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Further structural motifs from the reactions of thioamides with diiodine and the interhalogens iodine monobromide and iodine monochloride: an FT-Raman and crystallographic study †

Philip D. Boyle, Jill Christie, Thomas Dyer, Stephen M. Godfrey, Ian R. Howson, Christina McArthur, Bashie Omar, Robin G. Pritchard and Gareth Rh. Williams

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester, UK M60 1QD. E-mail: stephen.m.godfrey@umist.ac.uk; mcdigpb3@fs1.ch.umist.ac.uk

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The reactions of the thioamides thiourea, tu, 1-ethyl-2-thiourea, etu, 1,3-dimethyl-2-thiourea, dmtu, 1,3-diethyl-2-thiourea, detu, 3-methylbenzothiazole-2-thione, mbtt and 3-methylrhodanine, mrh, with one equivalent of diiodine have been studied; attempts have been made to characterise the resultant 1 : 1 addition products using FT-Raman spectroscopy. It has been shown that these materials lie on a CT–ionic borderline. The crystal structure of dmtu·I_2 has been determined and is shown to be ionic and of the form $[(dmtu)_2I]^+I_3^-$, an arrangement previously only rarely found in crystallographic reports. The reactions of etu and dmtu with iodine monobromide and iodine monochloride and of mbtt with iodine monobromide give 1 : 1 interhalogen addition products; initial FT-Raman investigations point to these adopting a CT 'spoke' structure. The reaction of tu with two equivalents of diiodine to give a bulk material of stoichiometry tu·I_4 has been studied in detail and shown to lead to a variety of novel polyiodide arrangements, the crystal structures of two of which are reported, $(tu)_2(I_2)_3$ and $(tu)_3(I_2)_5$, and compared to each other, the previously reported $(tu)_2I_2$ and to tu itself. These two structures represent further, previously unreported, structural motifs available for these highly complicated systems.

Introduction

The ability of molecules that contain Group 16 donor atoms to form CT complexes (and complexes exhibiting a variety of other structural motifs) with dihalogens and interhalogens has received renewed interest in recent years.[1] This is for two principal reasons. First, molecules such as 1,1,3,3-tetramethyl-2-thiourea have been shown to exhibit considerable antithyroid activity *via* I_2 complexation *in vivo*; existing sulfur atom-containing drugs such as chlorpromazine, promethazine and disulfiram are also capable of forming addition complexes with diiodine and may have secondary antithyroid acitivity.[2] Secondly, there is evidence of interesting electrical properties such as superconducting ability by sulfur–iodine complexes.[3] These properties have previously led us to investigate and characterise crystallographically dihalogen and interhalogen addition products of diorganosulfides,[4] diorganoselenides,[5] phosphine sulfides,[6] phosphine selenides,[7] diphenyldiselenium,[8] diphenylditellurium[9] and selenoamides.[10]

We turn our attention now to the reaction of diiodine and the interhalogens iodine monobromide and iodine monochloride with thioamides. Several groups have attempted to elucidate the array of possible structural motifs available for such addition complexes using purely spectroscopic methods such as UV-VIS,[11] IR[12] and FT-Raman[13] but, unfortunately, it is difficult confidently to assign a particular motif to a particular system without the aid of single crystal X-ray crystallography. This has led to a series of crystallographic reports which have identified the principal structural types as being 1 : 1 'spoke' adducts,[14] 2 : 1 'extended spoke' adducts,[15] ionic complexes[16] as well as curiosities such as the polyiodide arrangements of thioamides in 2 : 3[17] and 2 : 7[18] ratios with diiodine. There is also some evidence that 1 : 1 T-shaped adducts exist for thioamides[19] analogous to those of selenoamides.[20] Examples of the principal structural motifs are shown in Fig. 1. Spoke structures arise due to donation of electron density from the sulfur atom into the σ^* antibonding molecular orbital of the diiodine molecule. The effect of this is a lengthening of the double bond of the thione group, formation of a sulfur–iodine dative bond and a lengthening of the iodine–iodine bond distance. A direct relationship exists between these three bond distances: if d(S–I) is short then d(C–S) and d(I–I) will be long and the donation is considered strong; for weak complexes this is reversed, d(I–I) and d(C–S) are short (indicative of weak donation) and d(S–I) is long.‡ Which structural motif is favoured for a particular thioamide is not easily predicted, but it is thought that it depends in part on the molecule's donor strength: one might expect very strong donors to cause a large increase in d(I–I) such that the bond cleaves, oxidation to give tetravalent sulfur occurs and a T-shaped product is formed. This has been observed when selenoamides are treated with dibromine.[10b] Also of importance is the non-donating part of the molecule; when the carbon-sulfur distance lengthens a partial positive charge is imparted to the rest of the molecule. This explains why thioamides are particularly good donors: the positive charge is easily supported by nitrogen atoms (especially if they contain alkyl groups). Generally, the greater the stabilising ability of the N-alkyl or -aryl groups, the stronger one might expect the resulting diiodine complex to be.

Although there have been several crystallographic reports concerning diiodine complexes of thioamides, there have been none to our knowledge which features complexes of iodine monobromide or iodine monochloride. There have also been surprisingly few reports featuring simple thioamides based

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† Supplementary data available: Raman spectra of the adducts and peak tables available from BLDSC (SUPP. NO. 57712, 12 pp.). See Instructions for Authors, Issue 1 (http://www.rsc.org/dalton).

‡ For the molecules in ref. 14 d(C–S) varies from 1.64 to 1.72 Å, d(S–I) from 2.61 to 2.80 Å and d(I–I) from 2.75 to 2.98 Å.

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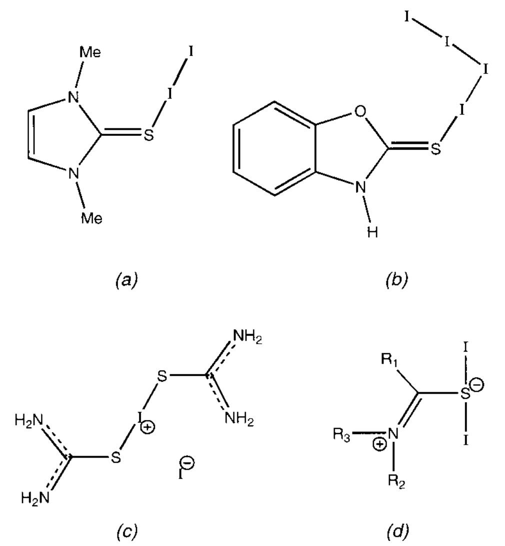

Fig. 1 Different structural motifs exhibited by diiodine–thioamide complexes: (*a*) the CT 'spoke' structure of 1,3-dimethylimidazole-2-thione–diiodine;[14a] (*b*) the CT 'extended spoke' structure of benzoxazole-2-thione bis(diiodine);[15] (*c*) the ionic structure of bis(thiourea)iodine(I) iodide;[16a] (*d*) a hypothetical T-shaped structure seen for selenoamide–diiodine[20,21] adducts but not, as yet, for thioamide-diiodine adducts.

around the thiourea molecule (the structure of the ionic 1 : 2 diiodine : thiourea complex, Fig. 1(*c*) being an exception.[16a]). In the study on antithyroid activity[2] it was simple di- and tetra-alkyl thioureas that were indicted as having the greatest efficacy in living systems; this is partly on account of their superior donor strength which appeared to be of importance to their activity during *in vivo* trials on rats. We decided, therefore, to examine the reactions of a range of simple and more complicated thioamides with diiodine, iodine monobromide and iodine monochloride with the aims of (*i*) establishing whether further structural motifs are possible for such systems, (*ii*) examining the donor power of such molecules with a view to predicting possible structure–activity relationships in anti-thyroid treatment, (*iii*) re-examining the role of Raman spectroscopy in the hope of finding a practical method of structure assignment without the need for single crystal X-ray diffraction. Fig. 2 shows the six molecules under investigation, together with their abbreviations as used in this report.

Results and discussion

The six thioamides illustrated in Fig. 2 were treated with one equivalent of diiodine and allowed to mix for *ca.* 2 d in dichloromethane or diethyl ether. Isolation afforded satisfactory yields of the darkly coloured 1 : 1 thioamide–diiodide adducts tu·I$_2$ **1**, etu·I$_2$ **2**, dmtu·I$_2$ **3**, detu·I$_2$ **4**, mbtt·I$_2$ **5** and mrh·I$_2$ **6**, the analytical data for which are displayed in Table 1. Spectra obtained from solid-state FT-Raman studies on **1**–**6** feature a series of prominent bands below 300 cm^{-1} that are absent for the parent thioamides, Table 2. Structural assignments were made as follows.

(*i*) I$_3^-$, as a symmetrical ion, would normally only exhibit one Raman active band, the ν_1 symmetric stretch, found at around 110 cm^{-1}.[22] However, when the ion is made asymmetric through distortion or interactions with other species, the ν_2 deformation vibration and ν_3 antisymmetric stretch at *ca.* 70 and 130–140 cm^{-1} respectively may also become Raman active.[13,21] The low frequency cut-off of our FT-Raman spectrometer is 100 cm^{-1}, so the ν_2 vibration cannot be observed. However, the bands at 137 and 108 cm^{-1} of **1** can be assigned to ν_3 and ν_1 of an I$_3^-$ moiety and suggest the adduct has an ionic structure.

(*ii*) 'Free' diiodine in the solid state exhibits a single Raman band at 180 cm^{-1};[23] this moves to a lower wavenumber upon

Table 1 Physical and analytical data for adducts **1**–**12**

Adduct	Solvent of preparation	Colour	mp/ °C	Yield (%)	Elemental analysis, % found (calc.) C	H	N	S	I	Br	Cl
1 Thiourea diiodide	CH$_2$Cl$_2$	Dark grey	83	80	3.7 (3.6)	1.2 (1.2)	8.4 (8.5)	9.9 (10.0)	76.8 (77.0)	—	—
2 1-Ethyl-2-thiourea diiodide	CH$_2$Cl$_2$	Brown	128	82	10.4 (10.1)	1.9 (2.2)	8.1 (7.8)	8.6 (9.0)	70.5 (70.9)	—	—
3 1,3-Dimethyl-2-thiourea diiodide	CH$_2$Cl$_2$	Purple	87	60	10.3 (10.1)	2.0 (2.2)	7.5 (7.8)	8.8 (9.0)	70.6 (70.9)	—	—
4 1,3-Diethyl-2-thiourea diiodide	CH$_2$Cl$_2$	Purple	72	56	15.5 (15.5)	2.9 (3.1)	6.9 (7.3)	7.8 (8.3)	65.8 (65.8)	—	—
5 3-Methylbenzothiazole-2-thione diiodide	Et$_2$O	Brown	116	75	21.6 (21.7)	1.3 (1.6)	3.5 (3.2)	14.7 (14.5)	56.9 (57.2)	—	—
6 3-Methylrhodanine diiodide	Et$_2$O	Brick-red	139	84	12.1 (12.0)	1.1 (1.3)	3.7 (3.5)	15.9 (16.0)	62.9 (63.3)	—	—
7 1-Ethyl-2-thiourea iodine monobromide	CH$_2$Cl$_2$	Yellow	175	77	11.7 (11.6)	2.4 (2.6)	9.4 (9.0)	9.8 (10.3)	39.8 (40.8)	26.1 (25.7)	—
8 1-Ethyl-2-thiourea iodine monochloride	CH$_2$Cl$_2$	Yellow	176	67	13.1 (13.5)	2.8 (3.0)	10.2 (10.5)	11.8 (12.0)	47.4 (47.6)	—	13.3 (13.3)
9 1,3-Dimethyl-2-thiourea iodine monobromide	CH$_2$Cl$_2$	Brown	132	65	11.8 (11.6)	2.3 (2.6)	9.0 (9.0)	10.0 (10.3)	40.4 (40.8)	26.0 (25.7)	—
10 1,3-Dimethyl-2-thiourea iodine monochloride	CH$_2$Cl$_2$	Brown	136	89	13.2 (13.5)	2.8 (3.0)	10.2 (10.5)	11.8 (12.0)	47.3 (47.6)	—	13.6 (13.3)
11 3-Methylbenzothiazole-2-thione iodine monobromide	Et$_2$O	Orange	147	73	24.7 (24.8)	1.8 (1.8)	3.7 (3.6)	16.0 (16.5)	32.2 (31.7)	20.4 (20.6)	—
12 Thiourea tetraiodide	CH$_2$Cl$_2$	Dark purple	77	58	2.3 (2.1)	0.6 (0.7)	5.1 (4.8)	6.0 (5.5)	86.4 (87.0)	—	—

Table 2 FT-Raman spectroscopic data and tentative structural assignments for adducts **1**–**6** and **9**–**12** (relative Raman peak heights where 100 is the maximum intensity are in parentheses)

Adduct	Raman bands in cm^{-1} (intensity), below 300 cm^{-1}	Structure assignment
1	219 (36), 137 (100), 108 (90)	Ionic: $[(tu)_2I]^+I_3^-$
2	161 (100)	Spoke: etu·I_2
3	159 (23), 144 (24), 113 (100)	Ionic–spoke mixture: $[(dmtu)_2I]^+I_3^-$ *and* dmtu·I_2
4	218 (121), 157 (100), 111 (86)	Ionic–spoke mixture: $[(detu)_2I]^+I_3^-$ *and* detu·I_2
5	157 (100)	Spoke: mbtt·I_2
6	150 (100)	Spoke: mrh·I_2
9	175 (100), 134 (24), 112 (22)	Ionic: $[(dmtu)_2I]^+IBr_2^-$
10	268 (16), 172 (100), 110 (30)	—
11	204 (11), 176 (100), 160 (59)	Mix of thione–spoke and dialkylsulfur–spoke for mbtt?
12	221 (36), 168 (100), 106 (6)	Extended spoke: tu·I_4

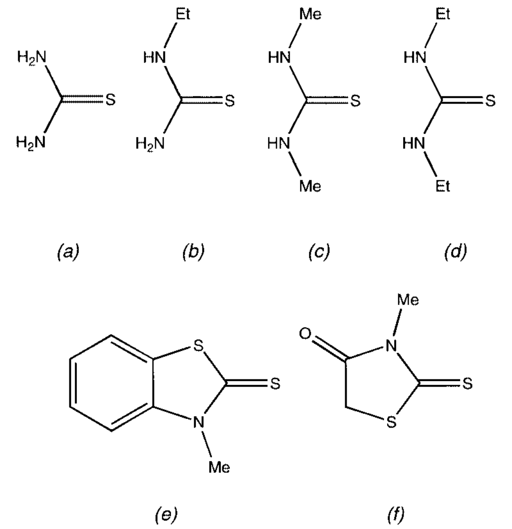

Fig. 2 The molecular structures of (*a*) thiourea, tu, (*b*) 1-ethyl-2-thiourea, etu, (*c*) 1,3-dimethyl-2-thiourea, dmtu, (*d*) 1,3-diethyl-2-thiourea, detu, (*e*) 3-methylbenzothiazole-2-thione, mbtt and (*f*) 3-methylrhodanine, mrh.

co-ordination to a donor atom, reflecting a reduction ion I–I bond order (and this is therefore a useful indicator of complex 'strength'). **2**, **5** and **6** exhibit single very strong bands at 161, 157 and 150 cm^{-1} respectively, which we assign to ν_1 (I–I) symmetric stretches. This implies spoke structures have been formed, with the donor ability of etu< mbtt < mrh.

(*iii*) For **3** and **4** the situation is less clear; their Raman spectra indicate spoke arrangements (from the bands at 159 and 157 cm^{-1} respectively) but the presence of I_3^- is also signalled in both cases (from bands at 113 and 144 cm^{-1} for **3** and 111 cm^{-1} for **4**). One explanation might be that both structural types are present, *i.e.* **3** and **4** lie on an ionic–CT 'borderline'. A further possibility is that the bands at 159 and 157 cm^{-1} are actually due to the δ(C–S–I) bend, which has been seen at 138,[24] 150 and 155 cm^{-1}[25] by other workers and that **3** and **4** adopt solely ionic structures. However, δ (C–S–I) bends are expected to be considerably less intense than ν_1 (I–I) and the bands in the region for **4** especially are very intense indeed.

It should be pointed out that C–S and S–I modes such as ν_1 (S–I) are notoriously difficult to assign and have not received attention in any of the previous studies that concern similar materials[13–19] to those presented here. This is likely to be a consequence of the low intensity of such modes when compared to the very intense I–I modes. Hence, an inability to resolve the many very weak bands that inhabit the fingerprint region makes positive assignment extremely difficult indeed. However, it is fortunately possible to assign a structure as ionic or spoke without having to assign S–I or C–S modes. This is because any band at *ca.* 110 cm^{-1} can unambiguously be assigned to a tri-iodide moiety; if the band is absent at that position but there is an intense band at 150–175 cm^{-1} we can assume the structure is spoke. In both cases, although we would expect very weak S–I and C–S modes to be present (and probably in very similar positions for each structural type), the fact that they are very difficult to assign is not problematic for the structural elucidation of these adducts.

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

I(1)–S(2)	2.602(4)	N(3)–C(4)	1.33(2)
I(1)–S(1)	2.654(4)	N(4)–C(4)	1.33(2)
I(2)–S(3)	2.623(4)	N(5)–C(7)	1.30(2)
I(2)–S(4)	2.634(4)	N(6)–C(7)	1.31(2)
S(1)–C(1)	1.728(13)	N(7)–C(10)	1.30(2)
S(2)–C(4)	1.715(14)	N(8)–C(10)	1.35(2)
S(3)–C(7)	1.747(12)	I(3)–I(4)	2.8787(13)
S(4)–C(10)	1.737(13)	I(4)–I(5)	2.9440(13)
N(1)–C(1)	1.32(2)	I(6)–I(7)	2.8874(14)
N(2)–C(1)	1.31(2)	I(7)–I(8)	2.9082(14)
S(2)–I(1)–S(1)	179.07(12)	C(1)–S(1)–I(1)	103.2(4)
S(3)–I(2)–S(4)	178.75(14)	C(4)–S(2)–I(1)	104.3(5)
I(3)–I(4)–I(5)	177.77(4)	C(7)–S(3)–I(2)	104.2(4)
I(6)–I(7)–I(8)	178.72(4)	C(10)–S(4)–I(2)	103.1(4)

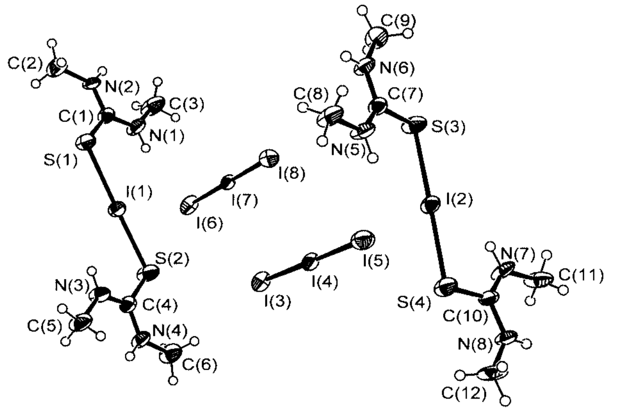

Fig. 3 Single-crystal structure of compound **3**. Two crystallographically independent $[(dmtu)_2I]^+$ cations and two I_3^- anions are present in the asymmetric unit.

Small purple crystals were produced by slowly cooling a dichloromethane solution of compound **3** from 30 to 5 °C. Examination by single-crystal X-ray diffraction revealed the ionic arrangement in Fig. 3; selected bond lengths and angles are displayed in Table 3. The structure consists of two crystallographically independent $[(dmtu)_2I]^+$ cations featuring almost linear S–I–S arrangements [S(2)–I(1)–S(1) 179.07(12), S(3)–I(2)–S(4) 178.75(14)°] and two independent I_3^- anions. It is in keeping with that of $(tu)_2I_2$[16a] (Fig. 1(*c*)) but with I_3^- as a counter ion rather than I^- and is, in fact, the first example of a $[(TA)_2I]^+I_3^-$ (TA = thioamide) 1 : 1 adduct structure to our knowledge. *d*(S–I) varies considerably, from 2.602(4) to 2.654(4) Å for the four SI bonds; the average of these (2.628 Å) is almost identical to the *d*(S–I) of 2.629 Å observed for $(tu)_2I_2$. This is perhaps surprising, as one might expect the two *N*-methyl groups of dmtu would make it a better donor molecule than tu, resulting in a stronger S–I bond on I_2 addition. Also of interest is the fact that asymmetry of 0.052(6) Å in the two bonds of the S–I–S system is exhibited by one of the independent cations, but is only 0.011(6) Å for the other. The CS distances for **3** also exhibit a range of values (1.715(14) to 1.747(12) Å), although the eight *d*(C–N) values are broadly similar taking standard deviation into account. There is little interaction between the central I^+ of the cation and the I_3^- anion; the shortest contacts between those species being

d(I(1)–I(4)) 4.090(4) Å and d(I(2)–I(7)) 4.142 Å, both only just within the sum of the van der Waals radii of two iodine atoms (4.30 Å) and far longer than d(I–I) in diiodine (2.66 Å).[26] However, there is asymmetry in both I_3^- ions; there is a difference in the two d(I–I) of 0.021(2) Å for one I_3^- ion and a significant 0.0652(2) Å for the other. This asymmetry should allow the asymmetric stretch to be observed in addition to the symmetric stretch in the Raman spectrum of **3**; it therefore seems likely that our assignment of the Raman bands at 144 and 113 cm^{-1} to the ν_3 and ν_1 stretches of the I_3^- ion is correct. However, further comment cannot be made on the presence or otherwise of a spoke structural isomer in the bulk material, for which the band at 159 cm^{-1} was assigned.

Three thioamides, etu, dmtu and mbtt, were treated with one stoichiometric equivalent of iodine monobromide in dichloromethane or diethyl ether for *ca.* 2 d; etu and dmtu were also treated with one equivalent of iodine monochloride under similar conditions. Five coloured compounds were isolated in satisfactory yields: etu·IBr **7**, etu·ICl **8**, dmtu·IBr **9**, dmtu·ICl **10** and mbtt·IBr **11**. Unfortunately, good Raman spectra were only obtained for **9**–**11** (Table 2). Structural assignment from these spectra proved to be difficult. IBr in the solid state exhibits a single band at 216 cm^{-1}[27] which moves to a lower wavenumber on co-ordination by a sulfur donor (*e.g.* to 184 cm^{-1} for the thioether crown–iodine monobromide complex [14]aneS$_4$·2IBr[28]). IBr_2^-, if symmetrical, tends to exhibit a single peak at around 160 cm^{-1} (attributable to ν_1)[22a,29] or, if unsymmetrical, two peaks at around 180 (ν_3) and 145 cm^{-1} (ν_1).[16c,22a] We therefore assign the bands at 175 and 134 cm^{-1} for **9** to the ν_3 and ν_1 stretches of an asymmetrical IBr_2^- ion, which implies an ionic structure of the form $[(dmtu)_2I]^+IBr_2^-$. This would mean **9** was isostructural with the ionic diiodine adduct of dmtu, **3**, Fig. 3, and represents the first description of a 1 : 1 thioamide–interhalogen adduct that does not exhibit a spoke motif. However, we are unable positively to assign the less intense band at 112 cm^{-1}, although it may simply be due to I_3^- moieties arising from 'halogen scrambling' of iodine monobromide. Similar treatment of the spectrum for **11** seems to imply the presence of two spoke moieties for the IBr adduct of mbtt. Examination of the structure of mbtt (Fig. 2) shows the presence of two possible donor atoms: a thione sulfur and a diorganosulfur. It seems feasible that both of these donor-sulfur atoms are capable of charge donation to an acceptor IBr molecule and that both structural isomers are present in the bulk material. This is speculative; however, the difference in wavenumber values of the two bands (*cf.* 176 and 160 cm^{-1}) could be interpreted as representative of two donor–acceptor situations: one weak and one strong. This may be representative of a further structural borderline for these subtle and sensitive systems. We have so far been unable to make any confident structural assignments from the Raman spectra for the iodine monochloride adduct, **10**.

All the structural assignments drawn from the Raman data are tentative. However, it would appear that several important effects are illustrated by the trends in Table 2. An ionic–CT borderline seems to be present, in which weak donors such as tu favour purely ionic systems, spoke–ionic 'mixes' form for stronger donors such as *N*-alkylated thioureas and purely spoke adducts are favoured by very good donors such as mbtt and mrh. As a tool for predicting structural type and elucidating previously unobserved effects (such as the possible formation of *both* ionic and CT 1 : 1 addition products) FT-Raman is of great use. However, we still feel that positive assignments cannot confidently be made without the aid of single crystal XRD determinations. The two methods are ideally used in tandem, as overreliance on XRD will not enable the full picture to be observed, as with the 'purely ionic structure' of **3** for which our FT-Raman studies seem to show is not a simple case.

Table 4 Selected bond lengths (Å) and angles (°) for $(tu)_2(I_2)_3$ **13**

S(1)–I(1)	2.5028(13)	S(1)–C(1)	1.735(5)
I(1)–I(2)	3.0538(5)	N(1)–C(1)	1.294(7)
I(2)–I(3)	3.407(5)	N(2)–C(1)	1.293(8)
I(3)–I(3)	2.7540(9)		
S(1)–I(1)–I(2)	176.04(4)	N(1)–C(1)–S(1)	124.2(4)
C(1)–S(1)–I(1)	104.7(2)	N(2)–C(1)–S(1)	115.7(5)
N(1)–C(1)–N(2)	120.2(6)		

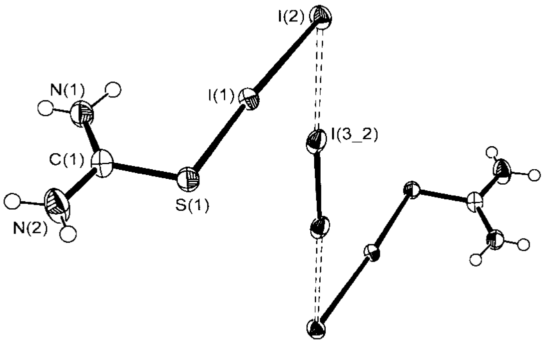

Fig. 4 Single-crystal structure of compound **13**. Two tu·I_2 spoke moieties link *via* a neutral I_2 molecule to form an extended chain of six iodine atoms.

We thought it would be of interest to examine the addition product(s) formed with an excess of diiodine. Diiodine and tu were treated in a 2 : 1 ratio for *ca.* 2 d in dichloromethane; isolation yielded a dark purple product of stoichiometry tu·I_4 **12**. Reaction of tu with three equivalents of diiodine yielded a product with the same stoichiometry and melting point as that of **12**, implying that two moles of diiodine is the maximum quantity that will complex with one mole of tu. The FT-Raman spectrum of **12** exhibited a very strong band at 168 cm^{-1} which we assigned to a slightly perturbed diiodine molecule (*cf.* 180 cm^{-1} for solid diiodine[23]). The band at 106 cm^{-1} is indicative of the symmetric stretch of an I–I–I system. We therefore initially assigned the structure of **12** as an 'extended spoke', as reported for benzoxazole-2-thione bis(diiodine), Fig. 1(*b*).[15] We sought confirmation of this, however, and attempted to grow crystals by slow cooling of a solution of **12** in dichloromethane from 30 to 5 °C. A suitable example was selected from the crop of small, purple crystals, but found by X-ray analysis to have the stoichiometry $(tu)_2(I_2)_3$ **13**, Fig. 4. Selected bond lengths and angles are displayed in Table 4. The structure can be seen to be essentially that of two 1 : 1 tu·I_2 spoke adducts linked *via* an additional diiodine molecule, the d(I–I) for which is 2.7540(9) Å, a value not appreciably longer than that for unco-ordinated diiodine (2.66 Å). That is, although co-ordination of one molecule of I_2 to a sulfur donor provokes a significant change in the I_2 bond order (d(I(1)–I(2) 3.0538(5) Å), co-ordination of a second I_2 molecule to the first does not; I(2) interacts only weakly with I(3) of the diiodine molecule (d(I(2)–I(3)) 3.407(5) Å). This explains the relatively small change in wavenumber of the Raman band assigned to the least perturbed I_2 molecule (*i.e.* from 180 for 'free' I_2 to 168 cm^{-1} for **12**), a phenomenon previously observed by other workers.[27] The S–I–I arrangement is nearly linear (S(1)–I(1)–I(2) 176.04(4)°) in keeping with spoke structures of other molecules containing a Group 15[30] or 16[4–7,14] donor atom. The structural motif S–I_2–I_2–I_2–S has never previously been reported to our knowledge.

The reaction was repeated and a further quantity of material with the same properties as those of **12** was allowed to cool slowly in dichloromethane. Purple crystals were again produced and a suitable candidate was selected; a single crystal X-ray diffraction study showed the stoichiometry this time to be $(tu)_3(I_2)_5$ **14**. The complicated arrangement of a tu·I_2 spoke moiety, a $[(tu)_2I_3]^+$ cation, an I_3^- anion and a neutral diiodine molecule is shown in Fig. 5; selected bond lengths and angles are displayed in Table 5. The tu·I_2 spoke can be considered a strong CT complex as d(I(6)–I(7)) has notably lengthened upon I_2 co-ordination to 3.0565(9) Å; we stated earlier that the range for d(I–I) in previously reported sulfur–diiodine CT adducts was 2.75 to 2.98 Å.[14] Hence, the tu·I_2 spoke moieties reported here as components of **13** and **14** represent very strong donor–acceptor systems indeed. This is of importance as it has been noted that strong complexes have the greatest efficacy as antithyroid treatments *in vivo*.[2] The S–I–I–I–S arrangement has not previously been reported; here it consists of a 'V-shaped' I–I–I moiety (I(2)–I(1)–I(3) 77.02(7)°) linking two tu molecules. The central iodine atom I(1) interacts weakly with I(4) of the diiodine molecule, as does I(7) of the tu·I_2 spoke with I(5); d(I(1)–I(4)) 3.247(1), d(I(5)–I(7) 3.491(1) Å. The I_3^- anion is essentially non-co-ordinating, although there are two very weak interactions to other iodine moieties in the structure; d(I(1)–I(10)) 3.850, d(I(7)–I(8)) 3.846 Å.

Table 6 compares selected bond lengths from compounds **13** and **14** to those reported for $(tu)_2I_2$[16a] and for tu itself.[31] The data reveal a surprising trend: as the I_2 : tu ratio increases from 1 : 2 to 3 : 2 to 5 : 3, d(S–I) becomes notably shorter. It is interesting that d(S–I) is especially short for the two S–I bonds of the $[(tu)_2I_3]^+$ cation; the SI bond can therefore be considered to be stronger in this novel arrangement than for spoke, extended spoke or ionic motifs.

Examination of the two structures **13** and **14** necessitated an alteration of our view of tu·I_4 **12**. Whilst it is perfectly possible that **12** indeed has an 'extended spoke' structure and that **13** and **14** are minor products, one should also consider the possibility that the bulk material **12** is simply made up of numerous different tu–polyiodide arrangements, of which **13** and **14** are just two examples. In that case, although our assignment of the bands at 168 and 106 cm^{-1} to a slightly perturbed I_2 molecule and an I–I–I moiety respectively would still be correct, it does not prove the existence of a discrete tu·I_4 molecule. Both **13** and **14** would be expected to show similar peaks in their Raman spectra as they each contain both kinds of species. Unfortunately, their crystals decomposed shortly after X-ray diffraction data collection, so Raman spectra were not obtained. Also, we were not confident that spectra collected from other crystals would necessarily be representative of **13** or **14**; however, we still think it likely that **12** largely consists of a tu·I_4 extended spoke, but with the presence of a series of polyiodide minor products.

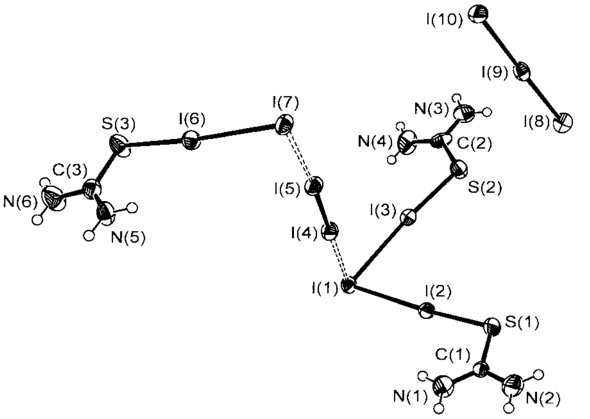

Fig. 5 Single-crystal structure of compound **14**. One tu·I_2 spoke moiety, one novel $[(tu)_2I_3]^+$ cation, one I_3^- anion and a neutral I_2 molecule are present in the asymmetric unit.

Table 5 Selected bond lengths (Å) and angles (°) for $(tu)_3(I_2)_5$ **14**

S(1)–I(2)	2.466(2)	I(9)–I(10)	2.922(1)
S(2)–I(3)	2.437(3)	S(1)–C(1)	1.71(1)
S(3)–I(6)	2.507(3)	S(2)–C(2)	1.70(1)
I(1)–I(2)	3.1457(9)	S(3)–C(3)	1.70(1)
I(1)–I(3)	3.168(1)	N(1)–C(1)	1.30(1)
I(1)–I(4)	3.247(1)	N(2)–C(1)	1.31(1)
I(4)–I(5)	2.756(1)	N(3)–C(2)	1.30(1)
I(5)–I(7)	3.491(1)	N(4)–C(2)	1.30(1)
I(6)–I(7)	3.0565(9)	N(5)–C(3)	1.30(1)
I(8)–9(9)	2.916(1)	N(6)–C(3)	1.30(1)
S(1)–I(2)–I(1)	176.08(7)	C(1)–S(1)–I(2)	104.1(3)
S(3)–I(6)–I(7)	173.69(7)	C(2)–S(2)–I(3)	105.7(4)
I(8)–I(9)–I(10)	177.43(3)	C(3)–S(3)–I(6)	105.2(3)

Conclusion

The main conclusions that we draw from the data presented here can be summarised as follows. (*i*) A range of thioamides are capable of forming 1 : 1 addition compounds with diiodine, iodine monobromide and iodine monochloride. Raman studies are useful in determining whether products adopt spoke or ionic structures; however results are sometimes inconclusive and structure assignment should be tentative. The fact that ν_1 (I–I) for an S–I–I system, ν_3 (I–I) for an asymmetric I_3^- anion and δ (C–S–I) all appear in a similar region (140–170, 130–140 and 140–155 cm^{-1} respectively) often makes positive assignment very difficult.

(*ii*) Single crystal X-ray diffraction is of great use, but reliance should not be absolute as the FT-Raman data imply there may be structural isomerism in these systems. However, our studies seem to show a predilection for ionic structures (previously only rarely crystallographically characterised[16]) by simple thiourea-based thioiamides, such as tu and dmtu, and a preference for spoke structures by heterocyclic thioamides such as mbtt and mrh.

(*iii*) Comparison of the crystal structure of compound **3** with $(tu)_2I_2$ seems to suggest that *N*-alkylation does not have as great an effect on d(S–I) as one might expect. This is important as it would allow solubility and toxicity considerations to take preference over the exact R groups present in an antithyroid candidate.

(*iv*) However, the novel crystal structures of compounds **13** and **14** show that the exact *stoichiometry* between the thioamide and diiodine has a pronounced affect on d(S–I) and therefore complex strength. In addition, there seems to be enormous structural diversity in polyiodide systems arising from reactions involving an excess of diiodine, such as that of tu with two equivalents of I_2 which leads to at least two different arrangements (*i.e.* **13** and **14**) and almost certainly many more to make up the bulk material of stoichiometry tu·I_4 **12**.

We hope soon to extent our studies to encompass a larger range of thioamides in the hope of elucidating the exact ionic–CT borderline and increasing the reliability of structural assignment through FT-Raman spectroscopy with a view to finding molecules with the strongest potential affinity for diiodine *in vivo*.

Table 6 A comparison of selected bond lengths (Å) in tu,[31] $(tu)_2I_2$,[16a] **13** and **14**

	tu	$(tu)_2I_2$[a]	13	14
S–I	—	2.629	2.5028(3)	2.437(3), 2.466(2), 2.507(3)
C–S	1.712(8)	1.724	1.735(5)	1.70(1), 1.70(1), 1.71(1)
C–N	1.332(6), 1.334(8)	1.296, 1.317	1.293(8), 1.294(7)	1.30(1), 1.30(1), 1.31(1), 1.30(1), 1.30(1), 1.30(1)

[a] No e.s.d.s were included in ref. 16 so regrettably they have not been included here.

Table 7 Crystal data and structure refinement for compounds **3**, **13** and **14**

	3	**13**	**14**
Empirical formula	$C_3H_8I_2N_2S$	$CH_4I_3N_2S$	$C_3H_{12}I_{10}N_6S_3$
M	715.95	228.41	1497.37
T/K	203(2)	203(2)	203(2)
Crystal system	$P2_1/c$	$C2/c$	$P\bar{1}$
Space group	Monoclinic	Monoclinic	Triclinic
a/Å	14.743(3)	14.019(2)	8.8406(10)
b/Å	16.368(2)	9.329(2)	11.215(2)
c/Å	15.231(2)	13.596(1)	15.454(2)
α/°	—	—	70.951(10)
β/°	90.29(2)	104.87(1)	85.298(10)
γ/°	—	—	74.08(2)
V/Å^3	3675.4(10)	1718.6(3)	1392.8(3)
Z	8	16	2
μ/mm^{-1}	6.996	11.067	11.352
Reflections collected/unique	6986/6451	1551/1487	5235/4888
R_{int}	0.0227	0.0142	0.0277
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0529, 0.1246	0.0230, 0.0554	0.0349, 0.0776
(all data)	0.0714, 0.1354	0.0276, 0.0571	0.0473, 0.0821

Experimental

All thioamides were obtained commercially from Aldrich and used as received. Compounds **1**–**4** were prepared by allowing the thioamides tu, etu, dmtu and detu to react with one equivalent of diiodine (Aldrich) in dichloromethane (BDH). The synthesis of **1** is typical: tu (1.000 g, 13.148 mmol) was dissolved in dichloromethane (*ca.* 50 cm^3) then diiodine added (3.337 g, 13.148 mmol). After *ca.* 2 d the resultant dark grey solid was isolated by filtration and dried *in vacuo*. Compounds **5** and **6** were prepared using mbtt and mrh in a similar manner except diethyl ether (BDH) was used instead of dichloromethane. Compound **12** was prepared in a similar manner to that of **1**, except that two equivalents of diiodine were used instead of one.

Compounds **7** to **11** are moisture sensitive; strictly anhydrous conditions must be observed for their successful synthesis. Dichloromethane (for **7**–**10**) was dried over calcium hydride and diethyl ether (for **11**) over sodium wire for 2 h then refluxed in an inert atmosphere (N_2) prior to use. Iodine monobromide (for **7**, **9** and **11**, Aldrich) was added as a solid and iodine monochloride (for **8** and **10**, Aldrich) as a liquid against a stream of dry nitrogen gas to the dichloromethane or diethyl ether solution of the appropriate thioamide. After *ca.* 2 d the resultant solid products were isolated using standard Schlenk filtration techniques and dried *in vacuo* before being transferred to pre-dried argon-filled ampoules which were then flame-sealed. All subsequent manipulations were carried out inside a glove-box.

Elemental analyses were performed by the analytical laboratory of this department. Analytical data for adducts **1**–**12**, including melting points and yields, are displayed in Table 1. The FT-Raman spectra were recorded in the range 3000–100 cm^{-1} at powers of 200–500 mW of incident light using a Nexus FT-Raman module with OMNIC 5 software. Spectra were recorded down to the low frequency cut-off point of 100 cm^{-1}. The spectrometer was fitted with an indium–gallium arsenide detector (RT) and operated *via* an Nd:YV04 laser source. The solid samples were introduced into a capillary tube and fitted into a compartment designed for 180° scattering geometry. No sample heating, decomposition or fluorescence was observed during any of the collections. Wavenumbers and relative intensities for bands observed at <300 cm^{-1} for **1**–**6** and **9**–**11** are displayed in Table 2. Full spectral traces and peak tables with intensities relative to 100 are included in the Supplementary Information.

X-Ray crystallography

The X-ray experiments for compounds **3**, **13** and **14** were carried out 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 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 7.

CCDC reference number 186/2110.

See http://www.rsc.org/suppdata/dt/b0/b004182n/ for crystallographic files in .cif format.

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References

1 J. Jeske, W.-W. du Mont and P. G. Jones, *Chem. Eur. J.*, 1999, **5**, 385; G. B. M. Vaughan, A. J. Mora, A. N. Finch, P. N. Gates and A. S. Muir, *J. Chem. Soc., Dalton Trans.*, 1999, 79; D. C. Apperley, N. Bricklebank, S. L. Burns, D. E. Hibbs, M. B. Hursthouse and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1998, 1289; A. J. Blake, F. A. Devillanova, A. Garau, L. M. Gilby, R. O. Gould, F. Isaia, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 2037; D. J. Williams, D. Vanderveer, B. R. Crouse, R. R. Raye, T. Carter, K. S. Hagen and M. Brewer, *Main Group Chem.*, 1997, **2**, 61.

2 C. Raby and J. Bauxeraud, *Eur. J. Med. Chem.*, 1980, **15**, 425; J. Buxderaud, A.-C. Absil, J. Claude, C. Raby, G. Catanzano and C. Beck, *Eur. J. Med. Chem.*, 1985, **20**, 43.

3 J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, New York, 1987; A. D. Yoffe, *Chem. Soc. Rev.*, 1976, **5**, 51; L. R. Greene and G. B. Street, *Chemistry and physics of one-dimensional metals*, Plenum, New York, 1977; H. Temkin, A. Watanabe and J. Tanaka, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 645; H. Temkin and G. B. Street, *Solid State Commun.*, 1978, **25**, 455; Z. Iqbal, R. H. Baughman, J. Kleppinger and A. G. MacDiarmid, *Solid State Commun.*, 1978, **25**, 409.

4 S. Sarwar, Ph.D Thesis, University of Manchester Institute of Science and Technology, 1997.

5 S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. Sarwar, *J. Chem. Soc., Dalton Trans.*, 1997, 1031.

6 W. I. Cross, S. M. Godfrey, S. L. Jackson, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1999, 2225.

7 S. M. Godfrey, S. L. Jackson, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1998, 4201.

8 P. D. Boyle, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Sheffield, *Chem. Commun.*, 1999, 2159.

9 P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, S. Sarwar and J. M. Sheffield, *Angew Chem.*, *Int. Ed.*, 2000, **39**, 1796.

10 (*a*) P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. J. Teat, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2219; (*b*) P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. J. Teat, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2845; (*c*) P. D. Boyle, S. M. Godfrey and R. G. Pritchard, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 4245.

11 F. Cristiani, F. A. Devillanova, A. Diaz and G. Verani, *J. Chem. Soc.*, *Perkin Trans. 2*, 1984, 1383; M. Cau, F. Cristiani, F. A. Devillanova and G. Verani, *J. Chem. Soc.*, *Perkin Trans. 2*, 1985, 749.

12 M. Bodelsen, G. Borch, P. Klæboe and P. H. Nielsen, *Acta Chem. Scand.*, *Ser. A*, 1980, **34**, 125.

13 P. Deplano, F. A. Devillanova, J. R. Ferraro, F. Isaia, V. Lippolis and M. L. Mercuri, *Appl. Spectrosc.*, 1992, **46**, 1625; P. Deplano, F. A. Devillanova, J. R. Ferraro, M. L. Mercuri, V. Lippolis and E. F. Trogu, *Appl. Spectrosc.*, 1994, **48**, 1236.

14 (*a*) F. Freeman, J. W. Ziller, H. N. Po and M. C. Keindl, *J. Am. Chem. Soc.*, 1988, **110**, 2586; (*b*) D. Atzei, P. Deplano, E. F. Trogu, F. Bigoli, M. A. Pellinghelli and A. Vacca, *Can. J. Chem.*, 1988, **66**, 1483; (*c*) D. Atzei, P. Deplano, E. F. Trogu, F. Bigoli, M. A. Pellinghelli, A. Sabatini and A. Vacca, *Can. J. Chem.*, 1989, **67**, 1416; (*d*) P. Cristiani, F. Demartin, F. A. Devillanova, F. Isaia, G. Saba and G. Verani, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 3553; (*e*) F. Bigoli, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *Can. J. Chem.*, 1995, **73**, 380; (*f*) F. Bigoli, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3583.

15 F. Cristiani, F. A. Devillanova, F. Isaia, V. Lippolis, G. Verani and F. Demartin, *Polyhedron*, 1995, **14**, 2937.

16 (*a*) H. Hope and G. Hung-Yin Lin, *Chem. Commun.*, 1970, 169; (*b*) G. Hung-Yin Lin and H. Hope, *Acta Crystallogr.*, *Sect. B*, 1972, **28**, 643; (*c*) F. Demartin, P. Deplano, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chem.*, 1993, **32**, 3694.

17 F. H. Herbstein and W. Schwotzer, *J. Am. Chem. Soc.*, 1984, **106**, 2367.

18 F. H. Herbstein and W. Schwotzer, *Angew. Chem.*, *Int. Ed. Engl.*, 1982, **21**, 219.

19 A. J. Arduengo and E. M. Burgess, *J. Am. Chem. Soc.*, 1977, **99**, 2376.

20 N. Kuhn, T. Kratz and G. Henkel, *Chem. Ber.*, 1994, **127**, 849; N. Kuhn, R. Fawzi, T. Kratz and M. Steimann, *Phosphorus Sulfur Silicon Relat. Elem.*, 1996, **112**, 225.

21 F. Bigoli, A. M. Pellinghelli, P. Deplano, F. A. Devillanova, V. Lippolis, M. L. Mercuri and E. F. Torgu, *Gazz. Chim. Ital.*, 1994, **124**, 445.

22 (*a*) A. G. Maki and R. Forneris, *Spectrochimica Acta*, *Part A*, 1967, **23**, 867; (*b*) G. A. Bowmaker and S. F. Hannan, *Aust. J. Chem.*, 1971, **24**, 2237; (*c*) W. Gabes and H. Gerding, *J. Mol. Struct.*, 1972, **14**, 267.

23 W. Holzer, W. F. Murphy and H. J. Bernstein, *J. Chem. Phys.*, 1970, **52**, 399.

24 S. Kato, Y. Komatsu, T. Murai, H. Hamaguchi, M. Tasumi and R. Okazaki, *Chem. Lett.*, 1986, 935.

25 R. Minkwitz, J. Nowicki, B. Jahnkow and M. Koch, *Z. Anorg. Allg. Chem.*, 1991, **596**, 77.

26 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd edn., 1997.

27 F. Cristiani, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chem.*, 1994, **33**, 6315.

28 A. J. Blake, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, S. Parsons and M. Schröder, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 525.

29 G. C. Haywood and P. J. Hendra, *Spectrochim. Acta*, *Part A*, 1967, **23**, 2309.

30 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1163; N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 101.

31 D. Mullen and E. Hellner, *Acta Crystallogr.*, *Sect. B*, 1978, **34**, 2789.

32 G. M. Sheldrick, SHELX 97, Programs for crystal structure analysis (release 97-2), University of Göttingen, 1998.