

The reaction of *N*-methylbenzothiazole-2-selone with the interhalogens iodine monobromide and iodine monochloride

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Received 19th March 1999, Accepted 13th May 1999

Two 1:1 interhalogen adducts of *N*-methylbenzothiazole-2-selone (mbts) have been prepared and crystallographically characterised: mbts·IBr (**1**) and mbts·ICl (**2**). Both exhibit the charge transfer 'spoke' structure consisting of a linear Se–I–X arrangement (X = Br or Cl) where $d(\text{C–Se})$ increases from that seen for mbts by 0.058(5) and 0.062(8) Å (**1** and **2** respectively); $d(\text{C–N})$ decreases by 0.019(4) and 0.019(9) Å. This indicates electron density moves towards the Se–I–X moiety upon co-ordination, causing a partial positive charge to reside on the nitrogen atom. The I–X bond lengthens with respect to the unco-ordinated species for both molecules. The addition of two equivalents of ICl to mbts gave a dark purple material of stoichiometry $\text{C}_8\text{H}_7\text{Cl}_{2.9}\text{I}_{1.1}\text{NSe}$ **3**; the fractional stoichiometry for iodine and chlorine may be indicative of 'halogen scrambling'. An additional product from this reaction was examined crystallographically and found to consist of the ion pair $[\text{C}_8\text{H}_7\text{NSCl}]^+[\text{ICl}_2]^-$ **4**, *i.e.* the C–Se double bond has been completely cleaved and replaced by a C–Cl single bond. The positive charge is again supported mostly by the nitrogen atom; $d(\text{C–N})$ decreases to 1.294(10) Å indicating a double bond.

Introduction

The ability of selenoamides to form 1:1 addition products with equimolar quantities of diiodine has been extensively investigated by Devillanova and co-workers^{1–7} who reported the charge transfer (CT) 'spoke' structure consisting of a linear Se–I–I arrangement and bent geometry at the selenium atom.^{4,7} Interestingly, however, variations in the organic fragment of the selenoamide can result in a T-shaped I–Se–I arrangement⁷ which contains a hypervalent selenium atom. A further structural type described is that of the ionic product from the 1:1 reaction of *N*-methylbenzothiazole-2-selone, mbts, with diiodine; this consists of an $[(\text{mbts})_2\text{I}]^+$ cation and I_3^- anion.⁵ Fig. 1 represents the three structural types so far elucidated for products of these reactions. Clearly, the nature of 1:1 selenoamide–diiodine addition compounds is highly dependent on subtle electronic effects from the organic fragment of the selenoamide employed.

Two further addition compounds of mbts have been described.⁵ The 2:1 reaction of mbts and diiodine produces an 'extended spoke' which is perhaps best thought of as an $[\text{mbts–I}]^+$ moiety strongly interacting with an I_3^- anion; *i.e.* the presence of *two* molecules of I_2 per mbts molecule produces a CT structure whereas *one* would appear not to. A directly comparable structure exists for the 2:1 addition product of mbts and IBr; here the $[\text{mbts–I}]^+$ moiety interacts (albeit weakly) with an IBr_2^- anion. Fig. 2 represents these two molecular structures. The carbon–selenium bond lengthens in all of the aforementioned molecules; however, it is noteworthy that the double bond character is essentially preserved, *e.g.* for the diiodine adduct of 5,5-dimethyl-2-selenoximidazolin-4-one, $d(\text{C–Se}) = 1.861(4)$ Å.* The exception to this is for the T-shaped adduct in Fig. 1 (b) where the $d(\text{C–Se})$ of 1.893(6) Å indicates a purely single bond.

We are currently engaged in a comprehensive study of the

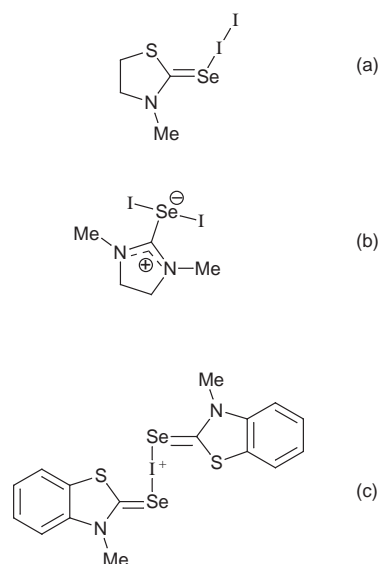


Fig. 1 The three types of 1:1 product from the reactions of selenoamides and diiodine: (a) the 'spoke' structure of *N*-methyl-1,3-thiazolidine-2-selone–diiodine; (b) the T-shape structure of (1,3-dimethylimidazolidin-2-yl)diodoselenium; (c) the ionic *N*-methylbenzothiazole-2-selone iodonium salt.

interaction of a variety of organo Group 15 and 16 compounds with dihalogen and interhalogen molecules and have also found that the geometrical nature of the adducts produced frequently varies with changes in organo-substituents. Further, the identity of the dihalogen and the solvent employed for the reaction is of importance. For example, Me_2Se reacts with diiodine to produce the CT adduct $\text{Me}_2\text{Se–I–I}$ whereas the same diorganoselenide reacts with dibromine or dichlorine to produce the disphenoidal 'see-saw' structure Me_2SeX_2 (X = Br or Cl).^{14,15} Additionally, Knobler and McCullough¹⁶ reported the crystal structure of the iodine monochloride complex of 1-oxa-4-selenacyclohexane, $\text{C}_4\text{H}_8\text{OSe–ICl}$, this is also a CT adduct con-

* Normal range for a carbon–selenium double bond taken as 1.817 to 1.866 Å based on crystallographic values reported in refs. 8–13.

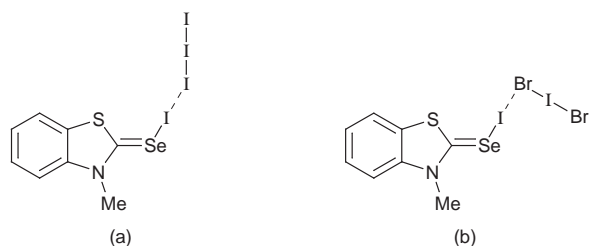


Fig. 2 The 'extended spoke' structures of (a) $\text{mbts}\cdot 2\text{I}_2$ and (b) $\text{mbts}\cdot 2\text{IBr}$.

taining the linear arrangement Se–I–Cl. More recently, we have extended our studies to investigate the reaction of certain tertiary phosphine chalcogenides with dihalogens. In all cases, reaction of R_3PSe with diiodine in a 1:1 stoichiometry produces the CT adducts R_3PSeI ,¹⁷ whereas the analogous reaction with dibromine produces the T-shaped adducts R_3PSeBr_2 .¹⁸ Reaction of R_3PSe with dichlorine appears to be rather complicated, but preliminary studies suggest that, rather than adduct formation occurring, cleavage of the phosphorus–selenium bond occurs to produce equimolar quantities of triorganophosphorus dichloride, R_3PCl_2 , and elemental selenium.¹⁹ These results illustrate the susceptibility of the phosphorus–selenium bond to cleavage when treated with the lighter dihalogens.

We have now turned our attention to the reaction of compounds containing a carbon–selenium double bond with dihalogens, principally to investigate the types of structures exhibited upon adduct formation and also to compare the nature of such adducts with those formed by the reaction of the analogous tertiary phosphine chalcogenides with dihalogens; *i.e.* to compare the reaction of compounds containing a carbon–selenium double bond with those containing a phosphorus–selenium double bond with dihalogens.

The reactions of selenoamides with interhalogens have been investigated far less than those with diiodine. In addition to the 2:1 'extended spoke' adduct in Fig. 2(b) the only other reports to our knowledge concern the crystallographic studies of the IBr spoke adduct of *N*-methyl-1,3-thiazolidine-2-selone⁴ and three intriguing products containing dications which bear the unusual –Se–Se– bridge.²⁰ The latter show again the importance of the organic fragment of the particular selenoamide employed and how this affects the nature of products formed. For example, the reaction of 1,3-dimethyl-4-imidazoline-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. A further curiosity is revealed 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 (Fig. 3).

The variety in structural types so far elucidated clearly show the difficulties in predicting the exact nature of products formed from reactions of selenoamides with dihalogens. These difficulties have prompted us to turn our investigations to the reactions of *mbts* with ICl and IBr in order to find out which (if any) of the above structural motifs are adopted by possible 1:1 addition products. In addition, we felt it would be useful to examine the 2:1 reaction of ICl with *mbts* in order to see if the product is isostructural with the $\text{mbts}\cdot 2\text{IBr}$ complex described by Devillanova and co-workers in ref. 5. Apart from this single structure, reactions of selenoamides with n I–X (where X = Br or Cl; $n > 1$) have received virtually no attention to date.

Results

The compound IBr was treated with *mbts* in a 1:1 ratio and ICl in 1:1 and 2:1 ratios; in each case, we employed dichloro-

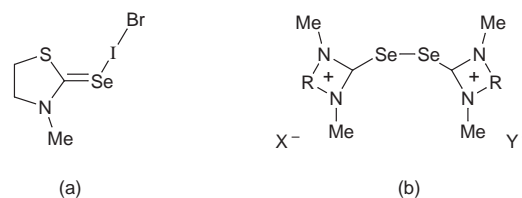


Fig. 3 a The CT 'spoke' structure of *N*-methyl-1,3-thiazolidine-2-selone–iodine monobromide. b Structure representing three products containing a dicationic Se–Se bridge: (i) $\text{R} = \text{CH}=\text{CH}$, $\text{X}, \text{Y} = \text{Br}$; (ii) $\text{R} = \text{CH}=\text{CH}$, $\text{X} = \text{Cl}$, $\text{Y} = \text{I}$; (iii) $\text{R} = \text{CH}_2\text{CH}_2$, $\text{X} = \text{Br}$, $\text{Y} = \text{IBr}_2$.

methane as the solvent and reaction times were approximately four days.

(i) The 1:1 adduct $\text{mbts}\cdot \text{IBr}$ **1** is a bright orange solid isolated in 72% yield which decomposes to a black tar at 138–139 °C. Elemental analysis, found % (calc. for $\text{C}_8\text{H}_7\text{BrINSSe}$): C, 21.9 (22.0); H, 1.4 (1.6); Br, 18.4 (18.4); I, 28.9 (29.2); N, 3.2 (3.2); S, 7.1 (7.4). Recrystallisation of **1** *via* the slow cooling of a solution in dichloromethane from 40 °C yielded small pale orange crystals, one of which was selected for analysis by single crystal X-ray diffraction. The structure of one molecule from the unit cell of **1** is illustrated in Fig. 4.

(ii) The 1:1 adduct $\text{mbts}\cdot \text{ICl}$ **2** is a yellow solid isolated in 77% yield which decomposes to a black tar at 165–167 °C. Elemental analysis, found % (calc. for $\text{C}_8\text{H}_7\text{ClINSSe}$): C, 24.7 (24.6); H, 1.7 (1.8); Cl, 8.8 (9.1); N, 3.6 (3.6); I, 32.2 (32.5); S, 8.2 (8.2). Recrystallisation of **2** by the same method as for **1** yielded small yellow needle crystals, one of which was selected for analysis by single crystal X-ray diffraction. The structure of one molecule from the unit cell of **2** is illustrated in Fig. 5.

(iii) The reaction of *mbts* with two equivalents of ICl resulted in a dark purple solid **3**, isolated in approximately 40% yield, which decomposed at 202 °C. Elemental analysis, found % (calc. for $\text{C}_8\text{H}_7\text{Cl}_{2.9}\text{I}_{1.1}\text{NSSe}$): C, 20.1 (20.4); H, 1.3 (1.5); Cl, 20.9 (21.8); I, 29.3 (29.7); N, 2.8 (3.0); S, 6.6 (6.8). Attempts to recrystallise **3** have so far failed; however, after isolation yellow crystals were produced in the dark purple filtrate by cooling to *ca.* 5 °C. X-Ray analysis of a single crystal showed the unit cell to contain a cationic organic species, $[\text{C}_8\text{H}_7\text{NSCl}]^+$ and the anion ICl_2^- , **4**. No selenium is present in this material so the compound cannot be thought of as representative of the purple bulk material. An ion pair from the unit cell of **4** is illustrated in Fig. 6.

Discussion

Table 1 lists selected bond lengths and angles for adducts **1**, **2** and **4** and compares them to those found⁸ for unco-ordinated *mbts*. Both **1** and **2** have a spoke structure based on a linear Se–I–X (X = Br or Cl) arrangement. The geometry at the selenium atom is bent. In each case, $d(\text{C}–\text{Se})$ has increased from the 1.817 Å seen for *mbts* † to 1.877(5) and 1.879(8) Å for **1** and **2** respectively. These distances are slightly beyond the normal range for carbon–selenium double bonds, but shorter than the accepted value of 1.893 Å for a truly single bond.²² It seems likely, therefore, that at least partial double-bond character is retained in the C–Se linkage. The increase in $d(\text{C}–\text{Se})$ is accompanied in both adducts by a reduction in $d(\text{C}–\text{N})$ of around 0.020 Å to 1.329(6) (**1**) and 1.329(10) Å (**2**). These values are at the lower end of the accepted scale for a C sp^2 –N single bond and at the top of that for a double bond. It can be postulated that upon co-ordination to the selenium atom by the interhalogen electron density moves towards the C–Se moiety away from the nitrogen atom. This effect is even more pronounced in the T-shaped selenium-brominating agents described by Akabori and co-

† All bond distances quoted here for *mbts* are averages of the distances for the two independent molecules in the unit cell reported in ref. 8. No standard deviations were given in that work, so cannot be included.

Table 1 Selected bond lengths (Å) and angles (°) for adducts **1**, **2** and **4**. A comparison with the average of those found for mbts⁸

	mbts ^a	1	2	4
Se(1)–I(1)	—	2.6360(8)	2.6186(10)	—
I(1)–Br(1)	—	2.8137(8)	—	—
I(1)–Cl(1)	—	—	2.691(2)	—
C(2)–Se(1)	1.817	1.877(5)	1.879(2)	—
C(2)–S(3)	1.723	1.706(5)	1.722(8)	1.696(8)
N(1)–C(2)	1.349	1.329(6)	1.329(10)	1.294(10)
N(1)–C(10)	1.443	1.464(6)	1.470(10)	1.464(9)
C(2)–Cl(1)	—	—	—	1.673(8)
I(1)–Cl(2)	—	—	—	2.559(2)
I(1)–Cl(3)	—	—	—	2.502(2)
Se(1)–I(1)–Br(1)	—	177.09(2)	—	—
Se(1)–I(1)–Cl(1)	—	—	178.76(5)	—
N(1)–C(2)–Se(1)	127.3	121.9(4)	122.1(6)	—
S(3)–C(2)–Se(1)	122.1	124.8(2)	124.8(5)	—
N(1)–C(2)–Cl(1)	—	—	—	123.1(6)
N(1)–C(2)–S(3)	110.5	113.2(4)	113.1(6)	116.0(6)
S(3)–C(2)–Cl(1)	—	—	—	121.0(5)
C(2)–Se(1)–I(1)	—	99.14(1)	100.6(3)	—
C(10)–N(1)–C(2)	121.9	122.3(4)	122.6(7)	122.6(7)
Cl(2)–I(1)–Cl(3)	—	—	—	179.19(8)

^a The value reported here is an average of the bond lengths found for each of the two crystallographically independent molecules in the unit cell in ref. 8. No standard deviations were given in that work.

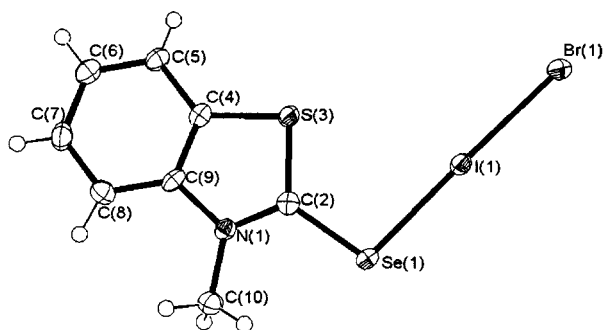


Fig. 4 An ORTEP²¹ drawing of one molecule of adduct **1**.

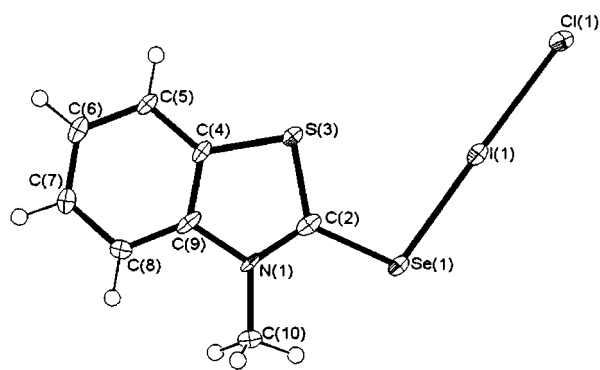


Fig. 5 An ORTEP drawing of one molecule of adduct **2**.

workers²³ here $d(\text{C}–\text{Se})$ is entirely single in character at 1.95(1) to 1.99(2) Å. Hence, those molecules are best described as zwitterionic, with positive charge residing on the nitrogen atom and negative charge on the SeBr_2 moiety. Adducts **1** and **2** can be thought of as being intermediate between the Akabori structure and the free mbts molecule.

An interesting difference between adducts **1** and **2** is the change that occurs in $d(\text{C}–\text{S})$ on co-ordination; it shows essentially no change in **2** as compared to mbts, but for **1** decreases by 0.017 Å. It is thought that this might be a consequence of crystal packing rather than any subtle electronic effects, this idea is supported when one examines the carbon–sulfur bond

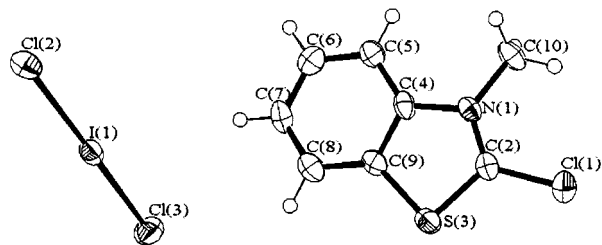


Fig. 6 An ORTEP drawing of the ion pair in the unit cell of adduct **4**.

length obtained by Devillanova and co-workers⁴ for $\text{mbts}\cdot 2\text{I}_2$. Three crystallographically discrete molecules are present in the unit cell;⁴ one of which has a $d(\text{C}–\text{S})$ higher than that of mbts, one lower and one similar. It would appear, therefore, that although carbon–selenium and carbon–nitrogen bond lengths can be usefully invoked when attempting to describe such adducts, carbon–sulfur bond lengths are not a reliable tool.

Both adducts **1** and **2** were obtained in high yield and elemental analyses found correspond well to calculated values. However, considerable structural variation has been encountered with such systems, as outlined in the Introduction, and it is appreciated that there is a small possibility that the structures described do not correspond to that of the bulk material. However, the ‘spoke’ structures of **1** and **2** are in keeping with those observed for similar materials^{4,7} which exhibit a diiodine spoke. We feel confident, therefore, that the structures reported herein are indeed representative of the bulk material.

The dark purple solid of stoichiometry $\text{C}_8\text{H}_7\text{Cl}_{2.5}\text{I}_{1.1}\text{NSeI}$ **3** obtained as the insoluble product from the 2:1 reaction with ICl can be rationalised if halogen scrambling has occurred. This is a phenomenon we have previously reported for the product of the reaction of triphenylphosphine with iodine monobromide, $\text{Ph}_3\text{PI}_{1.29}\text{Br}_{0.71}$. Alternatively, this material may consist of several minor products in addition to the bulk ‘mbts· ICl_3 ’; this could be an equally valid explanation of the relatively poor chlorine analysis. Powder diffraction has shown that no elemental selenium is present in **3** but, so far, recrystallisation attempts have failed and NMR and infrared techniques have been unhelpful in characterising this material. An interesting feature of the additional product, **4**, is that the selenium atom in mbts is replaced by a chlorine atom; the short $d(\text{C}–\text{N})$ bond length of 1.294(10) Å indicates a carbon–nitrogen double bond and $d(\text{C}–\text{S})$ also decreases to 1.696(8) Å. This may imply that the positive charge of the organic cation, although located mostly on the nitrogen atom, is at least partially distributed round the heterocyclic ring. This reaction would therefore seem at first glance to not be analogous to that undergone between mbts and two equivalents of IBr which forms the product in Fig. 2(b). However, the stoichiometry of the reaction leading to **3** and **4** seems to imply that other products may well form in the 2:1 ICl reaction. It is conceivable that the 2:1 adduct $[\text{mbts}–\text{I}]^+ [\text{ICl}_2]^-$ is one of these, or that it could be obtained if reaction conditions (such as solvent or reaction time) were adjusted. *Prima facie*, it would seem that mbts forms an extended spoke with two equivalents of I_2 or IBr but not (at least not to the same extent) with ICl. Obviously this is somewhat speculative, and we plan to examine the sensitive system of mbts and ICl further.

Conclusion

The direct reaction of mbts with equimolar quantities of IBr and ICl results in the quantitative formation of 1:1 adducts which exhibit the molecular ‘spoke’ structure. An increase of $d(\text{C}–\text{Se})$ is observed (accompanied by a reduction in $d(\text{C}–\text{N})$), but the double bond character of the carbon–selenium bond is essentially preserved. These two new adducts are therefore

Table 2 Crystal data and structure refinement for adducts **1**, **2** and **4**

	1	2	4
Empirical formula	C ₈ H ₇ BrINSSe	C ₈ H ₇ ClINSSe	C ₈ H ₇ Cl ₃ INS
<i>M</i>	434.98	390.52	382.46
<i>T/K</i>	173(2)	150(2)	203(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pnma</i>	<i>P</i> 2 ₁
<i>a</i> /Å	6.9764(13)	9.0950(2)	7.844(2)
<i>b</i> /Å	9.1423(19)	6.74600(10)	7.8546(10)
<i>c</i> /Å	17.817(5)	17.9527(4)	10.058(2)
β /°			92.860(10)
<i>V</i> /Å ³	1136.4(4)	1101.49(4)	618.9(2)
<i>Z</i>	4	4	2
<i>D</i> _c /mg m ⁻³	2.542	2.355	2.052
μ /mm ⁻¹	9.676	6.597	3.365
Reflections collected/unique	6711/2494	6175/1362	1252/1174
[<i>R</i> _{int}]	[0.0368]	[0.0561]	[0.0260]
Final <i>R</i> 1, <i>wR</i> 2 indices [<i>I</i> > 2σ(<i>I</i>) (all data)]	0.0251, 0.0543 0.0276, 0.0550	0.0466, 0.0912 0.0646, 0.0977	0.0301, 0.0728 0.0327, 0.0747

isostructural with the IBr complex of *N*-methyl-1,3-thiazolidine-2-selone.⁴ It should be of interest to extend the range of selenoamides under investigation to establish whether this is the only structural motif available for such products.

In addition, although previous workers have described the mbts·2IBr complex which consists of an 'extended spoke' arrangement (Fig. 2(b)), we have shown that the analogous reaction with ICl appears to be more complicated; a variety of products form, including the as yet unidentified material, **3**, and the ionic compound **4**. This is the first report to our knowledge which has shown that oxidation of the selenium atom in a selenoamide can occur by using two equivalents of an interhalogen. In addition, our studies and reports by other workers appear to suggest that this oxidation does not take place if only one equivalent of interhalogen is used. Therefore, whilst we do not dismiss the possibility that a 2:1 'extended spoke' adduct of mbts and ICl can form in a manner analogous to that with IBr, it seems fair to conclude that this is not necessarily the preferred reaction pathway for the mbts-ICl system. Our results lead us to suggest that subtle differences in acceptor abilities of IBr and ICl are of more importance for reactions involving two equivalents of interhalogen than for the corresponding equimolar reactions.

Experimental

Compounds **1–4** are moisture sensitive. 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. The compound mbts was obtained commercially (Aldrich) and used as received. Dichloromethane (BDH) was dried over calcium hydride and refluxed in an inert atmosphere (N₂) for at least two hours prior to use. The synthesis of mbts·IBr is typical: mbts (0.5 g, 2.19 mmol) was dissolved in dichloromethane (ca. 100 cm³) and subsequently iodine monobromide (Aldrich, 0.45 g, 2.19 mmol) added. After ca. 4 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 in the Results section.

X-Ray crystallography

The X-ray experiments for adducts **1** and **2** were carried out on Station 9.8 at the 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.

The X-ray diffraction experiment for adduct **4** was carried out at 203 K on a Nonius MACH 3 4-circle diffractometer using graphite monochromated Mo-K α radiation. The ω -2 θ scan technique was used to collect 1252 reflections with 2 θ ≤ 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 SHELXL 97 suite of programs²⁴ was used to solve the structures by direct methods and refined them using full-matrix least-squares. Crystallographic data are summarised in Table 2.

CCDC reference number 186/1465.

Acknowledgements

Two of us (P. D. B. and W. I. C.) are grateful to the EPSRC for research studentships. We also wish to thank Daresbury Laboratories (station 9.8) for use of their single crystal X-ray diffraction facility.

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Paper 9/02188D