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FULL PAPER

The reaction of *N*-methylbenzothiazole-2-selone and 1,1-dimethylselenourea with sulfuryl chloride and dichlorine†

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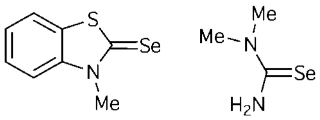
The reactions of *N*-methylbenzothiazole-2-selone, mbts, and 1,1-dimethylselenourea, dmsu, with dichlorine and the chlorinating agent SO_2Cl_2 have been investigated. In the 1 : 1 reactions spectroscopic evidence for the formation of 1 : 1 selenoamide•Cl_2 adducts was obtained; unfortunately, crystallisation attempts have so far been unsuccessful. A single crystal X-ray diffraction was performed, however, on an ionic minor product from the reaction of mbts with one equivalent of SO_2Cl_2. When two equivalents of SO_2Cl_2 or an excess of dichlorine gas were treated with mbts or dmsu a variety of ionic products were obtained, the exact nature of which varied depending upon which chlorinating agent is used, the identity of the selenoamide and the stoichiometry of the reactants. The reactions are therefore complicated and, in most cases, several products are obtained from a given reaction. This study represents the first reported reactions of selenoamides with chlorinating agents and two new selenium–chlorine binary anions have been crystallographically characterised for the first time, namely $Se_2Cl_4^{2-}$ and $SeCl_6^{2-}$.

Introduction

We are currently engaged in a comprehensive study of the interaction of a variety of organogroup 15 and 16 compounds with dihalogen and interhalogen molecules and have found that the geometrical nature of the adducts produced frequently varies with changes in organosubstituents, the nature of the donor atom, the identity of the halogen, and in some cases the solvent employed for the reaction. Thus, for example, triphenylarsine reacts with one equivalent of diiodine in diethyl ether to produce the four-co-ordinate CT adduct Ph_3As–I–I,[1] whereas the addition of one equivalent of dibromine results in the trigonal bipyramidal molecule Ph_3AsBr_2.[2] This latter reaction contrasts with that between triphenylphosphine and dibromine[3] which produces a CT adduct, Ph_3P–Br–Br, similar to that of triphenylarsine diiodide. More recently, we have extended our studies to the reaction of certain tertiary phosphine selenides with dihalogens and have found that these species react with diiodine to produce the CT compounds R_3PSe–I–I (geometry at selenium atom is bent).[4] However, reactions of the same compounds with dibromine produce the T-shaped compounds R_3PSeBr_2 which contain an approximately linear Br–Se–Br arrangement.[5]

We have now turned our attention to the reactions of dihalogens with selenoamides. The ability of selenoamides to form 1 : 1 adducts with diiodine has been investigated by Devillanova and co-workers;[6] in addition to CT products, however, there are several other structural motifs. These include T–shaped molecules containing an I–Se–I arrangement and ionic products containing an Se–I^+–Se linkage and an I_3^- counter ion. Recently[7] we reported the structures of the CT adducts of IBr and ICl with *N*-methylbenzothiazole-2-selone, mbts; this latter molecule was the first report of a 1 : 1 addition compound of ICl and a selenoamide to our knowledge. We have also described products from the reaction of some selenoamides with dibromine:[8] these are T-shaped addition compounds which we feel are best described as zwitterionic molecules with a negative charge residing on the Br–Se–Br moiety and a positive charge residing on one or distributed between two nitrogen atoms bound to an sp^2-hybridised carbon atom. However, other workers have interpreted these molecules in terms of a $SeBr_2$ acceptor stabilised by a carbene.[9,10]



Here, we present the results of our investigation into the reaction of two selenoamides, mbts and 1,1-dimethylselenourea, dmsu, with dichlorine and the chlorinating agent sulfuryl chloride, SO_2Cl_2. There are no reports to our knowledge concerning simple 1 : 1 adduct formation between Cl_2 and selenoamides or, indeed, any other molecule that contains a C=Se functional group. However, some structural investigations have been carried out on products from the reactions of dialkylselenium donor molecules with elemental chlorine. As early as 1942 the crystal structure of diphenylselenium dichloride, Ph_2SeCl_2, had been shown to consist of disphenoidal see-saw shaped molecules containing an almost linear Cl–Se–Cl arrangement.[11] Isostructural with this are di-*p*-tolylselenium dichloride, reported by the same workers,[12] 2-chloropropyl-*p*-tolylselenium dichloride described by Nyburg and co-workers[13] and 1,4-diselenane 1,1,4,4-tetrachloride described by Amendola *et al.*;[14] this molecule has two linear Cl–Se–Cl linkages. More recently, we have reported the see-saw structure of dimethylselenium dichloride, Me_2SeCl_2[15] (previously, Wynne and George had examined this molecule using Raman and IR techniques and assigned bands at 293 and 270 cm^{-1} to selenium–chlorine stretching modes[16]). Such molecules do not necessarily need to be prepared by direct reaction with elemental chlorine, however, and there are reports by separate groups which feature molecules analogous to those under discussion here, but which have been prepared *via* different routes.[17,18] All these molecules exhibit see-saw geometry, an

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4245/

almost linear Cl–Se–Cl arrangement and selenium–chlorine bond distances of between 2.25 and 2.40 Å.

We were surprised, therefore, to find no reports concerning adduct formation between C=Se donor groups and dichlorine, especially considering adducts of dialkylselenium molecules are relatively well known. A possible reason for this may be the strong oxidising power of dichlorine as compared with dibromine or diiodine. In two of our previous reports we described how addition of an excess of iodine monochloride or dibromine resulted in oxidation of the selenium atom and cleavage of the carbon–selenium double bond to produce an organic cation and ICl_2^- (ref. 7) or $SeBr_6^{2-}$, $Se_2Br_9^-$ and Br_3^- (ref. 8) as counter ions. This oxidation has not so far been observed for reactions involving an excess of diiodine or iodine monobromide,[6] and we hypothesised that the greater oxidising power of the dihalogen becomes important when two or more equivalents are added to selenoamides. Further, we noted that although oxidation has not been observed by us or reported by other workers for 1 : 1 reactions involving heavier dihalogens or interhalogens, the oxidising power of dichlorine is such that oxidation may well take place even when it reacts with selenoamides in only a 1 : 1 ratio.

This study, therefore, seeks to examine the reaction of mbts and dmsu with dichlorine, in order to show whether 1 : 1 addition products can indeed form, or whether oxidation will take place to produce organic cations and binary selenium–chlorine anions. However, as we have shown the ratio of dihalogen employed is of great importance, much of the work presented is concerned with reactions with SO_2Cl_2 rather than dichlorine gas. Another reason for this is that we felt it would be useful to compare the nature of products formed from the reaction of selenoamides with dichlorine to those formed on reaction with sulfuryl chloride: chlorination by the latter reagent will not require fission of a Cl–Cl bond.

Results and discussion

Sulfuryl chloride was treated with an equimolar quantity of mbts for *ca.* 3 d in dichloromethane. A green solid of stoichiometry mbts·Cl_2 **1** was recovered as the major product. The Raman spectrum of this material has strong bands at 279 and 260 cm^{-1} which are lower than, but in keeping with, the values observed by Wynne and George[16] for Me_2SeCl_2. That molecule was shown by us[15] to exhibit a see-saw geometry with an almost linear Cl–Se–Cl moiety; these Raman bands therefore imply that **1** also contains this arrangement. In addition, we were able to obtain a ^{13}C NMR of **1** which revealed a peak at δ 174.1, $^1J(^{13}C-^{77}Se) = 203.1$ Hz. In a previous report[8] we pointed out that this coupling constant is a useful guide to the degree of s character in the C–Se bond; *cf.* δ_{mbts} 185.4 [$^1J(^{13}C-^{77}Se) = 231.3$ Hz], $\delta_{mbts\cdot Br_2}$ 171.6 [$^1J(^{13}C-^{77}Se) = 194.1$ Hz]. That is, as the C–Se bond moves from sp^2 to sp^3 hybridisation the amount of s character is reduced: this is illustrated by a reduction in ^1J. These data seem to suggest that mbts·Br_2 and **1** have a similar CSe bond type in solution. In ref. 8 we reported that mbts·Br_2 has a zwitterionic structure, with a positive charge on the nitrogen atom and a negative charge residing on the linear Br–Se–Br moiety, the C–Se linkage changing from a double bond (in mbts) to a single bond on adduct formation; this is reflected in the reduction of the coupling constant. The Raman and NMR data presented here therefore seem to imply that **1** and mbts·Br_2 are isostructural. Unfortunately, we have been unable to obtain crystals from the bulk material that are of a sufficient quality to carry out an X-ray diffraction analysis to confirm this. However, pale yellow crystals were grown by slowly cooling the filtrate collected on isolation of **1** and a structure determination on a single crystal revealed the ionic structure, **2**, shown in Fig. 1. The carbon–selenium double bond has been cleaved and replaced by a carbon–chlorine single bond with a distance of 1.670(7) Å to produce the organic cation $[C_8H_7NSCl]^+$; *d*(C(2)–N(1)) has shortened to 1.309(9) Å, thus representing a double bond. The positive charge can be assumed to therefore reside on the nitrogen atom. A Cl^- anion balances the charge and has quite a strong interaction with the Cl atom of the cation, *d*(Cl(1) · · · Cl(2)) = 3.087(7) Å (*cf.* the sum of the van der Waals radii of two Cl atoms of 3.6 Å). Selected geometrical parameters for **2** are presented in Table 1. Within standard deviations, the bond distances for the $[C_8H_7NSCl]^+$ cation in **2** are almost identical to those for the same cation in the ionic compound $[C_8H_7NSCl][ICl_2]$ previously described by us.[7] A particular curiosity concerning **2** is the presence of one molecule of SO_2 per ion pair; there is a strong interaction between that molecule's sulfur atom and the chloride ion, *d*(Cl(2) · · · S(1)) = 2.827(8) Å. A similar $Cl^- \cdots SO_2$ interaction was described by Passmore and co-workers[20] for the SO_2 'solvated' structure of 1,3,2-benzodithiazolium chloride.

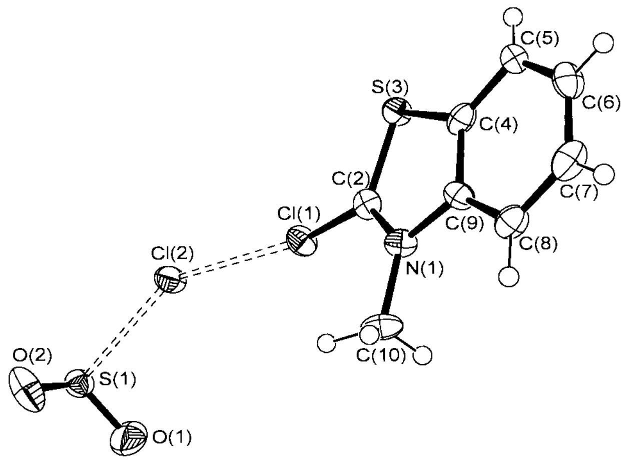


Fig. 1 An ORTEP[19] diagram of an ion pair from compound **2** with sulfur dioxide 'solvate'.

Table 1 Selected geometrical parameters (Å and °) for compound **2**

Cl(2)–C(2)	1.670(7)	S(3)–C(2)	1.697(7)
N(1)–C(2)	1.309(9)	S(1)–O(1)	1.420(6)
N(1)–C(10)	1.464(9)	S(1)–O(2)	1.410(6)
N(1)–C(2)–Cl(1)	124.0(5)	Cl(1)–C(2)–S(3)	120.8(4)
N(1)–C(2)–S(3)	115.2(5)	O(1)–S(1)–O(2)	116.4(5)

One equivalent of SO_2Cl_2 was treated with dmsu in a similar manner to mbts (above). After *ca.* 3 d a lemon solid of stoichiometry $C_3H_8N_2SeCl_2$ **3** was isolated. Unfortunately, we have so far been unable to elucidate this material's identity using spectroscopic techniques, and attempts at crystal growth have not been successful. It may also be noted that **3** analyses high for chlorine, most likely a consequence of an (as yet) unisolable minor product, perhaps of an ionic nature similar to **2**. It should be of considerable interest, therefore, to investigate **3** further to find out if it exhibits a T-shape geometry (as do Me_2SeCl_2 and **1**), or a yet different structural motif.

However, we were more successful when dmsu was treated with two equivalents of sulfuryl chloride. This reaction resulted in a lemon solid of stoichiometry $C_6H_{16}N_4SeCl_8$ **4**, from which a crop of small yellow needle crystals was obtained by slow cooling a saturated solution of **4** in dichloromethane to *ca.* 4 °C. One of these was examined by X-ray diffraction and found to have the ionic structure shown in Fig. 2 (selected geometrical parameters are in Table 2); *i.e.* **4** consists of two chloro-*N′*,*N′*-dimethylformamidinium ions counterbalanced by an $SeCl_6^{2-}$ anion. Also present in the asymmetric unit is one molecule of dichloromethane solvate. We believe that small amounts of microcrystalline, solvate-containing material may have been present in the initial yield of **4**; this might explain why the chlorine and carbon analyses are slightly higher than

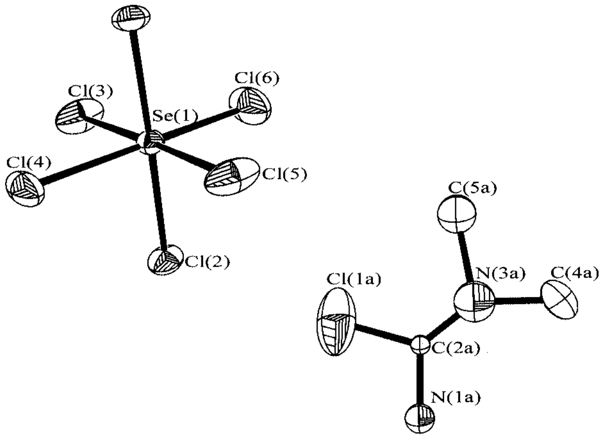


Fig. 2 An ORTEP diagram of an ion pair from compound **4**. The dichloromethane solvate has been omitted and only one disordered cationic component is shown for clarity.

Table 2 Selected geometrical parameters (Å and °) for compound **4**

Se(1)–Cl(2)	2.3736(8)	Se(1)–Cl(5)	2.535(2)
Se(1)–Cl(3)	2.285(2)	Se(1)–Cl(6)	2.226(2)
Se(1)–Cl(4)	2.601(2)		
Cl(6)–Se(1)–Cl(2)	90.65(5)	Cl(3)–Se(1)–Cl(4)	88.43(7)
Cl(6)–Se(1)–Cl(3)	92.25(6)	Cl(3)–Se(1)–Cl(5)	177.28(7)
Cl(6)–Se(1)–Cl(4)	179.32(7)	Cl(2)–Se(1)–Cl(4)	89.36(5)
Cl(6)–Se(1)–Cl(5)	90.47(7)	Cl(2)–Se(1)–Cl(5)	90.18(5)
Cl(3)–Se(1)–Cl(2)	89.79(5)	Cl(5)–Se(1)–Cl(4)	88.85(5)

expected. The organic cations are disordered (as was the case for its bromo-analogue in $[(H_2N)(Me_2N)CBr]_5[SeBr_6][Se_2Br_9][Br_3]_2$ previously described by us[8]); therefore little information regarding bond distances, angles, *etc.*, can be obtained. This cation has featured in only one other structural report to our knowledge,[21] although the similar tetramethylformamidinium analogue has been described by two separate research groups.[22,23] The $SeCl_6^{2-}$ anion surprisingly has not been previously described in a structural report as far as we know. Interestingly it contains two short, two medium and two longer Se–Cl bonds. Bond angles are close to 90 and 180°, giving a reasonably symmetric octahedral geometry. There is a long-range interaction between Cl(2) and the two available sites for Cl(1) of 3.395(8) and 3.264(8) Å for *d*(Cl(2)···Cl(1a)) and *d*(Cl(2)···Cl(1b)) respectively, which may stabilise the anion.

After isolation of compound **4** the filtrate was allowed to stand at *ca.* 4 °C and after several weeks tiny green crystals, **5**, formed, one of which was examined by single crystal X-ray diffraction. The structure is shown in Fig. 3 and selected geometrical parameters are displayed in Table 3. Compound **5** has a similar ionic arrangement to that of **4**, but with $Se_2Cl_4^{2-}$ rather than $SeCl_6^{2-}$ as a counter ion. This species is disordered: the anions stack along the *a* axis, with the Se atoms forming a 'column'. Crystallographically, each Se atom may occupy one of two sites (in the ratio 1:9), and Se–Se bonds are formed regardless of which site is occupied. The Cl atoms occupy one site only. Fig. 4 shows this arrangement; the anions in black depict the arrangement employed for 90% of the Se sites, those in grey show the alternative arrangement. Unusually, however, the organic cation is not disordered and geometrical parameters can be obtained. These values show that both C–N bonds have shortened and exhibit some double bond character, but *d*(C–NMe$_2$) is shortest at 1.292(3) Å (*cf.* *d*(C–NH$_2$) = 1.310(3) Å), implying that the methyl-bearing nitrogen atom bears most of the positive charge as one might expect. All geometrical parameters are in keeping with those reported for the same cation by Chivers *et al.*[21] The addition of two equivalents of sulfuryl chloride to dmsu does not, therefore, result in a T-shaped molecule with similar stoichiometry to that of **3**; rather, oxidation of the selenium atom and cleavage of the carbon–selenium double bond occur to yield the chloro-*N′*,*N′*-dimethylformamidinium cation. Our X-ray studies have shown that at least two selenium–chlorine binary anions are thermodynamically 'available' as counter ions; we do not exclude the possibility that other variations in the anion are possible, leading to further minor products.

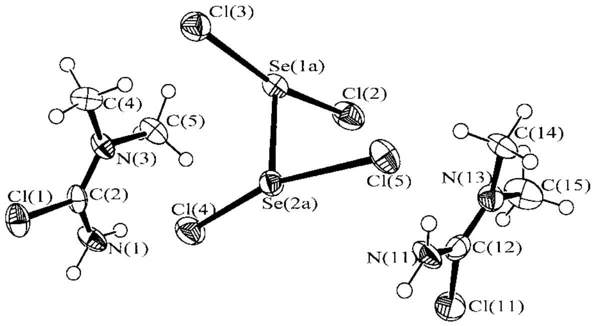


Fig. 3 An ORTEP diagram of the asymmetric unit of compound **5**.

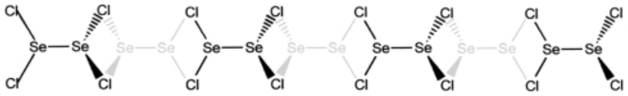


Fig. 4 Illustration of the two crystallographic sites available for the Se atoms of $Se_2Cl_4^{2-}$ in compound **5**. Note that the Cl positions are fixed. The sites in grey are occupied by 10% of the Se–Se units in the structure, the black sites are occupied by the remainder.

Table 3 Selected geometrical parameters (Å and °) for compound **5**

Se(1A)–Se(2A)	2.2642(5)	N(1)–C(2)	1.310(3)
Se(1A)–Cl(2)	2.4112(8)	N(3)–C(2)	1.292(3)
Se(1A)–Cl(3)	2.4843(8)	N(3)–C(4)	1.464(3)
Se(2A)–Cl(4)	2.2750(8)	N(3)–C(5)	1.465(3)
Se(1B)–Se(2B)	2.199(5)	Cl(11)–C(12)	1.702(2)
Se(1B)–Cl(2)	2.345(3)	N(11)–C(12)	1.309(3)
Se(1B)–Cl(3)	2.589(3)	N(13)–C(12)	1.297(3)
Se(2B)–Cl(4)	2.134(3)	N(13)–C(14)	1.471(3)
Cl(1)–C(2)	1.704(2)	N(13)–C(15)	1.474(4)
Se(2A)–Se(1A)–Cl(2)	97.74(3)	Se(1B)–Se(2B)–Cl(4)	100.2(2)
Se(2A)–Se(1A)–Cl(3)	95.77(3)	N(3)–C(2)–N(1)	124.6(2)
Cl(2)–Se(1A)–Cl(3)	166.44(3)	N(3)–C(2)–Cl(1)	118.6(2)
Se(1A)–Se(2A)–Cl(4)	99.87(3)	N(1)–C(2)–Cl(1)	116.8(2)
Se(2B)–Se(1B)–Cl(2)	105.3(2)	N(13)–C(12)–N(11)	124.2(2)
Se(2B)–Se(1B)–Cl(3)	93.60(14)	N(13)–C(12)–Cl(11)	119.1(2)
Cl(2)–Se(1B)–Cl(3)	160.27(15)	N(11)–C(12)–Cl(11)	116.7(2)

Having observed that the ratio of sulfuryl chloride to dmsu used is of great importance, we thought it likely that different products might result if dichlorine gas was used as a chlorinating agent instead. Previous studies have focussed on the structural diversity that arises on the reaction of selenoamides with a dihalogen or interhalogen;[1–9] some of this diversity could be said to arise as a consequence of the ease of fission of the halogen–halogen bond. Clearly, this is not a factor when using sulfuryl chloride. We allowed dmsu to react with an excess of dichlorine gas for *ca.* 3 d in dichloromethane; this yielded a bright yellow product of stoichiometry dmsu·Cl$_{5.3}$ **6**. Direct recrystallisation of **6** has so far failed, but small yellow needles were obtained by slow cooling the filtrate after isolation of the bulk material. Examination of one of these by X-ray diffraction showed it to have the ionic structure **7**, shown in Fig. 5; selected geometrical parameters are displayed in Table 4. It can be seen that **7** is indeed different to the other products of chlorination reactions of dmsu, *i.e.* **3**, **4** and **5**. The chloro-*N′*,*N′*-dimethylformamidinium cation is again a feature and is disordered due to it being situated on a crystallographic inversion centre. Of particular interest is the presence of yet another type of binary

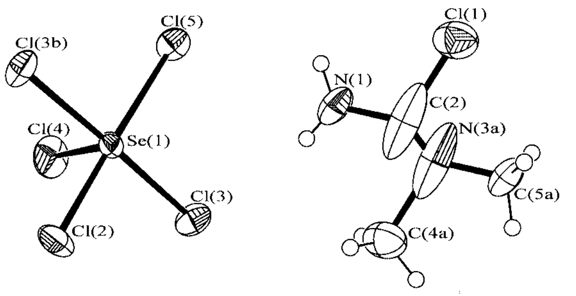


Fig. 5 An ORTEP diagram of an ion pair from compound **7**. Only one disordered cationic component is shown for clarity.

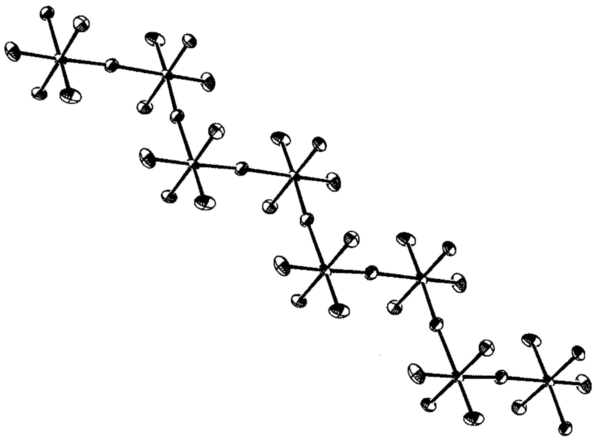
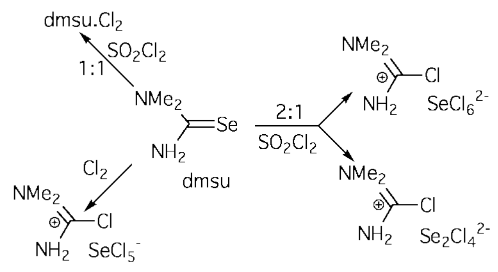


Fig. 6 An ORTEP diagram showing the 'polymeric' nature of linked $SeCl_5^-$ anions in compound **7**.

Table 4 Selected geometrical parameters (Å and °) for compound **7**

Se(1)–Cl(2)	2.257(2)	Se(1)–Cl(4)	2.161(2)
Se(1)–Cl(3)	2.3639(11)	Se(1)–Cl(5)	2.537(2)
Cl(2)–Se(1)–Cl(3)	89.28(4)	Cl(3)–Se(1)–Cl(4)	89.83(4)
Cl(2)–Se(1)–Cl(4)	92.55(9)	Cl(3)–Se(1)–Cl(5)	90.73(4)
Cl(2)–Se(1)–Cl(5)	176.45(8)	Cl(4)–Se(1)–Cl(5)	91.00(8)

anion, $SeCl_5^-$. This ion exhibits a reasonably diverse range of Se–Cl bond distances (two of 2.3639(11) and one each of 2.161(2), 2.257(2) and 2.537(2) Å). There are significant Se···Cl interactions between adjacent $SeCl_5^-$ units, which link to form a polymeric chain as illustrated in Fig. 6. The stoichiometry of **7** (*i.e.* $C_3H_8N_2SeCl_6$) is richer in chlorine than that of **6** (*i.e.* $C_3H_8N_2SeCl_{5.3}$) and so cannot be said to be truly representative of the bulk product. This might be a consequence of **6** containing a small amount of a chemically similar minor product; it is reasonable to speculate that minor products containing one or more anion(s) different to $SeCl_5^-$ would be difficult to remove from the bulk product using conventional techniques, and would have a marked effect on the chlorine analysis. Certainly, when two equivalents of sulfuryl chloride are treated with dmsu the products **4** and **5** are chemically very similar and should separation of those two species be necessary non-standard techniques would be required. Of course, it is possible that **6** and **7** are in fact unrelated compounds, and our studies are continuing to find out if this is the case or not. Scheme 1 summarises what is so far known about the reactions of dmsu with Cl_2 and SO_2Cl_2. Dichlorine gas was also treated with mbts to give a lemon solid of stoichiometry $C_8H_7NS{\cdot}SeCl_{5.5}$ **8**.



Scheme 1

Conclusion

In direct contrast to the reaction of diiodine or iodine monobromide with selenoamides (which produces 1 : 1 CT adducts regardless of the stoichiometry employed) and the reaction of Br_2 with selenoamides (which produces a bulk 1 : 1 addition product and ionic minor products) the reaction of Cl_2 or SO_2Cl_2 with selenoamides is complicated. Although it would appear that 1 : 1 addition compounds can be formed, carbon–selenium bond fission appears to be more favoured (compared to analogous reactions with the heavier dihalogens) and it seems unlikely that any of the reactions described herein results in the formation of a single product. These observations clearly illustrate how the oxidising power of a given dihalogen or interhalogen affects the nature of the product obtained when treated with a selenoamide.

The equimolar reaction of sulfuryl chloride with mbts or dmsu gives the 1 : 1 addition products **1** and **3**. Raman and ^{13}C NMR evidence seems to point strongly towards **1** being a T-shaped zwitterionic molecule with a linear Cl–Se–Cl arrangement supporting a negative charge and a positive charge residing on the nitrogen atom. That is, **1** appears to be an analogue of the mbts·Br_2 molecule previously described by us.[8] We hope to carry out further structural investigations to confirm the nature of **1** and **3**. Perhaps of greater interest, however, is the fact that an ionic minor product, **2**, also forms in the reaction that produces **1**. Previous reports have described how the addition of one equivalent of a dihalogen or interhalogen to a selenoamide gives 1 : 1 adducts,[6–10] but the addition of two equivalents results in C=Se bond cleavage to give an ionic product.[7–9] This study, therefore, represents the first report of C=Se bond cleavage occurring (albeit to give a minor product) from an equimolar reaction. In ref. 8 we pointed out that *d*(C–Se) gets longer as a more strongly oxidising dihalogen or interhalogen is used; ‡ we speculated that if dichlorine (or an equivalent such as sulfuryl chloride) were to be used, this bond would become especially long. This would make the Se atom particularly prone to oxidation and the C–Se bond very labile indeed. The fact that **2** was obtained from an equimolar reaction with SO_2Cl_2 appears to support this assertion.

Also of interest is the fact that the reaction of dmsu with two equivalents of sulfuryl chloride gives an ionic major product, **4**, in addition to an ionic minor product, **5**. A further ionic product, **7**, is obtained instead if one uses dichlorine instead of sulfuryl chloride. This illustrates two important points. First, there appears to be great subtlety in the conditions that govern which particular anions may form (*i.e.* in this work alone the organic cation is balanced by Cl^-, $Se_2Cl_4^{2-}$, $SeCl_5^{2-}$ or $SeCl_6^{2-}$). So far, we have been unable to predict which anions are likely to form for a given reaction, and our efforts are continuing in order to gain an understanding of the chemical factors that govern these systems. Secondly, our previous assertion[8] that the addition of an excess of a chlorinating agent would be likely to lead to an ionic compound as the bulk product, rather than just as a minor product, would seem to be correct.

The use of dichlorine to chlorinate dmsu and mbts has been shown to give different products than those from reactions using one or two equivalents of sulfuryl chloride. This

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‡ *d*(C–Se) for mbts, mbts·IBr and mbts·Br_2 are 1.817 (ref. 24), 1.877(5) (ref. 7) and 1.921(14) Å (ref. 8) respectively.

Table 5 Crystal data and structure refinement for compounds **2**, **4**, **5** and **7**

	2	**4**	**5**	**7**
Empirical formula	$C_8H_7Cl_2NO_2S_2$	$C_7H_{18}Cl_{10}N_4Se$	$C_6H_{16}Cl_6N_4Se_2$	$C_3H_8Cl_6N_2Se$
Formula weight	284.17	591.71	514.85	363.77
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pmn2_1$	$P2_1/n$	$Pnma$
a/Å	7.516(2)	13.974(3)	6.0267(10)	7.555(2)
b/Å	7.649(2)	7.633(2)	16.367(2)	15.516(2)
c/Å	18.973(3)	10.230(2)	18.116(2)	9.9151(10)
β/°	95.20(2)		97.80(2)	
V/Å^3	1086.3(4)	1091.1(4)	1770.5(4)	1162.3(4)
Z	4	2	4	4
μ/mm^{-1}	0.958	2.944	5.071	4.562
Total reflections	2033	1058	3388	2023
Unique reflections	1878	1058	3078	1058
	$[R_{int} = 0.0271]$	$[R_{int} = 0]$	$[R_{int} = 0.0381]$	$[R_{int} = 0.2288]$
Final $R1$, $wR2$ $[I > 2\sigma(I)]$	0.0689, 0.1480	0.0467, 0.1147	0.596, 0.1232	0.0549, 0.0909
(all data)	0.0893, 0.1582	0.0751, 0.1314	0.1207, 0.1484	0.2377, 0.1400

would seem to suggest that Cl–Cl bond cleavage is of some importance. We plan to extend the range of selenoamides and chlorinating agents under investigation; an understanding of the rules that govern particular product formation will hopefully allow a rational synthesis of a wide range of products to be carried out. At present, to our knowledge, the only selenium–chlorine binary anions to have been previously structurally characterised are $SeCl_4^{2-}$ (ref. 25 and 26), $SeCl_5^-$ (ref. 27), $Se_2Cl_6^{2-}$ (refs. 26, 28 and 29), $Se_2Cl_9^{2-}$ (ref. 30) and $Se_2Cl_{10}^{2-}$ (refs. 30 and 31). We have now added $Se_2Cl_4^{2-}$ and $SeCl_6^{2-}$ to this list. It seems likely that, by variation of conditions such as stoichiometry, solvent, reaction time, chlorinating agent and selenoamide used, it should be possible to produce further new and exciting structural varieties of the form $Se_aX_b^{n-}$ (where a, b are integers; $n = 1$ or 2).

Experimental

The selenoamide dmsu and compounds **1** to **8** are moisture sensitive; strictly anaerobic and anhydrous conditions must be observed for their successful synthesis. Subsequent manipulation of these products was carried out inside a Vacuum Atmospheres HE-493 glove-box. We obtained dmsu and mbts commercially (Aldrich) and used them as received; dichlorine was dried by bubbling through concentrated sulfuric acid prior to use. Dichloromethane (BDH) was dried over calcium hydride and refluxed in an inert atmosphere (N_2) for two hours prior to use. The synthesis of **1** is typical: mbts (0.500 g, 2.191 mmol) was dissolved in dichloromethane (*ca.* 70 cm^3) then SO_2Cl_2 was added as a 1 M solution in dichloromethane (2.19 cm^3, 2.191 mmol). After *ca.* 3 d the resultant green solid was isolated using standard Schlenk techniques and dried *in vacuo* before being transferred to pre-dried argon-filled ampoules which were then flame-sealed. Elemental analyses were performed by the analytical laboratory of this department and are listed below. The ^{13}C NMR spectrum was recorded in $(CD_3)_2SO$ using a Bruker AM400 spectrometer operating at 100.6 MHz and referenced to Me_4Si. The FT-Raman spectrum was recorded in the range 400–250 cm^{-1} at a power of 100 mW and no decomposition of the sample was observed during aquisition.

N-Methylbenzothiazole-2-selone dichloride **1**. Green solid, 47%, mp 201–203 °C (found: C, 31.5; H, 2.3; Cl, 24.5; N, 4.6; S, 10.4. $C_8H_7Cl_2NSSe$ requires C, 32.1; H, 2.3; Cl, 23.7; N, 4.7; S, 10.7%). FT-Raman (cm^{-1}): 279s and 260s. ^{13}C NMR (dmso): δ 174.1 (J(CSe) 203.1 Hz, C(2)).

1,1-Dimethylselenourea dichloride **3**. Lemon solid, 71%, mp 133–135 °C (found: C, 16.8; H, 3.6; Cl, 34.1; N, 12.7. $C_3H_8Cl_2N_2Se$ requires C, 16.2; H, 3.6; Cl, 31.9; N, 12.6%).

Bis(chloro-*N*′,*N*′-dimethylformamidinium) hexachloroselenate(IV) **4**. Lemon solid, 43% (found: C, 15.7; H, 3.5; Cl, 56.8; N, 11.9. $C_6H_{16}Cl_8N_4Se$ requires C, 14.2; H, 3.2; Cl, 56.0; N, 11.1%).

Compound **6**. Yellow solid, 90% (found: C, 10.4; H, 2.3; Cl, 54.4; N, 7.9. $C_3H_8Cl_{5.3}N_2Se$ requires C, 10.6; H, 2.4; Cl, 55.4; N, 8.3%).

Compound **8**. Lemon solid, 52%, mp 205–206 °C (found: C, 22.7; H, 1.7; Cl, 46.0; N, 3.3; S, 7.5. $C_8H_7Cl_{5.5}NSSe$ requires C, 22.7; H, 1.7; Cl, 46.0; N, 3.3; S, 7.6%).

X-Ray crystallography

The X-ray experiments for compounds **2**, **4**, **5** and **7** were carried out at 203 K on a Nonius MAC3 4-circle diffractometer using graphite monochromated Mo-Kα radiation. Three standard reflections were measured every 3 h and showed no significant decay. An absorption correction using the ψ-scan method was applied in each case. The cations in **4** are quadruply disordered and the hydrogen atoms were ignored. Chemically similar distances were constrained to be equal using the DFIX command. The cation in **7** is also disordered as its site is centred on a crystallographic inversion centre; however, in this case hydrogen atoms were able to be constrained to chemically reasonable positions. The $Se_2Cl_4^{2-}$ anion has the unusual kind of disorder discussed in the Results and discussion section and illustrated by Fig. 4. The SHELX 97 suite of programs[32] was used to solve the structures by direct methods and for refinement using full-matrix least squares. Crystallographic data are summarised in Table 5.

CCDC reference number 186/1683.

See http://www.rsc.org/suppdata/dt/1999/4245/ for crystallographic files in .cif format.

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