characterised including (1,3,6,7-tetrathiopentalene-2,5-bisthione)·I_2 [97], Fig. 27, dithiolodithiole·I_2 [98], 1,3-dithiolane-2-thione·I_2 [99], 1,3-dithiole-2-thione·I_2 [100] and, more recently, 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione·I_2 [101].

The I–I bond distance lengthens to 2.808(3)–2.843(2) Å for these molecules; this means the donor ability of 'thiones' (perhaps more precisely considered to be di and trithioesters) is somewhere in between those of tertiary phosphine sulfides and thioamides. However, there is data for only a small number of molecules (all of a similar type) so this cannot be assumed to be the case for all thione systems; certainly one might expect a degree of overlap between the stability of CT diiodine adducts of phosphine sulfides, thiones and thioamides depending on the exact R groups present in a particular donor molecule.

The only reports of thione adducts *not* featuring diiodine concern the IBr and Br_2 1:1 addition products formed on reaction with 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione [101]. The iodine monobromide adduct is a linear CT spoke system, isostructural with the diiodine adducts, but the dibromide compound is T-shaped in a similar manner to some thioamide·Br_2 [76], selenoamide·Br_2 [88–93] and phosphine selenide·Br_2 [57] adducts. It exhibits a CS distance that has lengthened from a double bond in the parent molecule to a single bond in the product. Fig. 28 illustrates these two structures. Interestingly, the 1:1 dibromide compound only forms when toluene is used; the use of dichloromethane results in cleavage of the C=S bond to produce a brominated cation balanced by bromide anions. This is a further example of structural dependency on the particular solvent employed.

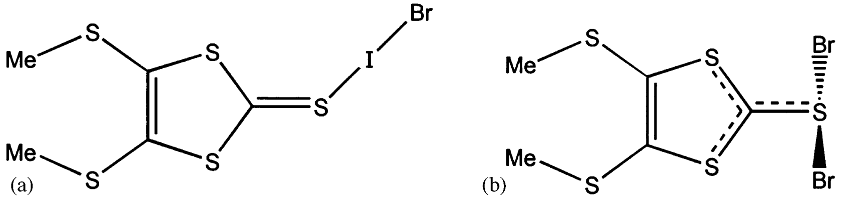


Fig. 28. The 1:1 adducts of 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione with (a) IBr and (b) Br_2.

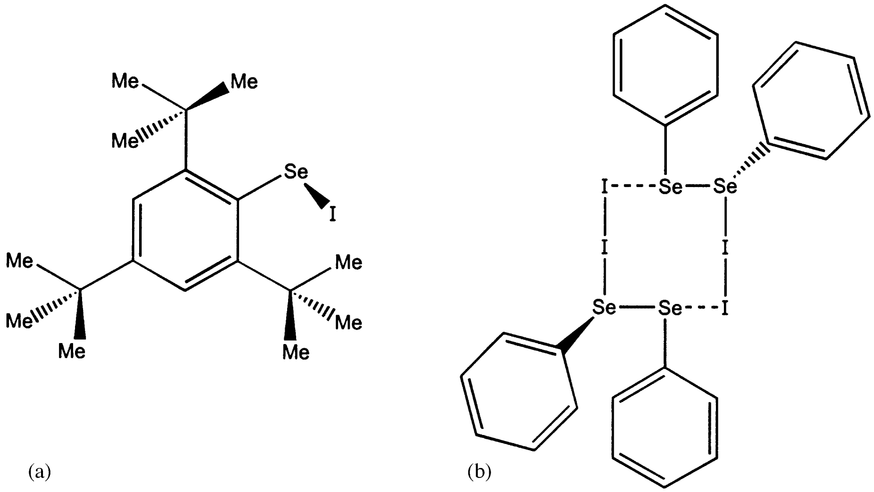
8. The reaction of R_2Se_2 with dihalogens and interhalogens

The reaction of diorgano diselenides with dihalogens and interhalogens has received only very limited crystallographic attention; however, there are a few crystallographic reports concerning addition products of these unusual donor compounds that merit comment.

It has been found [102,103] that the presence of bulky R groups appears to allow diorgano diselenides to react with diiodine to give stable iodoselanes such as 2,4,6-tri-*tert*-butylphenyl(iodo)selenide; that molecule has been crystallographically characterised [102] and is illustrated in Fig. 29a. This compound is remarkable in that it contains a rare covalent selenium–iodine bond (*d*(Se–I) 2.529 Å). However, diphenyl diselenide reacts with diiodine to form a 1:1 adduct that exists as a dimer in its crystalline solid state, Fig. 29b [104]. This dimer can be seen to exhibit a 'square' arrangement and *d*(Se–Se) lengthens from 2.29 (in Ph_2Se_2 [105]) to 2.347 Å as a result of CT from the selenium donor to the diiodine acceptor molecule. A notable difference between this molecule and CT adducts of, say, diorgano selenides is that although one of the selenium atoms of Ph_2Se_2 acts as a conventional electron donor, the other acts as a weak acceptor.

It appears, therefore, that sterically crowded diorgano diselenides form iodoselenides (with covalent Se–I bonds) on reaction with diiodine, whereas those with less bulky substituents such as phenyl groups form CT adducts [106]. However, a further structural type has been shown to exist — that of the diiodine complex of bis(2,4,6-triisopropylphenyl) diselenide, which consists of a diiodine molecule linking two diselenide molecules [107]. This compound should be thought of as only a very weak CT diiodine adduct as *d*(I–I) is only 2.772(2) Å implying that very little CT donation from the diselenide has occurred.

To date there have been no published crystallographic reports concerning the interaction of diorgano diselenides with dibromine, dichlorine or chlorinating agents, difluorine or fluorinating agents or the interhalogens iodine monobromide and iodine monochloride. However, work has been recently conducted in this area at UMIST and preliminary studies show that molecules such as Ph_2Se_2 react with IBr to give a CT adduct that adopts a dimer arrangement similar to that of $Ph_2Se_2I_2$; reaction with Br_2 or Cl_2 in diethyl ether at RT produces a novel $Ph_4Se_4X_4$ ($X = Br$, Cl) structure containing a planar Se_4 square, Fig. 30 [108]. Also of relevance is the reaction of materials such as $Ph_2Se_2I_2$ with phosphines to form pseudohalogen addition products of the form $R_3PSe(Ph)I$ [78,109].



(a) (b)

Fig. 29. The molecular structure of (a) the stable iodoselenide 2,4,6-*tert*-butylphenyl(iodo)selenide and (b) the dimeric 'square' arrangement of $Ph_2Se_2I_2$.

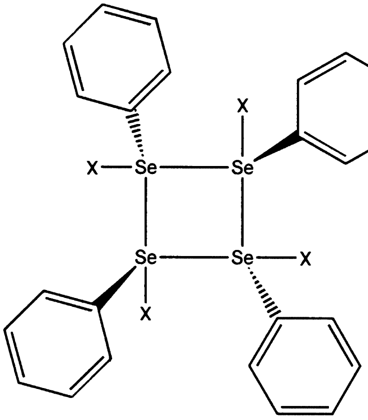


Fig. 30. 'Selenium squares' arising from the 1:1 addition of X_2 to Ph_2Se_2 to give $Ph_4Se_4X_4$ ($X_2 = Br_2$, Cl_2).

Although tellurium compounds are not within the scope of this review, of some relevance is a recent paper [110] that has shown crystallographically that diphenyl ditellurium, Ph_2Te_2, reacts with a stoichiometric equivalent of diiodine to form the novel compound $Ph_4Te_4I_4$ which features a Te_4 square consisting of individual PhTeI units linked through weak Te–Te bonds, Fig. 31. *d*(Te–Te) has lengthened (from 2.705(1) Å in Ph_2Te_2 [109]) to 3.125(2)–3.175(2) Å. It is very interesting that compounds of similar stoichiometry, i.e. PhTeI ($Ph_4Te_4I_4$) and PhSeI ($Ph_2Se_2I_2$) exhibit such different structural motifs in the solid state (c.f. Fig. 31 with Fig. 29b). This once again highlights the importance of the donor atom in organo Group 16-dihalide chemistry. There is also some unpublished ^{13}C-NMR, Raman and powder diffraction evidence to suggest that compounds of the form R_2Te_2IBr and $R_2Te_2Br_2$ are isostructural with this species [108]. Further, $Ph_4Te_4I_4$ has been shown

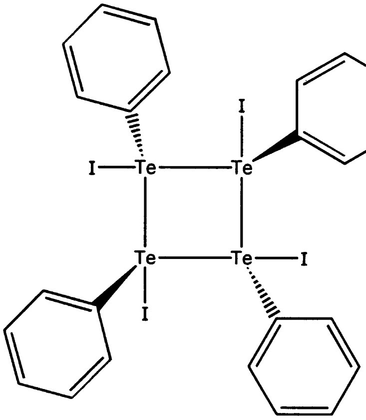


Fig. 31. The 'tellurium square' structure of $Ph_4Te_4I_4$.

to react with four equivalents of triphenyl phosphine to produce the pseudohalogen adduct $Ph_3PTe(I)Ph$ [110].

9. Potential applications of sulfur and selenium donor–dihalogen acceptor complexes

It can be seen from Sections 2–8 that Group 16 donor complexes with dihalogen and interhalogen acceptor molecules show remarkable structural diversity, with compounds exhibiting CT spoke [6–13,17–19,22,30–34,36,53,55,56,65–70,78,81,84,97–101], extended spoke [71,84], polyiodide [3b, 52, 58, 64, 73–75, 78, 83], see-saw [20,34,38–41,44–48], ionic [3b,58,72,73,78], T-shaped [57,76–78,82,83,88–93,101], mixed-valence [85], dication-bridged [78,85,87], dimeric [104,108] and chalcogen square [108,110] motifs. The nature of the compound is dependent on R-groups, the donor atom, the acceptor molecule, the solvent employed and the precise reaction stoichiometry. This goes someway to explaining the fascination these subtle systems have held for main group chemists in recent years.

However, in addition to purely structural interest, there are numerous potential applications for these systems that embrace fields as diverse as medicine, electronics and synthetic organic and inorganic chemistry, and indeed several researchers have already begun to investigate the role of Group 16–dihalogen and interhalogen complexes in these areas.

9.1. Oxidation of unactivated metal powders

One of the main reasons for the recent renewed interest in main group dihalogen and interhalogen addition complexes is the recently reported ability of Group 15 adducts to oxidise a wide range of unactivated metal powders. Although elemental metals have been successfully used as reagents before, it is usually under extreme conditions such as in metal vapour synthesis or by using a pre-activated metal [111] such as very finely dispersed nickel. The usual route to, for example, a metal–phosphine complex, is therefore to react a metal halide salt with the desired phosphine. However, this method is far from ideal as the salts must be rigorously dried and reaction times are typically long. Workers at UMIST showed that Group 15–dihalogen adducts of the form R_3PX_2 ($X = I$, Br) are capable of forming novel metal phosphine complexes through the one-step oxidation of iron [112], nickel [113], cobalt [114], manganese [115], zinc [116], tin [117] and even gold [118]. This route has also been shown to work for tertiary arsines and stibines to produce complexes such as $[ZnI_2(AsMe_3)_2]$ [119], $[NiI_3(AsMe_3)_2]$ [120] and $[CoI_3(SbPh_3)_2]$ [121]. In addition to being a useful new synthetic route to known compounds, this method has proved to be of great utility in the synthesis of previously unavailable materials, such as a surprising trigonal bipyramidal d^8 Au(III) complex [118], $[(Me_3As)_2AuI_3]$.

However, so far there have been no published reports of this novel synthetic route being applied to Group 16–dihalogen adducts, although Me_2SeI_2 has been found to react with unactivated cobalt metal powder to give the first simple Co(II) selenoether complex and the first tetrahedral Co(II) selenium complex to be crystallographically characterised, $(Me_2Se)_2CoI_2$, Fig. 32 [108].

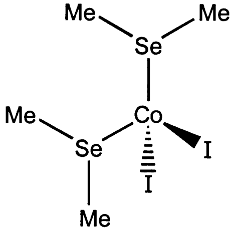


Fig. 32. The tetrahedral structure of $(Me_2Se)_2CoI_2$.

It seems likely that other Group 16–dihalogen and interhalogen adducts will react with unactivated metals in a similar manner. It should be of interest, therefore, to investigate the reactions of molecules similar to those described in Sections 2–8 with a wide range of unactivated main group and transition metals with a view to finding a novel synthetic route analogous to that already well established for Group 15 adducts.

9.2. Synthetic antithyroids

The thyroid gland naturally produces the hormones triiodothyronine and tetraiodothyronine (T_3 and T_4) [122]. However, excessive production of these essential hormones leads to a condition known as *hyperthyroidism*, typified by a variety of metabolic and autoimmune disorders such as Graves' disease. Current treatment tends to be by surgery (i.e. thyroidectomy — complete removal of the thyroid gland) or by the use of radioactive ^{131}I to selectively destroy thyroid tissue. The use of drugs (synthetic *antithyroid* drugs, SAT) is effective in only around half of cases, other patients require a more severe treatment.

It is known that the production of T_3 and T_4 in vivo includes a step that involves the oxidation of I^- to I_2 and ultimately to I^+; this process is catalysed by the enzyme *thyroid peroxidase* (TPO). It has been proposed [123] that SAT drugs work by inhibiting TPO, although the precise mode of action is still controversial [124]. However, French researchers pointed out that SAT drugs containing sulfur donor atoms form CT adducts with diiodine and that the values of the formation constants, K_c, are always high for molecules that possess antithyroid activity [125]. Further, they investigated the structure–activity relationship of SAT drugs in rats [126] and proposed a mechanism whereby $SAT \cdot I_2$ complexes in vivo allow the generation of I_3^- ions, which are incapable of being used in the biological synthesis of T_3 and T_4. Hence, thyroid activity is slowed.

It was also shown [126] that a direct link exists between the strength of the $SAT \cdot I_2$ complex and the efficacy of the drug in vivo. Therefore, very strong Group 16 donors could be designed with a view to finding new and more efficient SAT drugs. It is also of obvious importance that the exact structural nature of the donor–acceptor systems be established. It is interesting that simple thioamides (Section 5.1) such as *N*-alkylated thioureas were indicted as having the greatest SAT efficacy; this is likely to be a consequence of their superior donor ability with respect to other types of sulfur donor molecule. More recent work [127] has concentrated on the antithyroid drug methimazole (a sulfur donor molecule) and its behaviour as a 'diiodine sponge' in vivo.

9.3. Electrical conductors [128]

It has been known since 1975 that $(SN)_x$ is superconductive at 0.3 K [129]; this was, in fact, the first superconducting inorganic polymer to be discovered. Since then, it has been noted that the addition of acceptors such as bromine to form complexes such as $(SNBr_{0.4})_x$ increases the electrical conductivity of $(SN)_x$ by an order of magnitude; a similar effect is noted if iodine is used [130,131]. It is a good conductor because of the presence of one unpaired electron associated with each S–N unit and because the polymer chains are parallel with good overlap between π orbitals which creates a pathway for conduction through the length of the chain. It has been established using Raman spectroscopy [132] that the bromine moiety is present as Br_3^- or Br_5^- and that the iodine moiety is present as I_5^-. The bromination reaction involves a CT process that delocalises the polymeric cation and the counter anion of the dopant.

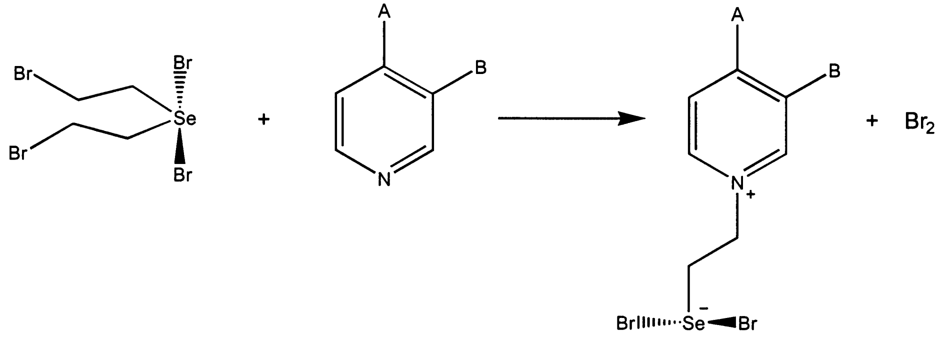
However, $(SN)_x$ and doped $(SN)_x$ are difficult and dangerous to work with (they are synthesised from explosive intermediates [133]) and there are obvious benefits to be gained from designing new polyhalide systems with inorganic polymers and other compounds with a view to improving the range of superconducting materials available. Polyiodide acceptor complexes have already been described here [3b, 52, 58, 64, 73–75, 78, 83] but clearly the range of compounds so far examined is limited.

It is hoped that by examining Group 16–dihalide systems that a further understanding of the synthesis, characterisation and electrical applications of these materials may be obtained.

9.4. Reagents for organic synthesis

Dibromide and dichloride 1:1 addition products of diorgano Group 16 donor molecules have been known since the 19th century [134], although their precise structure had not been investigated until recently. One application of these materials has been in the isolation [135], purification [136] and characterisation [137] of the parent diorgano sulfide, selenide or telluride; these processes being aided by the ease of separation of the dihalogen adducts with respect to the desired parent compounds.

However, it has also been found by several groups that dihalogen compounds of Group 16 donor molecules have enormous utility as reagents in organic synthesis. Akabori et al. investigated the reactivity of dialkylselenium dihalides in the selective reduction of tertiary amides to the corresponding amines [48,138,139], the one-pot preparation of 2,5-bis(alkoxymethyl) tetrahydroselenophenes [140], the formation of T-shaped compounds with pyridine derivatives [141,142], the ring-opening of cyclic ethers [143] and the alkoxyselenation of cyclohexene [144]. Scheme 2 outlines the reaction of bis(2-bromoethyl) selenium dibromide with pyridine derivatives to form T-shaped hypervalent selenium coordination compounds.



Scheme 2. Akabori's method of producing T-shaped dibromide compounds (A = H, CN; B = H, Br).

Engman found that diorganoselenium dichloride species (Section 3.4) were valuable reagents in selenoxide elimination reactions [145] (e.g. to prepare 2-chloro-1-olefins [146] or vinylic chlorides [147]) and in the synthesis of enones [148] and vinylic and allylic acetates [149]. He also pointed out that sodium ascorbate mildly reduces diorganoselenium dihalides back to diorgano selenides [150].

Other workers have described the role of diorgano Group 16 compounds in the synthesis of α-halo-β,γ-unsaturated esters [151], *N*-sulfonyldiarylselenimides [152] and β-bromoselenonium salts [153], as well as for the conversion of alcohols into alkyl chlorides [154], the electrophilic chlorination of toluene [155] and the functionalisation of cyclohexane [156].

Clearly, therefore, materials such as those described herein are extraordinarily versatile reagents for a whole variety of systems; it seems likely that further research will produce a range of new synthetic applications. However, progress in mechanistic studies appears to have been hindered by a lack of understanding of the precise structural nature of these addition compounds. For example, in a report describing the electrophilic addition of bromodimethylsulfonium bromide to olefins [157] the structure of Me_2SBr_2 was assumed to be the ionic arrangement $[Me_2S\text{–}Br]^+Br^-$ and was featured in the proposed mechanism in this form. However, it has since been shown that Me_2SBr_2 actually exhibits a linear CT spoke structure [22] — a fact that may be of importance in determining exactly how this, and similar reagents, actually work. It seems obvious then, that further work should be carried out to improve the understanding of the subtle effects that govern the structural nature of sulfur and selenium–dihalogen addition products.

10. Conclusions

It is clearly illustrated from this review, the great structural diversity exhibited by sulfur and selenium donor molecules upon reaction with dihalogens, which explains the considerable recent interest in such systems. Whilst much is now known concerning the solid-state structure of these dihalogen adducts, some of the more complicated systems (e.g. the reaction of selenoamides with dihalogens) require further investigation. This, together with a detailed investigation of several potential applications for these materials, will ensure that further reports concerning these systems should continue to be of broad interest for some time.

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