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Reaction of dimethylselenourea and selenourea with dibromine to produce selenourea–dibromine, the 'T'-shaped 1:1 molecular adduct *N*,*N*-dimethyl-2-selenourea–dibromine, its solvent of crystallisation-containing analogue and the unusual ionic compound $5[(H_2N)(Me_2N)CBr]^+[SeBr_6]^{2-}[Se_2Br_9]^-2[Br_3]^-$. A low temperature crystallographic reinvestigation of *N*-methylbenzothiazole-2-selone–dibromine

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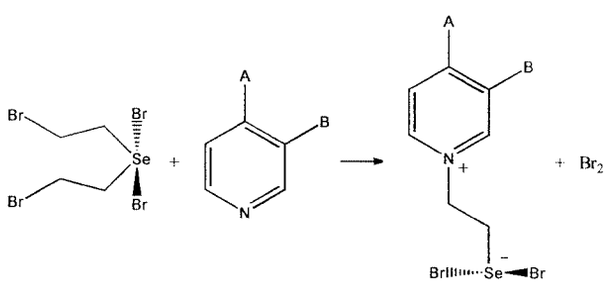
The reactions of the selenoamides *N*,*N*-dimethyl-2-selenourea, dmsu, selenourea, su and *N*-methylbenzothiazole-2-selone, mbts, with dibromine has been studied. In all reactions the bulk product formed is the 1:1 T-shaped addition compound, selenoamide·Br_2. The crystal structure of dmsu·Br_2 **1** has been determined and compared to its solvated analogue, dmsu·Br_2·CH_2Cl_2. Despite the different crystal packing in these two adducts, an asymmetry in *d*(Se–Br) is exhibited by both, ruling out the possibility that differences in Se–Br bond lengths are attributed solely to crystal packing forces. Both structures are essentially zwitterionic, a negative charge resides on the $SeBr_2$ moiety and the positive charge is supported by the two nitrogen atoms. The recently reported mbts·Br_2, previously described as a carbene interacting with $SeBr_2$, was reinvestigated. Considering findings from a low temperature X-ray study and the ^{13}C NMR spectrum, this compound is in fact also best described as zwitterionic, analogous to **1** and previously described structures. An interesting minor product from the reaction of two equivalents of dibromine with dmsu has also been characterised crystallographically. This complicated ionic structure of formula $5[(H_2N)(Me_2N)CBr]^+$-$[SeBr_6]^{2-}[Se_2Br_9]^-2[Br_3]^-$ illustrates the susceptibility of certain selenoamides to carbon–selenium bond cleavage when a dihalogen that is more strongly oxidising than I_2 or IBr is treated with them in a stoichiometric ratio greater than 1:1. This curious (and disordered) structure represents the first report of the anion $[Se_2Br_9]^-$.

Introduction

We are currently engaged in a comprehensive study of the interaction of a variety of organo Group 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, Me_2Se reacts with diiodine to produce the charge-transfer (CT) adduct Me_2Se–I–I whereas with dibromine or dichlorine it produces the disphenoidal 'see-saw' structure Me_2SeX_2 (X = Cl or Br).[1] On the other hand, other workers have shown crystallographically that dimethyl sulfide reacts with dibromine to form the CT compound Me_2S–Br–Br.[2] More recently, we have extended our studies to investigate the reaction of certain tertiary phosphine selenides with dihalogens and have found that these species react with diiodine to produce the CT compounds R_3PSeI_2 (geometry at selenium atom is bent).[3] However, reactions of the same compounds with dibromine produce the T-shaped compounds R_3PSeBr_2.[4]

We have now turned our attention to the reaction of selenoamides with dihalogens. The ability of selenoamides to form CT adducts with diiodine (and to a lesser extent, iodine monobromide) has been investigated by Devillanova and co-workers[5] and several crystal structures of such compounds have been reported. Initial reports concluded that the 1:1 adducts formed from the reaction of selenoamides with I_2 or IBr feature the linear arrangement Se–I–X (X = I or Br), as expected for a CT complex. Despite the fact that some lengthening of the carbon–selenium bond was noted upon adduct formation, the double bond character of the C=Se bond was essentially retained. Interestingly, the same workers also discovered that, by varying the nature of the selenoamide, a 'T'-shaped geometry could be observed; thus, reaction of *N*-methyl-1,3-thiazolidine-2-selone with I_2 produces the CT adduct, but that of 1,3-dimethyl-4-imidazoline-2-selone resulted in a 'T'-shaped compound featuring an I–Se–I linkage. Recently, we have investigated[6] the isostructural mbts·IBr and mbts·ICl molecules (mbts = *N*-methylbenzothiazole-2-selone), the latter representing the first crystallographic report of a selenoamide–iodine monochloride CT adduct to our knowledge. More intriguing is the reaction of mbts with two equivalents of ICl mentioned in the same study; one might expect an 'extended chain' arrangement to result, as was found by Devillanova for mbts·2IBr: that structure consists of a cationic $[mbts–I]^+$ moiety strongly interacting with an $[IBr_2]^-$ anion. However, we found that cleavage of the carbon–selenium bond occurs and a mixture of products results. Clearly, these systems lie close to important structural and geometrical borderlines and further investigation into the subtle electronic and steric effects that govern the exact nature of adducts formed on reaction with dihalogens or interhalogens is warranted.

Here, we present the results of our investigation into the reaction of some selenoamides with dibromine. Until recently, there had been no reports to our knowledge concerning simple 1 : 1 adduct formation between selenoamides and X_2 (where X = Br, Cl or F), or indeed between X_2 and molecules (other than selenoamides) that contain a C=Se functional group. However, very recently the interaction of selenoamides with dibromine has become a topical area. Williams *et al.*[7] described an aromatic selenoamide–dibromine adduct with a T-shaped Br–Se–Br arrangement. These workers interpreted this molecule as a stable aromatic heterocycle carbene complex of selenium(II) bromide. They also assigned a negative charge to the Br–Se–Br moiety; the C–Se linkage is described as a single bond and a positive charge is supported by the aromatic ring. Additionally, Devillanova *et al.*[8] reported the structure of the T-shaped 1 : 1 dibromine adduct of mbts for which they described the C–Se linkage as a double bond, with no negative charge on the Br–Se–Br moiety. Hence, these workers felt that a carbene–$SeBr_2$ complex is an appropriate description for this type of adduct, but imply that carbene stabilisation is achieved from substantial back bonding by the $SeBr_2$ moiety to give essentially a carbon–selenium double bond. In addition, these workers made no comment concerning a possible zwitterionic structure for the adduct. Akabori and Takanohashi[9] have extensively studied the organic synthetic reagent bis(2-bromoethyl)selenium dibromide. This versatile reagent is prepared from the reaction of elemental selenium, dibromine and ethylene in carbon tetrachloride[10] and has found use, in conjunction with $NaBH_4$, for the selective reduction of tertiary amides or nitrile compounds to the corresponding amine,[9] as well as a variety of other novel synthetic reactions.[11] It also has relevance to our studies as it is said to form hypervalent 'T'-shaped selenium co-ordination compounds[12] on reaction with pyridine and substituted pyridines according to Scheme 1. These products are not described in



(**1a**, A, B = H; **1b**, A = H, B = Br; **1c**, A = CN, B = H)

Scheme 1

terms of a carbene-acceptor system, but as purely zwitterionic, with the positive charge residing mostly on the nitrogen atom and the negative charge on the Br–Se–Br moiety: an orbitally deficient 3 centre–2 electron system that arises from the overlap of np_σ orbitals. These products were not made *via* direct addition of bromine to a C=Se functional group, however, so cannot necessarily be relied upon when predicting or rationalising the nature of products formed from the reaction of selenoamides with Br_2. Similarly, the 'T'-shaped molecule Se_3C–$SeBr_2$ reported by Larsen and Henriksen[13] was prepared by the reaction of CSe_2 with Se_2Br_2 in the presence of bromide ions, rather than by 1 : 1 dibromine addition. These workers offered no opinion regarding the distribution of charge around this unusual molecule. Fig. 1 illustrates three of the molecules under discussion which, together with the product in Scheme 1, represent the diversity of structural forms assigned to these T-shaped species. It would appear, therefore, that disagreement exists as to the exact structural nature of these T-shaped adducts, *i.e.* 'purely' carbene *versus* 'purely' zwitterionic forms. This may, in part, be due to the lack of consensus regarding which bond

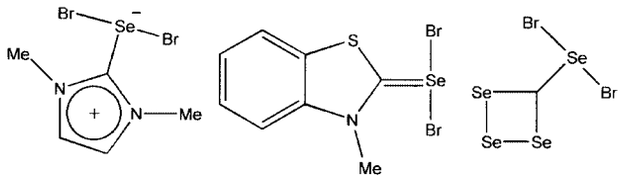


Fig. 1 Three T-shaped molecules containing a Br–Se–Br arrangement; the structures shown here are those assigned by the authors of the reports in which they appear, refs. 7, 8 and 13 respectively.

distances constitute a single or a double carbon–selenium bond. A search of crystallographic reports reveals the normal range for all types of C–Se linkage to be 1.70 to 1.95 Å; however, there is no clear dividing line where one can categorically state whether a particular distance represents a single or a double bond. A further complication with molecules such as mbts is that one can envisage some delocalisation occurring about the selenoamide group, resulting in only small changes in bond order upon adduct formation.

This study, therefore, seeks to address the problem by adding to the rather limited number of selenoamide–dibromine adducts known and to carry out a more rigorous examination of the changes in geometrical parameters that occur on adduct formation. This should hopefully provide a definitive description for these subtle and topical systems. Although this is of significant interest in itself, the long-term aim of this research is to provide a new synthetic route to metal–selenium complexes. This could be analogous to the successful method previously described by us for oxidising metal powders with dihalogen adducts of tertiary phosphines, arsines and stibines to produce novel metal complexes,[14] some with unusual geometries and/or high oxidation states. We are interested, therefore, not only in the synthesis of new 1 : 1 selenoamide addition compounds with dihalogens and the rationalisation of their geometries and charge distribution about the molecules, but also in their possible use as agents for the oxidation of unactivated metal powders.

Results and discussion

The selenoamides selenourea (su) and *N*,*N*-dimethylselenourea (dmsu) were treated with dibromine in a 1 : 1 ratio in dichloromethane solution; reaction times were *ca.* 2 d. In each case an approximately quantitative yield of an orange 1 : 1 selenoamide–dibromine adduct was isolated, *i.e.* dmsu·Br_2 **1** and su·Br_2 **2**. We also reacted dmsu with two equivalents of dibromine to find out if a 1 : 2 adduct can form, as was seen for certain selenoamides with diiodine and iodine monobromide.[5a] However, this also produced a 1 : 1 adduct of stoichiometry dmsu·Br_2 **3**. Analytical data and a powder diffraction comparison showed **1** and **3** to be identical. That is, the nature of the bulk product appears to be independent of whether one or two equivalents of dibromine are used. This was also found by Devillanova to be the case for the reaction of mbts with dibromine,[8] strongly suggesting that 'extended chain' structures of the type reported for mbts·$2I_2$ and mbts·2IBr[5a] do not occur for dibromine addition reactions.

Pale yellow crystals were prepared by slowly cooling a solution of compound **1** in dichloromethane from 30 to *ca.* 5 °C and leaving to stand at this temperature for *ca.* 5 d. On examination by single crystal X-ray diffraction the molecular geometry was seen to be T-shaped. Fig. 2 shows one molecule from the unit cell: *d*(C–Se) has lengthened from the 1.866 Å in dmsu reported by Zingaro and co-workers[16] (no standard deviations were included in this work) to 1.943(4) Å (Table 1); this increase without doubt represents a change from a carbon–selenium double bond to a (long) single bond. A negative charge must therefore reside on the Br–Se–Br moiety. Correspondingly, both carbon–nitrogen bonds shorten and adopt some C=N double

Table 1 A comparison of selected geometrical parameters (Å and °) for dmsu, **1** and **5**

	dmsu [16,a]	**1**	**5**
Se(1)–C(2)	1.866	1.943(4)	1.943(8)
Se(1)–Br(2)	—	2.4408(6)	2.433(1)
Se(1)–Br(1)	—	2.7623(6)	2.755(1)
N(1)–C(2)	1.329	1.309(5)	1.31(1)
N(3)–C(2)	1.324	1.312(5)	1.29(1)
N(3)–C(5)	1.458	1.461(5)	1.47(1)
N(3)–C(4)	1.463	1.470(5)	1.48(1)
C(6)–Cl(1)	—	—	1.77(1)
C(6)–Cl(2)	—	—	1.75(1)
C(2)–Se(1)–Br(2)	—	90.6(1)	89.4(2)
C(2)–Se(1)–Br(1)	—	85.4(1)	84.0(2)
Br(2)–Se(1)–Br(1)	—	174.11(2)	173.30(4)
N(3)–C(2)–N(1)	118.56	121.9(4)	122.1(7)
N(3)–C(2)–Se(1)	124.62	122.0(3)	122.3(6)
N(1)–C(2)–Se(1)	116.81	116.1(3)	115.6(6)
C(2)–N(3)–C(4)	121.16	119.9(3)	119.7(7)
C(2)–N(3)–C(5)	122.51	125.5(3)	124.6(7)
C(4)–N(3)–C(5)	116.25	114.6(3)	115.7(7)
Cl(2)–C(6)–Cl(1)	—	—	111.4(6)

[a] Values reported in ref. 16 contain no standard deviations so they cannot be included here.

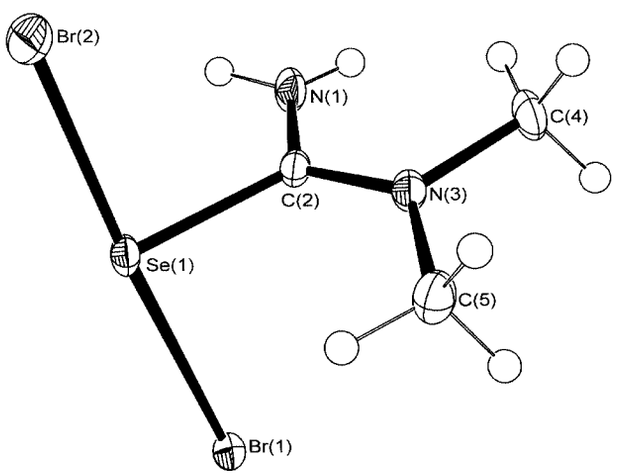


Fig. 2 An ORTEP [15] drawing of one molecule of compound **1**.

bond character (*d*(C2–N3) = 1.312(5), *d*(C2–N1) = 1.309(5) Å). Within experimental error, one cannot conclude which of the two nitrogen atoms bears the most positive charge: one might expect it to reside mostly (but not completely) on the methyl group-bearing nitrogen atom, due to the added inductive effects present to stabilise the positive charge. Unfortunately this cannot be proved or disproved from the data presented here. Nevertheless, this molecule can be unquestionably described as zwitterionic. A further point of interest is the asymmetry of the selenium–bromine bond distances. A large difference between *d*(Se1–Br1) and *d*(Se1–Br2) of 0.3215(6) Å is seen; this is almost three times the difference seen for one of the molecules in the asymmetric unit of mbts·Br_2 [8] or for CBr_2Se_4.[13]

Attempts to grow crystals from a dichloromethane solution of compound **2** have so far failed. It seems likely, however, that this adduct would adopt the same structure as **1**. It would be useful to examine a single crystal, though, in order to make a comparison of geometrical parameters between dibromine adducts of the similar selenoamides, su and dmsu. It seems likely that positive charge will not mostly reside on a single nitrogen atom in **2** but be distributed evenly between both of them. The absence of inductive groups on either nitrogen atom may make such a molecule less stable than the dmsu analogue and will almost certainly have an effect on the distribution of charge (and therefore on bond distances) about

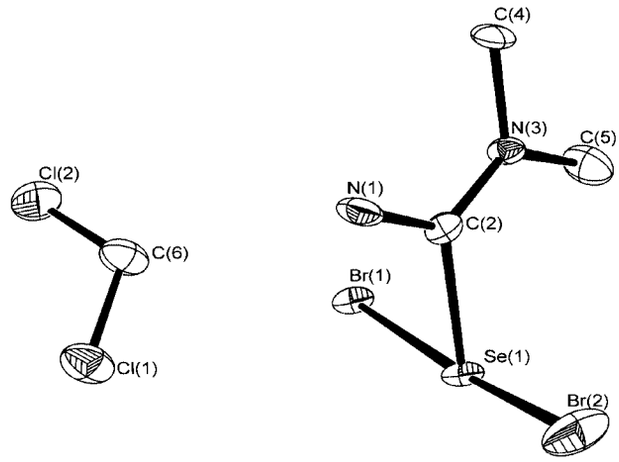


Fig. 3 An ORTEP drawing of the asymmetric unit of compound **5**, comprising of one molecule of dmsu and its solvate, CH_2Cl_2.

the molecule. We hope shortly to examine a wider range of selenoamides so a more thorough investigation can be made into the effect of *N*-alkyl groups of selenoamides on adduct formation with dihalogens.

It was then decided to attempt to treat compound **1** with nickel powder. Previous reports by us have described how triorganophosphine diiodide and dibromide adducts have found utility for formation of novel nickel complexes featuring high oxidation states [17] or surprising *trans* arrangements.[18] We therefore hope to develop an analogous route to transition metal–selenoamide complexes using selenoamide–dihalogen adducts. Unactivated nickel metal powder was treated with two equivalents of **1** in dichloromethane for *ca.* 5 d. The bulk product was a green powder with the empirical formula $C_6H_{16}Br_4N_4NiSe_2$ **4**; so far, the structure of this material has yet to be elucidated. However, small yellow crystals formed in the filtrate after isolation and standing at room temperature for *ca.* 7 d; one was examined by single crystal X-ray diffraction and found to be the starting material dmsu·Br_2 but, unlike **1**, one molecule of CH_2Cl_2 solvent is present in the asymmetric unit. Fig. 3 shows the asymmetric unit for this material, **5**. A comparison of the structure and packing of **1** with **5**, its solvent-of-crystallisation-containing analogue, can therefore be made (Fig. 4). The molecules of dmsu·Br_2 in **1** appear to orientate with 'pairs' of Br–Se–Br moieties of neighbouring molecules lying parallel to each other; in **5**, however, the presence of CH_2Cl_2 solvent molecules results in a different arrangement. Table 1 compares geometrical parameters for **1** and **5** with those previously reported for dmsu.[16] It can be seen that there are few significant differences in bond lengths or angles between dmsu·Br_2 molecules from the two structures. Interestingly, the asymmetry of the Br–Se–Br moiety is identical at 0.3215(6) Å for each structure; this asymmetry is therefore not solely a crystal packing phenomenon in this case. In ref. 12(*a*), Akabori and co-workers reasoned that the asymmetry in the Br–Se–Br moiety can be explained if one considers the longer (and therefore weaker) Se–Br bond to arise due to the relative proximity of the positive nitrogen atom to the bromine atom of the long Se–Br bond as compared with the short Se–Br bond's bromine atom. Although this theory holds for the non-planar T-shaped molecules described in that report (where the pyridinium moiety is clearly orientated much nearer to one side of the Br–Se–Br moiety), it cannot be applied to the planar dmsu·Br_2 molecules in **1** or **5**; here the positive charge cannot be considered to be closer to one side of the Br–Se–Br moiety than the other. We would therefore suggest that the effect of the positive nitrogen atom is not as influential as previously thought.[12a]

Having established that dmsu·Br_2 is a zwitterionic molecule (in both its solvent- and non-solvent-containing forms) we were

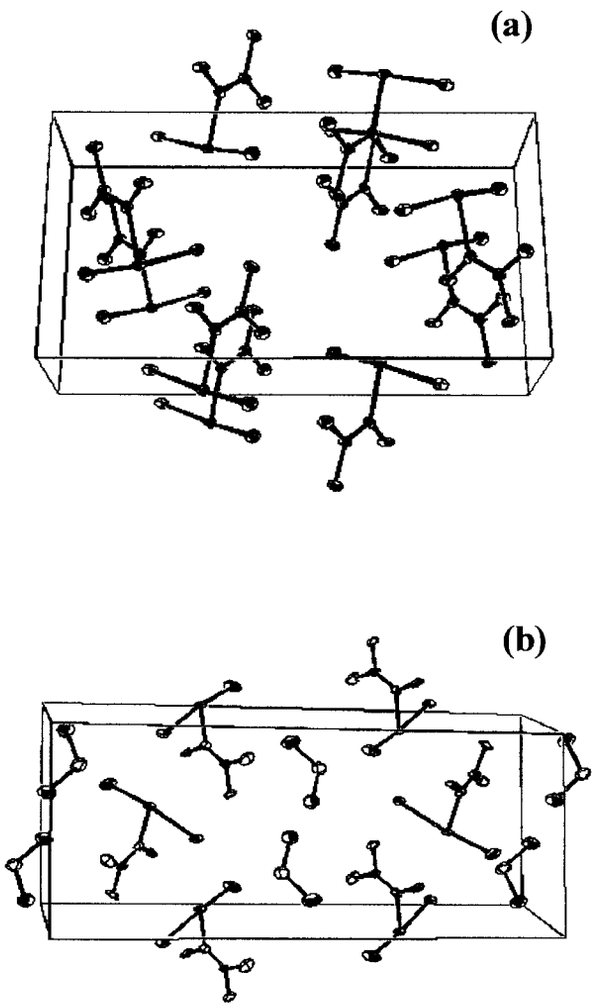


Fig. 4 The crystal packing of (*a*) compound **1** and (*b*) **5**.

intrigued as to why mbts·Br_2 was reported[8] as having essentially the same C–Se and C–N bond orders as mbts. As stated earlier, defining a carbon–selenium bond as single or double is problematic. We therefore felt it would be of interest to re-examine the structure of mbts·Br_2 reported by Devillanova *et al.*[8] at low temperature (*ca.* 200 K). One equivalent of dibromine was added to a solution of mbts in dichloromethane and allowed to react for *ca.* 2 d to produce mbts·Br_2 **6**. Small pale orange crystals were obtained on recrystallising the orange bulk product from slowly cooling a solution of dichloromethane from *ca.* 30 to *ca.* 5 °C. A single crystal was selected for X-ray diffraction analysis and the asymmetric unit (except the disordered dichloromethane solvent of crystallisation) is shown in Fig. 5. Selected geometrical parameters are displayed in Table 2, along with reported parameters for mbts[19] and the mbts·Br_2 structure at RT in ref. 8. We found the structure of **6** to be essentially the same as this latter structure; *i.e.* the unit cell consists of four pairs of crystallographically independent mbts·Br_2 molecules and two disordered dichloromethane ('solvent of crystallisation') molecules. Interestingly, the differences between the two independent mbts·Br_2 molecules in **6** are more pronounced for certain geometrical parameters than in its RT analogue, *e.g.* the difference in *d*(Se–C) between independent molecules is negligible (within experimental error) at RT but is 0.05(1) Å at −70 °C. The two Se–Br bonds in one of the mbts·Br_2 molecules in **6** are essentially symmetrical, but show a significant difference of 0.109(1) Å in the other. A similar order of Br–Se–Br asymmetry was found, but not commented on, for the RT structure by Devillanova *et al.*[8] We find it remarkable that only one of the independent molecules in the asymmetric unit shows an asymmetric effect and the other is symmetrical, if packing

Table 2 Selected geometrical parameters (Å and °) for compound **6**. A comparison with mbts[19] and mbts·Br_2 (examined at RT)[8]

	mbts	mbts·Br_2	**6**
Se(1)–C(2)	1.819	1.916(10)	1.921(14)
	1.815	1.908(10)	1.87(2)
Se(1)–Br(2)	—	2.564(2)	2.551(3)
		2.612(2)	2.602(3)
Se(1)–Br(1)	—	2.571(2)	2.557(3)
		2.510(2)	2.494(3)
S(3)–C(2)	1.719	1.687(10)	1.69(2)
	1.726	1.701(10)	1.71(2)
S(3)–C(4)	1.743	1.727(10)	1.783(14)
	1.733	1.734(10)	1.72(2)
N(1)–C(2)	1.359	1.303(11)	1.27(2)
	1.339	1.309(12)	1.32(2)
N(1)–C(9)	1.399	1.420(12)	1.39(2)
	1.390	1.392(12)	1.39(2)
N(1)–C(10)	1.456	1.453(12)	1.44(2)
	1.430	1.442(13)	1.41(2)
C(2)–Se(1)–Br(2)	—	87.2(3)	86.6(5)
		88.9(3)	89.2(5)
C(2)–Se(1)–Br(1)	—	86.5(3)	87.1(5)
		86.2(3)	86.0(5)
Br(2)–Se(1)–Br(1)	—	173.6(1)	173.6(1)
		175.1(1)	175.2(1)
C(2)–S(3)–C(4)	93	90	89.4(7)
	92	89	92.1(7)
C(2)–N(1)–C(9)	115	115	113.5(1)
	114	113	113.2(1)
C(2)–N(1)–C(10)	123	124	125.0(1)
	123	126	124.4(1)
C(9)–N(1)–C(10)	122	121	121.3(13)
	122	121	122(2)
N(1)–C(2)–S(3)	110	112	114.0(11)
	111	115	112.0(12)
N(1)–C(2)–Se(1)	127	127	126.2(13)
	128	124	126.9(13)
S(3)–C(2)–Se(1)	123	120	119.8(8)
	121	121	120.8(9)

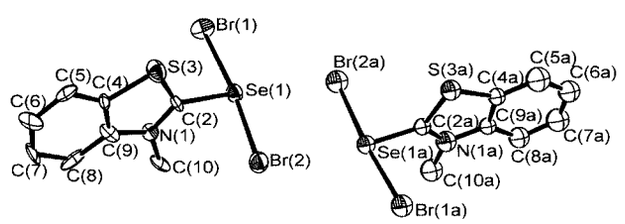


Fig. 5 An ORTEP drawing of the two discrete molecules of mbts·Br_2 (the molecule of dichloromethane solvate is omitted for clarity) from the asymmetric unit of compound **6**.

interactions are discounted as for dmsu·Br_2 (**1** and **5**). A close examination of our structure did indeed reveal some long range interactions (*d*(Br2–Se1A) = 3.461(3), *d*(Se1–Br2A) = 3.446(3), *d*(Br1–Br1*) = 3.678 Å); however, although these interactions perhaps help to explain why one molecule is asymmetric, they do not satisfactorily explain why the other is not. In addition, Akabori's theory[12a] that the positive moiety of the molecule is highly influential cannot be invoked (as it cannot be for **1** and **5**) due to the planar nature of the mbts molecule. This asymmetric effect is, therefore, a curious phenomenon that has so far not been completely explained by current thinking, and which merits further investigation.

The prime reason for the reinvestigation of mbts·Br_2 is to provide a definitive model for this type of 1 : 1 adduct. As **6** and the RT analogue each contain two independent mbts·Br_2 molecules, four C–Se bond lengths are available for examination: *d*(C–Se) = 1.921(14) and 1.870(15) Å at −70 °C and 1.916(10) and 1.908(10) Å at RT. With perhaps the exception of the second value, these all represent relatively long Se–C linkages. A search of the references containing crystallographic examples

of Se–C single and double bonds[16,19,20] seems to suggest a general consensus that a distance of 1.817 to 1.866 Å represents a double bond, single bonds generally being from 1.870 to 1.950 Å.† This would assign the C(2)–Se(1) linkage as a single bond. However, further information is obtained if one examines the bond distances from C(2) to N(1). If a zwitterionic model is employed, then as *d*(C–Se) lengthens from a double to a single bond one would expect *d*(C–N) to correspondingly shorten from a single to a double bond. The values for *d*(C2–N1) of 1.271(16) and 1.324(17) Å obtained by us for **6** and of 1.303(11) and 1.309(12) Å by Devillanova *et al.* show that this is indeed the case. That is, if Devillanova's carbene model for the mbts·Br_2 molecule were correct, then C(2) would have a total of five bonds: a double to Se(1), a double to N(1) and a single to S(3). We therefore find it far more likely that a zwitterionic structure is a more accurate model. Final proof of this was obtained by a comparison of $^1J(^{13}C–^{77}Se)$ for unco-ordinated mbts with that for **6**. We found this coupling constant to be 231.3 and 194.1 Hz for mbts and **6**, respectively, *i.e.* the value is lowered on co-ordination of mbts to dibromine. This tells us that the amount of s character in the C–Se bond is decreased on adduct formation, *i.e.* the bond moves from sp^2 to sp^3 hybridisation. This is in complete agreement with the bond length data for this molecule. We therefore feel that **6** is unquestionably a zwitterionic molecule, with the negative charge residing on the $SeBr_2$ moiety and the positive charge supported by the nitrogen atom. This means that it is isostructural with dmsu·Br_2 (**1** and **5**). Further, one might expect all selenoamide–dibromine T-shaped adducts to adopt this arrangement; future investigations will no doubt test the validity of this statement.

A previous report by us[6] describes how the addition of one equivalent of iodine monochloride to mbts produces a simple, spoke adduct, whereas two equivalents lead to cleavage of the carbon–selenium double bond and formation of the ionic compound $[C_8H_7NSCl]^+[ICl_2]^-$. Additionally, the ionic structure of 2-bromo-*N*-methylthiazolidinium hexabromoselenate has been described:[8] on reaction of *N*-methylthiazolidine-2-selone with dibromine, C=Se bond cleavage and the formation of a bromoorganic cation occurs. We felt it was important to investigate this phenomenon further so the reaction of dmsu with two equivalents of dibromine was repeated to again produce **3**. After isolation of the bulk 1:1 addition product we left the filtrate to stand for *ca.* 5 d and tiny red crystals were produced. One was examined by single crystal X-ray diffraction using a synchrotron source and found to have the ionic structure shown in Fig. 6. The stoichiometric formula of this material is $5[(H_2N)(Me_2N)CBr]^+[SeBr_6]^{2-}[Se_2Br_9]^-2[Br_3]^-$ **7**. Selected geometrical parameters from this curious arrangement are displayed in Table 3. Three different anions are present in the unit cell: *(a)* the well known octahedral $SeBr_6^{2-}$ on a centre of symmetry; *(b)* linear Br_3^- anions which show an asymmetry in Br–Br distances (difference between *d*(Br1–Br2) and *d*(Br2–Br3) is 0.317(1) Å) and *(c)* sitting on a crystallographic twofold axis, the previously unreported $Se_2Br_9^-$. This latter species consists of two selenium atoms each bound to three 'terminal' bromine atoms by three relatively short bonds (*d*(Se–Br) = 2.375(1) to 2.398(1) Å) and linked to each other by three longer 'bridging' bonds *via* bromine atoms (*d*(Se–Br) = 2.843(1) to 2.868(1) Å). One of the terminal bromine atoms, Br(10), has a long range interaction with Br(3) of the neighbouring Br_3^- anion (*d*(Br3–Br10) = 3.056 Å); therefore, the asymmetry of that anion can be attributed, at least in part, to the interaction of a Br_3^- bromine atom with a terminal bromine atom in the $Se_2Br_9^-$ anion. The overall charge of −1 for this anion cannot be assigned solely to one or other of the selenium centres. The species can be considered to have a structure closer to that described for the $Se_2Br_{10}^{2-}$ anion[21] than for $Se_2Br_8^{2-}$.[21] That is, in $Se_2Br_{10}^{2-}$, both selenium atoms in the anion are in almost identical environments (as is the case for $Se_2Br_9^-$) and each centre can be thought of as supporting one negative charge each. In $Se_2Br_8^{2-}$, however, one Se atom has bonds to six Br atoms and the other has bonds to just four; the former selenium centre supports both negative charges. Fig. 7 illustrates this point.

Oxidation of the selenium atom and cleavage of the carbon–selenium double bond has occurred to produce a cationic organic fragment containing a carbon–bromine single bond. For three of the cations' bromine atoms, a long interaction to another bromine atom in a neighbouring anion occurs: *(i)* Br(41) is 3.163(1) Å from Br(1) in the Br_3^- anion; *(ii)* Br(61) is 3.071(1) Å from Br(4) in $SeBr_6^{2-}$ and *(iii)* Br(81) is 3.003(1) Å from Br(8), a bridging bromine atom in $Se_2Br_9^-$. The effect of these long, but significant interactions is likely to be stabilisation of the positive charges residing on the cations.

† These values based on C(sp^2)–Se linkages. As C(2) has only three bonds in the molecules under discussion here, it seems justified to assume that sp^2 hybridisation for that atom is retained on adduct formation, regardless of whether the zwitterionic or carbene model is used to interpret the structure.

Table 3 Selected geometrical parameters (Å and °) for compound **7**. Figures marked with an asterisk are the values for the rigid group used to refine the individual atomic coordinates in the disordered $[(H_2N)(Me_2N)CBr]^+$ cation sites. Each of the cations in the asymmetric unit will therefore share these values. These are listed for just one of the cations to avoid duplication

Br(1)–Br(2)	2.427(1)	C(22)–Br(21)	1.8325*
Br(2)–Br(3)	2.744(1)	C(22)–N(21)	1.3240*
Se(1)–Br(4)	2.5820(1)	C(22)–N(23)	1.2826*
Se(1)–Br(5)	2.5664(8)	N(23)–C(24)	1.4615*
Se(1)–Br(6)	2.5673(8)	N(23)–C(25)	1.4529*
Se(2)–Br(7)	2.375(1)	Br(3)–Br(10)	3.056(1)
Se(2)–Br(9)	2.386(1)	Br(1)–Br(41)	3.163(1)
Se(2)–Br(10)	2.398(1)	Br(4)–Br(61)	3.071(1)
Se(2)–Br(8)	2.843(1)	Br(8)–Br(81)	3.003(1)
Se(2)–Br(11)	2.868(1)		
Br(1)–Br(2)–Br(3)	177.20(5)	C(22)–N(23)–C(25)	123.2*
Br(5)–Se(1)–Br(6)	90.73(3)	C(22)–N(23)–C(24)	119.7*
Br(5)–Se(1)–Br(4)	90.35(3)	C(25)–N(23)–C(24)	117.1*
Br(6)–Se(1)–Br(4)	89.62(3)	N(23)–C(22)–N(21)	125.0*
Br(7)–Se(2)–Br(9)	96.11(4)	N(23)–C(22)–Br(21)	119.7*
Br(7)–Se(2)–Br(10)	95.94(4)	N(21)–C(22)–Br(21)	115.3*
Br(9)–Se(2)–Br(10)	94.11(4)		

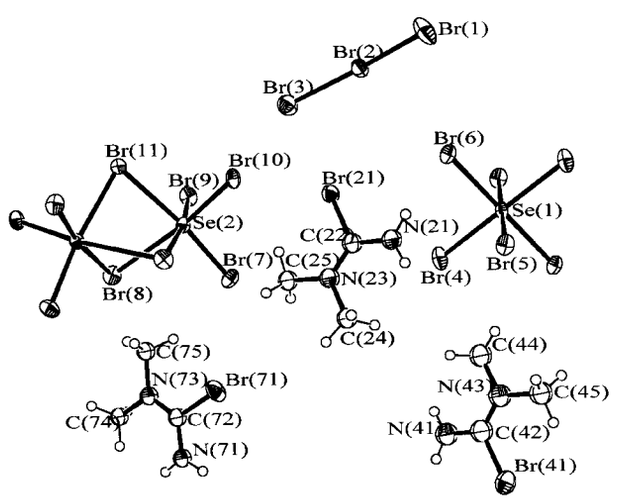


Fig. 6 The asymmetric unit of compound **7**, including labelling scheme (symmetry-related atoms are unlabelled). Each cation site contains several disordered $[(H_2N)(Me_2N)CBr]^+$ species with a total charge of +1; only one cation is illustrated per site for clarity. The formula for this compound is $5[(H_2N)(Me_2N)CBr]^+[SeBr_6]^{2-}[Se_2Br_9]^-2[Br_3]^-$; *i.e.* a full representation of this stoichiometry features two more symmetry generated cations and one more Br_3^- anion than shown here. These have also been omitted for clarity.

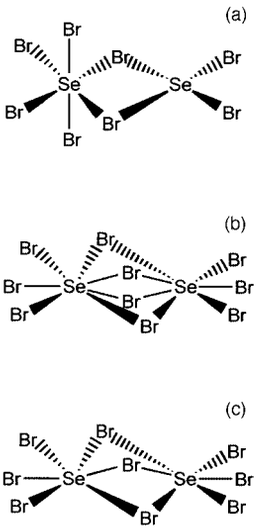


Fig. 7 A comparison of the structures of the known[21,22] binary selenium–bromine anions (a) $Se_2Br_8^{2-}$ and (b) $Se_2Br_{10}^{2-}$ with (c) $Se_2Br_9^-$.

The mechanism that allows for such a dramatic reaction on addition of two equivalents of bromine to dmsu, but not for the 1:1 reaction, is not yet known. It is likely that other products, so far unidentified, from this reaction form and it would be of great interest to isolate and examine these by similar methods to enable a complete stoichiometric equation for the reaction to be written. Although oxidation of the selenium atom and cleavage of the C=Se bond produced 2 $[C_4H_7BrNS]^+[SeBr_6]^{2-}$ as a single product in ref. 8, it would appear that formation of the octahedral $SeBr_6^{2-}$ anion is not the only driving force for this kind of reaction: we have shown that at least two other anions can be produced. Considering the variety of binary selenium–bromine anions known, it seems likely that yet more anions can form, depending on the exact selenoamide used, ratio of dibromine and possibly solvent. As one previously unknown anion has now been produced *via* this method, we intend to extend our studies fully to investigate this novel pathway to see if other, previously unknown, binary anions can indeed be formed.

Conclusion

In contrast to the reaction of diiodine or iodine monobromide with selenoamides, which produces the 1:1 or 2:1 CT adducts quantitatively, the reaction of dibromine with these compounds is more complicated, especially in the 2:1 dibromine:selenoamide ratio. In the case of the selenoamides dmsu and mbts, reaction with dibromine in both the 1:1 and 2:1 stoichiometric ratios produces a bulk product which proved to be the T-shaped 1:1 addition compounds. In each case, the carbon–selenium bond distance lengthens indicating a formal change from a double to a single bond and a negative charge resides on the $SeBr_2$ moiety. This change in bond order is also shown by a reduction in the $^1J(^{13}C–^{77}Se)$ coupling constant on coordination. The positive charge is supported by one or both nitrogen atoms (depending on the parent selenoamide) and a double bond is formed between the nitrogen atom and the carbon bound to the selenium. All of the adducts described seem therefore to be zwitterionic. This is in agreement with previous studies by Akabori and co-workers,[12] but contrasts with a recent report concerning the structure of mbts·Br_2 by Devillanova *et al.*[8] who described this adduct as essentially unchanged at the selenium centre (*i.e.* the carbon–selenium bond retains its double bond character). We feel that this adduct is also better described as zwitterionic in agreement with the other structures reported in this work and the previous reports of Akabori concerning similar compounds. However, it is feasible that Devillanova's model of a carbene-stabilised $SeBr_2$ acceptor is not a wholly incorrect approach if taken to its extreme. Those workers represented the C–Se bond as a double one, implying the $SeBr_2$ moiety engages in fairly substantial back donation to the singlet carbene: this doesn't fit with the data. However, it is perfectly reasonable that the nitrogen atom will donate a lone pair to the 'singlet carbene', with little or no back donation from the $SeBr_2$ required for carbene stabilisation. This model (taken to its extreme) would result in a greatly contracted C–N bond and lengthened C–Se bond, which is what is observed. It cannot be said from data reported so far, therefore, whether the mbts·Br_2 and dmsu·Br_2 molecules are 'purely' zwitterionic or very extreme carbene–acceptor systems. What is clear, however, is that a substantial positive charge is located on the nitrogen atom(s) and a corresponding negative charge resides on the $SeBr_2$ moiety. This view is consistent with that described by Williams *et al.*[7] for the first adduct in Fig. 1. These workers appreciated that the lengthening of the C–Se bond implies that substantial negative charge moves to the $SeBr_2$ moiety; in addition, formation of an aromatic ring occurs, which supports a positive charge. However, this molecule was described as (presumably a very extreme) carbene–acceptor system and not in terms of a zwitterion. Clearly, the borderline between extreme carbene–acceptor and zwitterionic forms is a difficult one to define. Akabori has shown that, in certain cases, there is no need to invoke a carbene–acceptor model, *i.e.* when there is no option of carbene stabilisation by heteroatoms bound to the 'donor'-carbon atom. Those molecules must, therefore, fall in the 'pure' zwitterionic class. This leads us to suggest that a zwitterionic model is perhaps a simpler and more accurate way of describing such molecules, including those adducts reported by Williams *et al.*[7] and Devillanova *et al.*[8]

Attempts to grow crystals of a nickel–selenoamide complex produced crystals of **5**, the T-shaped dmsu·Br_2 zwitterionic molecule seen for **1**, but with one molecule of dichloromethane in the unit cell. The presence of this solvent of crystallisation removes the interaction between adjacent Br–Se–Br moieties, preventing them 'pairing-up', but has little effect on the geometrical parameters of the dmsu·Br_2 molecule. The asymmetry of *d*(Se–Br) in the Br–Se–Br arrangement is especially pronounced at 0.321(6) Å (almost three times that seen by us and Devillanova *et al.*[8] for mbts·Br_2 and by other workers for bis-(2-bromoethyl)selenium dibromide[12] and for CSe_4Br_2[13]) and is almost identical in both **1** and **5**. This effect cannot, therefore, just be attributed to packing effects. In addition, of the two independent mbts·Br_2 molecules in the asymmetric unit of **6**, asymmetry does not occur in the molecule with the greater positive charge on the nitrogen atom (as implied by the longer *d*(C–Se) and shorter *d*(C–N) than for the other independent molecule). This, coupled with the fact that mbts and dmsu are planar selenoamides, leads us to suggest that the effect of the positive charge on the nitrogen atom on the asymmetry of the two Se–Br bonds is not as influential as suggested by Akabori and co-workers.[12a] These workers also raised the possibility that one of the Br atoms actually acted as a slightly independent anion to an 'SeBr' moiety as a result of this 'influence'. Although the data here reduce the importance of the N atom's positive charge, we do not rule out the possibility that one of the Br atoms does indeed act as an anion stabilising an 'SeBr' acceptor, and that this may go some way to explaining the asymmetric effect. However, this would not explain the absence of asymmetry in one of the independent molecules in the crystal structure of **6**.

Reaction of dmsu or mbts with two equivalents of dibromine yields the 1:1 adduct as the major product; however, carbon–selenium bond cleavage also occurs to produce complex arrangements of organic cations and inorganic anions, such as that seen for **7**. One of these anions, $Se_2Br_9^-$, has not appeared

Table 4 Crystal data and structure refinement for compounds **1**, **5**–**7**

	1	**5**	**6**	**7**
Empirical formula	$C_3H_8Br_2N_2Se$	$C_4H_{10}Br_2Cl_2N_2Se$	$C_{17}H_{16}Br_4Cl_2N_2S_2Se_2$	$C_{15}H_{40}Br_{26}N_{10}Se_3$
Formula weight	310.89	395.82	860.88	2675.11
T/K	150(2)	203(2)	203(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a/Å	6.0102(4)	5.972(1)	12.265(3)	10.5396(14)
b/Å	15.697(1)	22.241(2)	13.625(3)	17.097(3)
c/Å	8.7387(6)	8.947(1)	14.222(3)	33.115(3)
β/°	102.250(2)	104.503(10)	90.73(3)	93.67(1)
V/Å^3	805.7(1)	1150.5(3)	2376.3(8)	5955.2(13)
Z	4	4	4	4
D_c/mg m^{-3}	2.563	2.285	2.288	2.984
Reflections collected/unique	4024/1786 [R_{int} = 0.0399]	2212/2011 [R_{int} = 0.0448]	4381/4181 [R_{int} = 0.1110]	14840/6296 [R_{int} = 0.0373]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0374, 0.0892	0.0466, 0.0930	0.0759, 0.0587	0.0458, 0.1199
(all data)	0.0396, 0.0901	0.0861, 0.1074	0.2352, 0.0839	0.0647, 0.1267

in a previous report to our knowledge; this species can be considered to have a structure in keeping with the known species $Se_2Br_{10}^{2-}$ rather than with $Se_2Br_8^{2-}$.[21,22] The replacement of the Se atom in dmsu with a Br atom produces a cationic molecule stabilised, in part, by long range bromine–bromine interactions with neighbouring anions. This replacement is analogous to that of Se in mbts with a Cl atom when mbts was treated with two equivalents of ICl.[6] It would seem, therefore, that although adduct formation occurs when selenoamide and dihalogen are treated in a 1:1 ratio, in a 1:2 ratio C=Se bond cleavage can occur and, as yet unpredictable, ionic complexes are produced. We believe this to be a consequence of the greater oxidising power/acceptor ability of Br_2 and ICl as compared to I_2 and IBr; Devillanova and co-workers[5a] have shown that reaction of two equivalents of these latter molecules with mbts produce structures of the form $[mbts–I]^+[X–I–X]^-$ (X = I or Br) with strong interaction between cation and anion to form an 'extended spoke' arrangement. It would appear from our investigations that this arrangement is not available for products of the reaction of selenoamides with ICl or Br_2. There is, therefore, another previously unrecognised borderline that exists for these systems: dihalogen molecules with relatively high acceptor ability appear fully to oxidise the selenium centre of the selenoamide when treated in a 1:2 ratio; those with lower acceptor ability do not. This is not too surprising if one considers the fact that the change in d(C–Se) upon forming 1:1 adducts is greater when the selenoamide is treated with a more strongly oxidising dihalogen. It seems likely that this effect is even more pronounced when an *excess* of strongly oxidising dihalogen is used. A further effect is likely to be the stability of binary selenium halide anions formed: binary selenium–iodine species are notoriously unstable and so are not available as products to drive non-stoichiometric addition reactions with diiodine. Conversely, binary selenium–bromine species are well known and show great variety. One might expect that, due to these two effects (*i.e.* dihalogen or interhalogen oxidising power and stability of binary anions), the reaction of selenoamides with an excess of dichlorine is likely to produce ionic compounds as the bulk product, rather than just minor products as have been described by us for dibromine and iodine monochloride. This will form the basis of a forthcoming paper.

Experimental

Compounds **1**–**7** are moisture sensitive, as are the selenoamides su and dmsu. Therefore, strictly anaerobic and anhydrous conditions must be observed for their successful synthesis. Any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glove-box. We obtained su, dmsu and mbts commercially (Aldrich) and they were used as received. Dichloromethane (BDH) was dried over calcium hydride and refluxed in an inert atmosphere (N_2) for at least two hours prior to use. The synthesis of dmsu·Br_2 is typical: dmsu (0.500 g, 3.310 mmol) was dissolved in dichloromethane (*ca.* 100 cm^3) and subsequently dibromine (Aldrich, 0.529 g, 0.170 cm^3, 3.310 mmol) was added. After *ca.* 2 d the resultant orange solid was isolated using standard Schlenk techniques and dried *in vacuo*. It was then transferred to pre-dried argon-filled ampoules that were flame-sealed. Elemental analyses were performed by the analytical laboratory of this department and are listed below. The ^{13}C NMR spectra were recorded in $(CD_3)_2SO$ using a Bruker AM400 spectrometer operating at 100.6 MHz and referenced to Me_4Si.

Compound **1**, dimethylselenourea–dibromine: orange solid, 95%, mp 139–141 °C (Found: C, 11.6; H, 2.5; Br, 51.5; N, 8.4. $C_3H_8Br_2N_2Se$ requires C, 11.6; H, 2.6; Br, 51.7; N, 9.0%). Compound **2**, selenourea–dibromine: orange solid, 82%, mp 162 °C (Found: C, 4.3; H, 1.2; Br, 56.1; N, 9.9. $CH_4Br_2N_2Se$ requires C, 4.2; H, 1.4; Br, 56.5; N, 9.9%). Compound **3**, *N*,*N*-dimethylselenourea–dibromine: orange solid, 92%, mp 137–140 °C (Found: C, 11.7; H, 2.4; Br, 50.7; N, 8.6%). Compound **4**, green solid (structure unknown), 82.2%, mp 196 °C (Found: C, 10.7; H, 2.2; Br, 46.6; Ni, 9.2. $C_6H_{16}Br_4N_4NiSe_2$ requires C, 10.6; H, 2.4; Br, 47.0; Ni, 8.6%). Compound **6**, *N*-methylbenzothiazole-2-selone–dibromine: orange solid, 65%, mp 214–216 °C (Found: C, 24.0; H, 1.8; Br, 41.6; N, 3.4; S, 7.7. $C_8H_7Br_2NSSe$ requires C, 24.7; H, 1.8; Br, 41.2; N, 3.4; S, 7.8%). ^{13}C NMR spectrum (dmso): δ 171.6 (J(CSe) 194.1 Hz, C(2)). *N*-Methylbenzothiazole-2-selone: ^{13}C NMR spectrum (dmso) δ 185.4 (J(CSe) 231.3 Hz, C(2)).

X-Ray crystallography

The X-ray experiments for compounds **1** and **7** were carried out at low temperature at Station 9.8 at Daresbury Laboratory on a Siemens SMART CCD diffractometer using silicon 111 monochromated synchrotron radiation of wavelength 0.68620 Å. Diffraction measurement employed ω rotation with narrow frames. An absorption correction using an empirical ellipsoidal method was applied. Extreme disorder of the $[(H_2N)(Me_2N)CBr]^+$ cations in **7** made it impossible to refine individual atomic coordinates. All the cations were therefore refined as rigid groups.

The X-ray diffraction experiments for compounds **5** and **6** were carried out on a Nonius MAC3 4-circle diffractometer using graphite monochromated Mo-K_α radiation. The ω–2θ scan technique was used to collect reflections with $1 \leq 2\theta \leq 50°$. Three standard reflections were measured every 3 h and showed no significant decay. The intensities were corrected for Lorentz-polarisation effects. An absorption correction using the ψ-scan method was applied.

The SHELX 97 suite of programs[23] was used to solve the structures by direct methods and for refinement using full-

matrix least squares. Crystallographic data are summarised in Table 4.

CCDC reference number 186/1526.

See http://www.rsc.org/suppdata/dt/1999/2845/ for crystallographic files in .cif format.

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