

# Metal Iodides in Polyiodide Networks – The Structural Chemistry of Complex Thallium Iodides with Excess Iodine

Per H. Svensson,<sup>[a]</sup> Günther Raud,<sup>[b]</sup> and Lars Kloo\*<sup>[c]</sup>

**Keywords:** Polyiodides / Iodine / Thallium / NMR spectroscopy

The  $\text{TlI}/(\text{R}_3\text{S})\text{I}_x$  systems ( $\text{R} = \text{Me}/\text{Et}$ ,  $x = 3, 5, 7$ ) have been investigated by means of Raman, far-IR,  $^{205}\text{Tl}$  NMR spectroscopy and X-ray diffraction. The reaction between  $(\text{Me}_3\text{S})\text{I}_7$  and  $\text{TlI}$  results in the polyiodide compound  $(\text{Me}_3\text{S})_3\text{I}_{26}$ . Raman spectra also reveal the presence of a solid thallium- and iodine-containing product. However, all attempts to structurally characterise this product were unsuccessful. The com-

pound  $(\text{Et}_3\text{S})\text{TlI}_4$  is obtained from the reaction between  $(\text{Et}_3\text{S})\text{I}_7$  and  $\text{TlI}$ .  $^{205}\text{Tl}$  NMR spectra show that  $\text{Tl}^{\text{III}}$  is present in the reaction mixtures of  $\text{TlI}/(\text{R}_3\text{S})\text{I}_x$  and that the peak assigned to  $\text{TlI}_4$  in the  $\text{TlI}/(\text{Et}_3\text{S})\text{I}_7$  system splits upon heating. This effect is reversible and indicates an equilibrium between two  $\text{Tl}^{\text{III}}$  species.

## Introduction

Iodine ( $\text{I}_2$ ) and the ions  $\text{I}^-$  and  $\text{I}_3^-$  can be regarded as the “building blocks” of polyiodides and by combination of these it is possible to rationalise almost all known polyiodide fragments (viz.  $\text{I}_5^-$ ,  $\text{I}_7^-$ ,  $\text{I}_8^{2-}$  and  $\text{I}_9^-$ ). The smaller polyiodides can easily be made with many different cations. However, the larger polyiodides usually have to be stabilised with quite bulky and/or polarisable cations. Many of the larger polyiodides consist of long chains, layers or intercalated structures, which in many cases are electronically conducting and even superconducting.<sup>[1–4]</sup>

A still greater variety of iodine-rich compounds with interesting structural properties can be achieved by the incorporation of metal centres into the polyiodide structures. The inclusion of different metal compounds gives endless possibilities for structural variation. Wells’ salt ( $\text{K}_3\text{Pb}_2\text{I}_8 \cdot 4\text{H}_2\text{O}$ ) is an early example of such a substance, though not structurally characterised until 1984 by Tebbe.<sup>[5,6]</sup> Recently, several late transition metals have been incorporated into polyiodide networks.<sup>[7–11]</sup> The exchange of linear  $\text{I}-\text{M}-\text{I}$  units for  $\text{I}-\text{I}-\text{I}$  units has also been shown for  $\text{M} = \text{Au}$ .<sup>[10]</sup>

According to the literature, less, if any, effort has been devoted to heavy main-group metals in this context. These metal ions, being borderline cases between hard and soft acceptors by the hard-soft acid-base formalism, are capable of forming iodide complexes in different or sometimes mixed oxidation states.

Thallium, with its most common oxidation states +I and +III, forms several well-known, non-polyiodide compounds and complexes, such as  $\text{TlI}$  and  $\text{TlI}_4$ . A  $\text{TlI}_6^{3-}$  ion has not been verified, though its bromide congener  $\text{TlBr}_6^{3-}$  was identified.<sup>[12]</sup> The compound  $\text{TlI}_3$  actually consists of  $\text{Tl}^+$  and  $\text{I}_3^-$  units.<sup>[13,14]</sup> Another less conventional property of thallium is that it is softer in the oxidation state +III than in +I. These facts indicate that the possibility of  $\text{Tl}^{\text{III}}$  oxidising  $\text{I}^-$  must be taken into account, even though the converse, iodine oxidation of  $\text{Tl}^{\text{I}}$  to  $\text{Tl}^{\text{III}}$ , can be induced by the right choice of ligands and reaction conditions.<sup>[14,15]</sup> Polyiodides incorporating only thallium are rather rare ( $\text{TlI}_3$  and  $\text{Tl}_3\text{I}_4$ )<sup>3</sup>, but they readily form  $(\text{Tl}_6\text{I}_6\text{M}_x)[\text{I}_4^{2-}]$  compounds if mixed with other metals ( $\text{M} = \text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Au}^+$ ,  $\text{Ag}^+$ ).<sup>[16]</sup>

In this work, we have investigated the possibility of incorporating thallium into polyiodide networks via the reaction between  $\text{Tl}$  or  $\text{TlI}$  and the polyiodide melts of trialkylsulfonium iodide. The results have been analysed by means of X-ray diffraction, Raman, IR and  $^{205}\text{Tl}$  NMR spectroscopy.

## Results and Discussion

### Spectroscopic Studies

The Raman spectrum of the reaction mixture between  $\text{TlI}$  and  $(\text{Me}_3\text{S})\text{I}_7$  (molar ratio 1:3) displays a broad peak at  $176\text{ cm}^{-1}$ , almost identical to that of pure  $(\text{Me}_3\text{S})\text{I}_7$  (Figure 1, top). The very strong peak from the heptaiodide makes it difficult to extract any information about the reaction mixture by means of Raman and far-IR spectroscopy. However, the absence of  $\text{TlI}$  ( $103\text{ cm}^{-1}$  and  $86\text{ cm}^{-1}$ ) indicates that a reaction has taken place. The far-IR spectrum shows very similar spectral features to that of unchanged  $(\text{Me}_3\text{S})\text{I}_7$ . There are some weak extra bands, but they are difficult to assign. The Raman spectrum of the solid thal-

<sup>[a]</sup> Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

<sup>[b]</sup> Inorganic Chemistry 1, Lund University, P. O. Box 124, 22100 Lund, Sweden

<sup>[c]</sup> Inorganic Chemistry, Department of Chemistry, Royal Institute of Technology, 10044 Stockholm, Sweden  
Fax: (internat.) + 46-8/790-9349  
E-mail: Larsa@inorg.kth.se

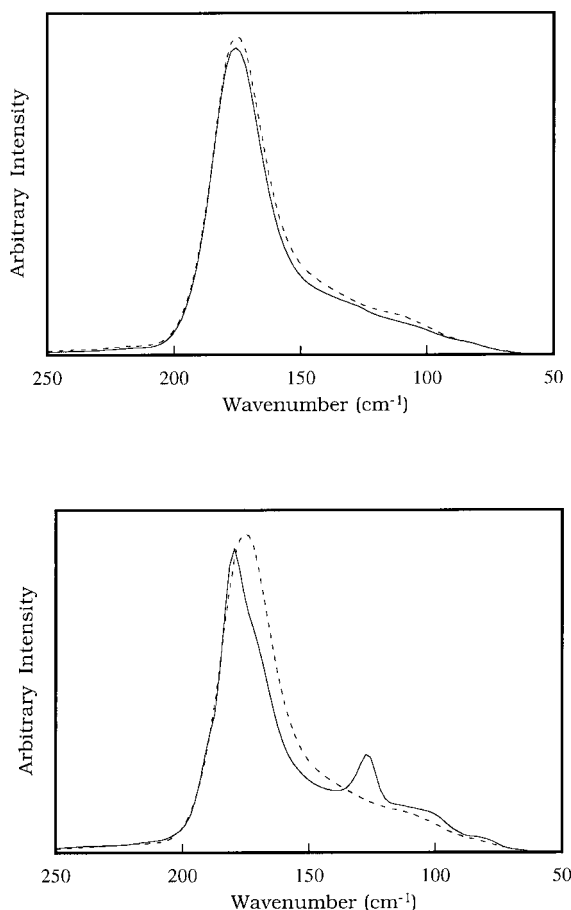


Figure 1. The Raman spectra of the reaction mixture; top: TlI and (Me<sub>3</sub>S)I<sub>7</sub> (—), bottom: the decomposed solid product (---); (---) denotes a pure (Me<sub>3</sub>S)I<sub>7</sub> melt

lium-containing product separated from the reaction melt shows the same spectral features as the reaction mixture. However, if the solid product is left to decompose under ambient conditions its Raman spectrum changes (Figure 1, bottom). Two new peaks are observed at 105 and 128 cm<sup>-1</sup>. The latter peak corresponds favourably to the asymmetric stretch of TlI<sub>4</sub><sup>-</sup>, while the former is in the region where both TlI and triiodide ions normally give rise to spectral features.<sup>[12,17–22]</sup> This implies that the solid product has decomposed to TlI<sub>4</sub><sup>-</sup> and possibly TlI or I<sub>3</sub><sup>-</sup>.

The vibrational spectra of the reaction mixture from TlI and (Et<sub>3</sub>S)I<sub>7</sub> (molar ratio 1:3) show spectral features that differ from the analogous mixture with (Me<sub>3</sub>S)I<sub>7</sub> (Figure 2, top). The Raman spectrum displays a distinct peak at 130 cm<sup>-1</sup> which is not seen in (Me<sub>3</sub>S)I<sub>7</sub>. This peak corresponds favourably with the asymmetric stretch of TlI<sub>4</sub><sup>-</sup>.<sup>[12,17–22]</sup> The symmetric stretch of TlI<sub>4</sub><sup>-</sup>, which should appear around 150 cm<sup>-1</sup>, is probably masked by the strong polyiodide bands. The far-IR spectrum also displays differences with respect to the pure polyiodide system. These can also be assigned to TlI<sub>4</sub><sup>-</sup> ions. The Raman spectra of the crystals obtained from the synthesis show that the spectral features of the polyiodides have decreased in intensity and as a consequence it is possible to identify a peak at 156 cm<sup>-1</sup> corresponding to the symmetric stretch of TlI<sub>4</sub><sup>-</sup> (Figure 2, bot-

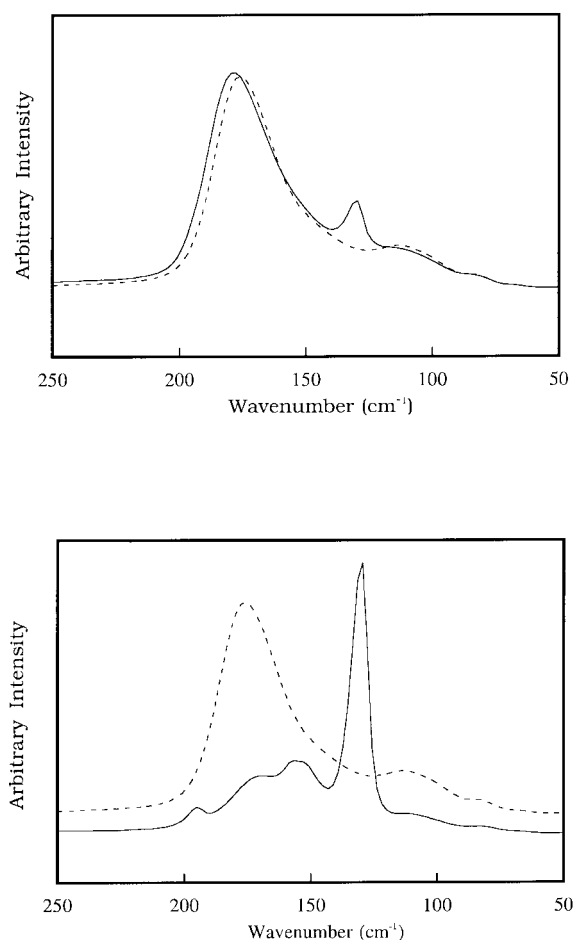


Figure 2. The Raman spectra of the reaction mixture; top: TlI and (Et<sub>3</sub>S)I<sub>7</sub> (—), bottom: the solid product (---); (---) denotes the spectrum of pure (Et<sub>3</sub>S)I<sub>7</sub> melt

tom). A weak band at 196 cm<sup>-1</sup> is also observed; it may be the overtone of the  $\nu_1$  of TlI<sub>4</sub><sup>-</sup> or I<sub>3</sub><sup>-</sup>, or the  $\nu_1$  of iodine. The spectral features of the crystals after some days under ambient conditions are invariant, thus indicating that the compound is stable under these conditions.

### Structural Investigation

The only product that could be isolated and fully characterised from the reaction between TlI and (Me<sub>3</sub>S)I<sub>7</sub> was found to be a polyiodide compound with no incorporation of thallium, (Me<sub>3</sub>S)<sub>3</sub>I<sub>26</sub> (**1**). However, there must be at least two different products under the chosen set of conditions: a polyiodide of the (Me<sub>3</sub>S)I/I<sub>2</sub> system, and a thallium compound (whose spectral properties were discussed above). The structure of the thallium-containing compound could not be characterised because of its thermal instability (loss of I<sub>2</sub>).

The structure of **1** can be described in terms of a pyramidal I<sub>7</sub><sup>-</sup> ion, V/L-shaped I<sub>5</sub><sup>-</sup> ions, intercalated iodine and Me<sub>3</sub>S<sup>+</sup> cations (Figure 3 and Figure 4). The intramolecular I–I distances for the penta- and hepta-iodides are in the range 2.75–3.29 Å (Table 1). The two independent I<sub>5</sub><sup>-</sup> ions are at the limit where they may be regarded either as two I<sub>2</sub> molecules coordinating to an iodide ion (V-shaped) or as a

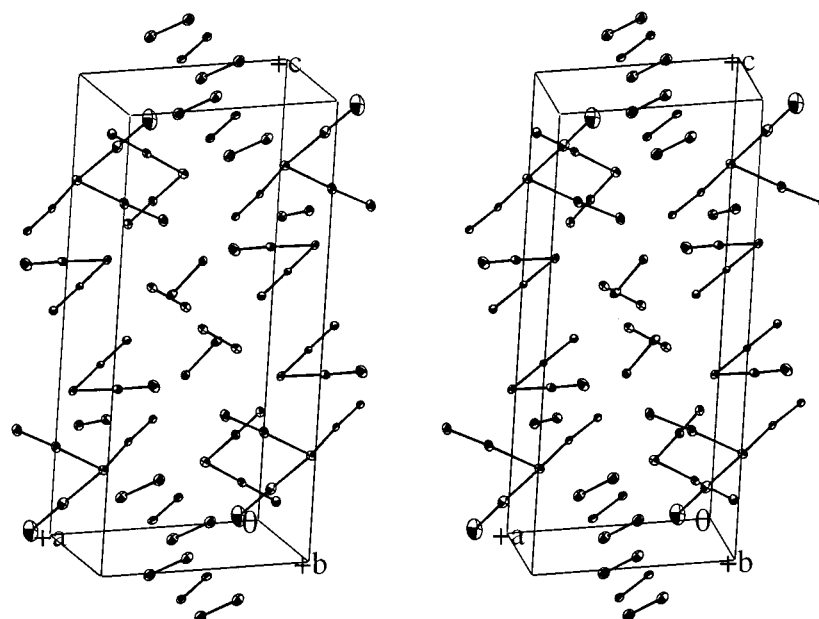


Figure 3. Stereoscopic view of the crystal structure of **1**; the cations are omitted for clarity

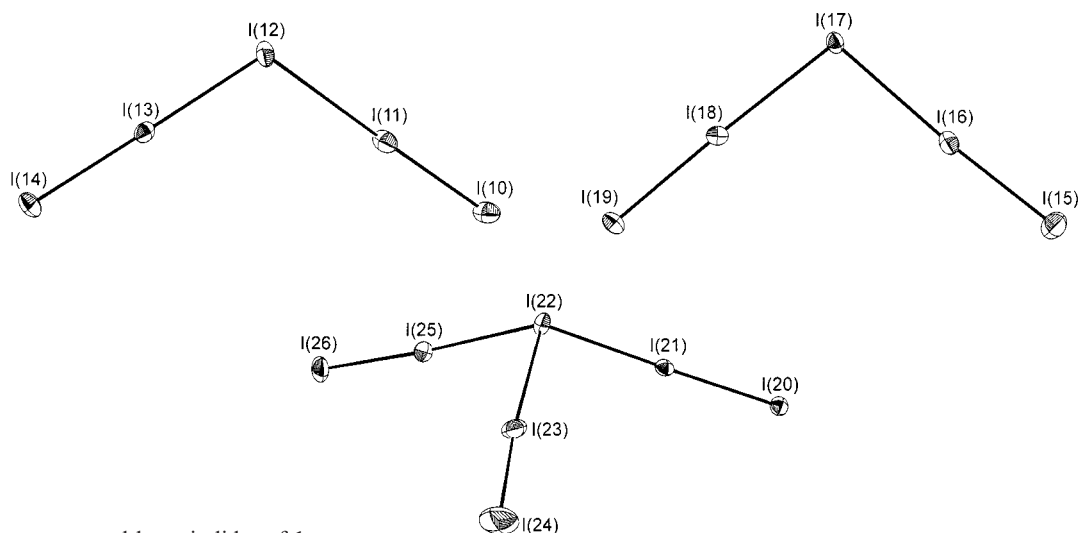


Figure 4. The penta- and hepta-iodides of **1**

triiodide coordinated to an  $I_2$  molecule (L-shaped). If the latter description is chosen, the very asymmetric triiodides I(12)–I(13)–I(14) [I(12)–I(13) 3.007(4) and I(13)–I(14) 2.843(4) Å] and I(17)–I(18)–I(19) [I(17)–I(18) 3.089(4) and I(18)–I(19) 2.805 Å] are linked to the iodine molecules I(10)–I(11) [2.751(4) Å] and I(15)–I(16) [2.790(4) Å], respectively. The triiodides are slightly bent [I(12)–I(13)–I(14) 179.3(1)° and I(17)–I(18)–I(19) 178.1(1)°].

The  $I_7^-$  anion can be described in terms of two  $I_2$  molecules I(23)–I(24) [distance 2.748(5) Å] and I(25)–I(26) [distance 2.748(4) Å] coordinating to an asymmetric triiodide I(20)–I(21)–I(22) [distances 2.811(4) Å and 3.069(4) Å and angle 176.10(10)°]. The top angles of the “pyramid” are 94.8(1)° and 91.7(1)° [I(21)–I(22)–I(23) and I(23)–I(22)–I(25), respectively]. Consequently, with this description the formula of **1** can be written as  $(Me_3S)_3[I_7(I_5)_2] \cdot 9/2 I_2$ . A comparison with structurally characterised penta-iodides and

hepta-iodides shows that the geometrical parameters of **1** are of normal magnitude.<sup>[23,24]</sup>

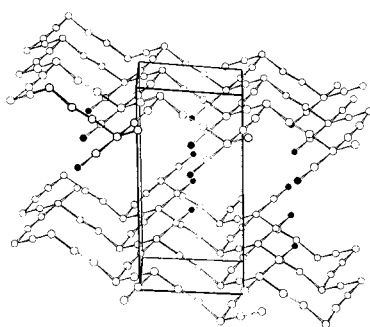
The intramolecular I–I distances of the intercalated  $I_2$  units [I(1)–I(2), I(3)–I(4), I(5)–I(6), I(7)–I(8) and I(9)–I(9\*)] vary from 2.73 to 2.77 Å. Pure iodine has intramolecular distances significantly shorter [2.715(6) Å in the solid state and 2.667(2) Å in the gas phase],<sup>[25,26]</sup> thus indicating a substantial charge-transfer interaction. The intermolecular I–I distances of the intercalated  $I_2$  molecules are 3.36 Å and greater.

With the limits between intra- and intermolecular distance applied above it is easy to describe and visualise the structure of **1**. However, the situation becomes much more complicated if the limit for intramolecular distances is increased. Intermolecular I–I distances in the range 3.5–3.7 Å have been regarded as secondary bonds (van der Waals diameter of iodine 4.30 Å) and if the limit is set to 3.7 Å

in **1**, the structure instead adopts a complicated network structure.<sup>[27,28]</sup> This structure is difficult to visualise but it is possible to give a general understanding of its constitution by dividing the network into two layers. The first layer is parallel to the *ab* plane and is constructed of the penta-iodide I(10)–I(11)–I(12)–I(13)–I(14) and two of the “in-

Table 1. Selected bond lengths and angles for **1** and **2**

<b>1</b>	
I(3)–I(4)	2.736(4)
I(5)–I(6)	2.749(4)
I(7)–I(8)	2.732(4)
I(9)–I(9)	2.771(4)
I(10)–I(11)	2.744(5)
I(11)–I(12)	2.751(4)
I(12)–I(13)	3.286(4)
I(13)–I(14)	3.007(4)
I(15)–I(16)	2.843(4)
I(16)–I(17)	2.791(4)
I(17)–I(18)	3.139(4)
I(18)–I(19)	3.089(4)
I(20)–I(21)	2.805(4)
I(21)–I(22)	2.811(4)
I(22)–I(23)	3.069(4)
I(22)–I(25)	3.226(4)
I(23)–I(24)	3.290(4)
I(25)–I(26)	2.746(5)
I(1)–I(22)	2.749(4)
I(2)–I(20)	3.388(5)
I(3)–I(20)	3.517(4)
I(8)–I(14)	3.367(4)
I(4)–I(19)	3.395(4)
I(9)–I(17)	3.644(4)
I(5)–I(12)	3.424(4)
I(10)–I(17)	3.380(4)
I(6)–I(14)	3.538(5)
I(7)–I(12)	3.458(4)
I(9)–I(26)	3.356(4)
I(10)–I(11)–I(12)	3.532(5)
I(11)–I(12)–I(13)	178.78(9)
I(12)–I(13)–I(14)	112.5(1)
I(20)–I(21)–I(22)	179.3(1)
I(15)–I(16)–I(17)	176.10(10)
I(16)–I(17)–I(18)	175.1(1)
I(17)–I(18)–I(19)	100.8(1)
I(21)–I(22)–I(23)	178.1(1)
I(22)–I(23)–I(24)	94.8(1)
I(22)–I(25)–I(26)	175.7(1)
I(23)–I(22)–I(25)	176.4(1)
	91.7(1)
<b>2</b>	
Tl–I(1)	2.757(1)
I(1)–Tl–I(1)	109.47(7)

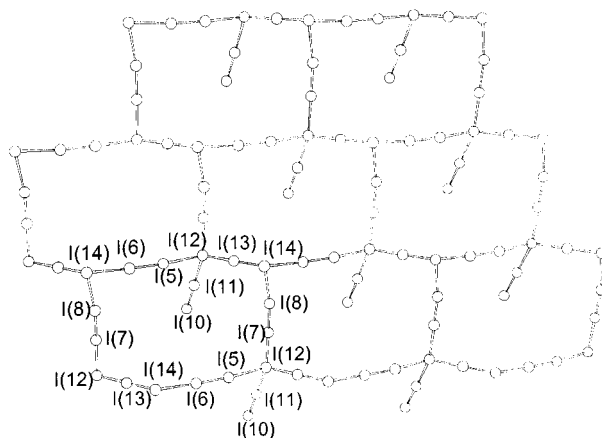
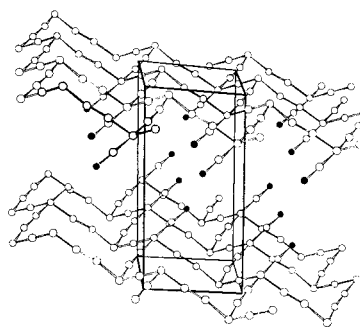
Figure 6. Stereoscopic view of the I<sub>16</sub> layer in the network of **1**; the layer-connecting iodine atoms I(10) are marked black

tercalated” iodine molecules I(5)–I(6) and I(7)–I(8) (Figures 5 and 6). The penta-iodide and the I(5)–I(6) iodine form edge-sharing, rectangular I<sub>16</sub> units, while the iodine I(7)–I(8) and the “leg” of the penta-iodide I(10)–I(11) are not incorporated into the rectangular framework. The second layer is built up from I<sub>51</sub> units, which are connected to each other through all edges (Figure 7). This layer intersects an equivalent layer in a chain-like manner.

The two layers are only connected to each other by I(17) which is linked to the free leg of the L-shaped penta-iodide I(10) [I(10)–I(17)]. Figure 8 shows how this connection ties the whole network together.

The highly crosslinked network of **1** is quite surprising considering the small cation used. There are few other polyiodides known in the literature that form extended, three-dimensional networks. All these have very bulky cations. There are some polyiodides that constitute network structures with metal centres incorporated, with the same type of cation as in **1**. These networks do not have any structural similarity with **1**, but they share the property of being highly connected and unstable under ambient conditions.<sup>[8–9]</sup>

The solid product from the reaction between TII and (Et<sub>3</sub>S)I<sub>7</sub> (molar ratio of 1:3) was identified as (Et<sub>3</sub>S)[TII<sub>4</sub>] (**2**) (Figure 9). The structure of **2** consists of tetrahedral TII<sub>4</sub><sup>–</sup> anions with Tl–I distances of 2.757(1) Å and I–Tl–I angles of 109.47(7)°, which agrees with mean values found in literature. X-ray diffraction studies on similar compounds have shown the anion to be sensitive to distortion,

Figure 5. The I<sub>16</sub> layer in the network of **1**

especially by smaller cations (such as  $\text{Cs}[\text{TlI}_4]$ )<sup>[18]</sup> or for reasons of asymmetric coordination.<sup>[15]</sup> A directly related compound is  $(\text{Bu}_4\text{N})[\text{TlI}_4]$ ,<sup>[17]</sup> which shows a slight distortion of the anion, even though the ammonium cation is bulkier than  $\text{Et}_3\text{S}^+$ .

Thallium deviates from the other members of group 13, being averse to the oxidation state +III.<sup>[29]</sup> This fact, which has often been regarded as an inert-pair effect, makes  $\text{Tl}^{\text{III}}$  compounds strongly oxidising in all kinds of solvents.<sup>[29]</sup> However, the favoured  $\text{Tl}^{\text{I}}$  has to compete with the strong Lewis acidity of  $\text{Tl}^{\text{III}}$ , exemplified by the stability of the  $\text{TlI}_4^-$  complex anion. The absence of any other known  $\text{Tl}^{\text{III}}$  complexes with iodide is a consequence of thallium's reluctance to form  $\text{Tl}-\text{Tl}$  or halogen-bridged compounds, in contrast to the other elements in group 13.<sup>[29]</sup> The equilibrium between redox behaviour and complex formation, going

from a weakly complex-forming  $\text{Tl}^{\text{I}}$  to a strongly complex-forming  $\text{Tl}^{\text{III}}$ , is affected by solvent properties, iodine and iodide concentration and not the least by lattice energies of the solid compounds that may be formed.<sup>[29]</sup>

In this work two iodides  $[\text{TlI}]$  and  $(\text{Me}_3\text{S})\text{I}$  or  $(\text{Et}_3\text{S})\text{I}$  are present which complicates the situation even further. Not only because the iodide will interfere by “pushing the system away” from the desired  $\text{Tl}^{\text{I}}$  compounds in many solvents, but also because there is a new contribution to the lattice energy to be expected for every possible precipitate.

All these factors, summed up for the  $\text{TlI}/(\text{R}_3\text{S})\text{I}/\text{I}_2^-$  system, demand a finely tuned choice of cation size and symmetry, and stoichiometric composition of the reaction mixture. This enables a balance between the two extreme results of all parameters [Equation (1)].



Reported syntheses with thallium most often lead to products to the right-hand side of Equation (1), due to the extreme stability of this complex anion.<sup>[29]</sup> Another system offering a choice between the left- and right-hand side of Equation (1) is reported by Tebbe et al.<sup>[15]</sup> Here, a crown ether is used to stabilise and increase the bulkiness of the, otherwise rare,  $\text{TlI}_2^+$  cation. This large cation forms compounds with  $\text{TlI}_4^-$  as well as polyiodide anions. The variable in these syntheses is the iodine concentration in the solvent used.

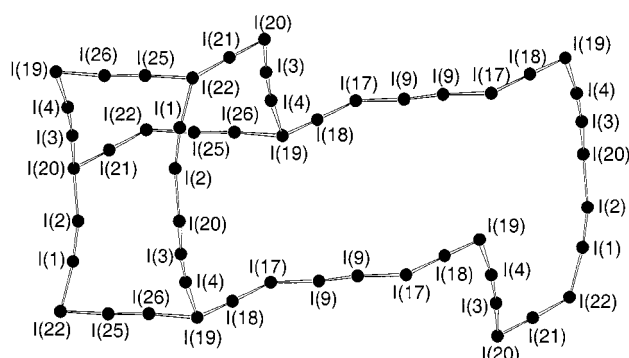


Figure 7. One of the  $\text{I}_{51}$  units that assemble the second layer

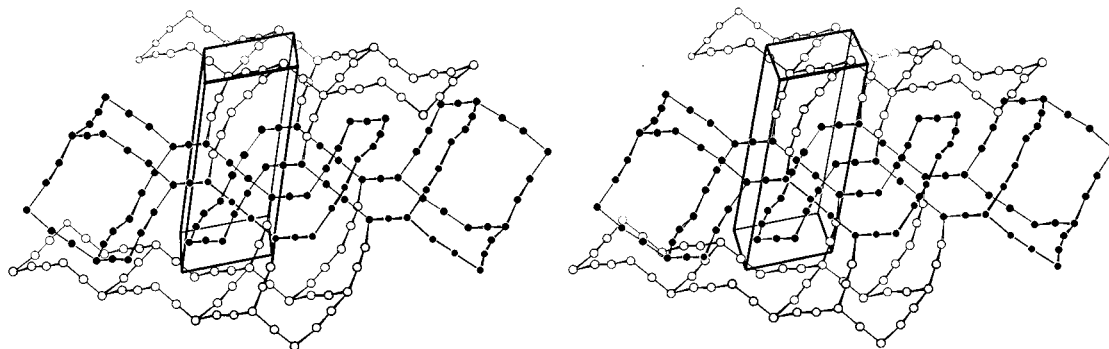


Figure 8. Stereoscopic view illustrating how the two layers are connected

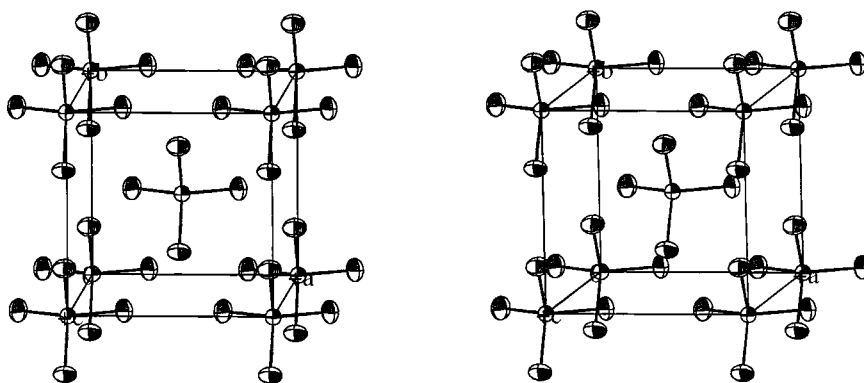


Figure 9. Stereoscopic view of the crystal structure of **2**; the cations are omitted for clarity



Under our choice of conditions, the shift in cation size going from  $R = \text{Me}$  to  $R = \text{Et}$  proved successful in the formation of both a polyiodide compound (compound **1**) and a  $\text{TI}^{\text{III}}$  iodide complex (compound **2**). The stability of the crystalline products obey the established trends of both the  $\text{TI}/\text{I}_2$  and polyiodide systems: i.e. large cations (i) stabilise polyiodides<sup>[1–4]</sup> and (ii) push  $\text{TII}/\text{I}$  towards  $\text{TII}_4^-$ .<sup>[17,30]</sup> Following the decomposition process with Raman spectroscopy, a minor change in the  $\text{I}_2/\text{I}^-$  ratio, caused by the removal of  $\text{I}_2$ , causes compound **1** to collapse. This shifts the equilibrium towards the production of  $\text{TII}_4^-$  [Equation (2) and (3)]. Compound **2**, on the contrary, is stable and resembles the congeners with other cations.

The oxidation of  $\text{TI}^{\text{I}}$  to  $\text{TI}^{\text{III}}$  results in the reduction of iodine to two iodide ions. Consequently, an increase in the iodide activity is obtained [Equation (2)]. However, the complex formation of  $\text{TII}_4^-$  requires four iodide ions [Equation (3)]. Thus, the  $\text{I}_2/\text{I}^-$  ratio is increased overall. This may explain why larger polyiodides such as  $(\text{Me}_3\text{S})_3\text{I}_{26}$  are formed by reaction with  $\text{TII}$ .



The structural and spectroscopic data obtained do not reveal which thallium species is present in the  $\text{TII}/(\text{Me}_3\text{S})\text{I}_7$  reaction mixture.

### <sup>205</sup>Tl NMR Investigations

Different mixtures of  $\text{TII}$  and  $(\text{Et}_3\text{S})\text{I}_7$  in the composition range 1:5 to 1:40 and temperature range 20 to 90 °C were investigated. Group-13 elements normally display a large chemical shift separation between the formal oxidation

states +I and +III; at least as long as the ligands are relatively hard, viz.  $\text{Cl}^-$  or  $\text{Br}^-$ .

However, very soft ligands, such as  $\text{I}^-$ , have a tendency to decrease the chemical shift separation between formally  $\text{TI}^{\text{I}}$  and  $\text{TI}^{\text{III}}$  making unambiguous assignments of peaks in the NMR spectra more difficult. For  $\text{TI}^{\text{III}}$  a decrease is seen for the chemical shift according to the series  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ .<sup>[31]</sup> This series is reversed for  $\text{TI}^{\text{I}}$  and the increase in chemical shift is coupled with growing covalency of the  $\text{TI}^+-\text{X}^-$  bond.<sup>[31]</sup>

A mixture rich in  $(\text{Et}_3\text{S})\text{I}_7$  (1:6), preheated to 90 °C and cooled to room temperature, produces a single NMR peak at  $\delta = -1414$ . With the vibrational spectroscopy results in mind, this peak is assigned to  $\text{TII}_4^-$ . Dilution with respect to  $(\text{Et}_3\text{S})\text{I}_7$  continuously shifts the frequency down to  $\delta \approx -1350$  (at 1:40). The corresponding  $\text{TII}-(\text{Me}_3\text{S})\text{I}_7$  mixtures are not liquid at room temperature and unchanged  $\text{TII}$  can be observed visually. A 1:20 mixture displays a  $\text{TII}_4^-$  peak at  $\delta = -1368$  and a broad band (about 6 kHz) at  $\delta = -1180$  assigned to  $\text{TII}_3$ .<sup>[32]</sup>

The same features are shown by  $\text{TII}-(\text{Et}_3\text{S})\text{I}_7$  mixtures which had not been previously treated at 90 °C. The two peaks appear at  $\delta = -1400$  and  $-1188$ . A gradual increase in temperature up to 90 °C produces three spectral effects (Figure 10).

(1) The intensity of the broad band decreases and disappears after some time at 90 °C. Cooling shows that this change is reversible and suggests a simple temperature-dependent complex equilibrium.

(2) Both the broad band and the  $\text{TII}_4^-$  peak move to more negative chemical shifts (about  $-1.5 \text{ ppm}/^\circ\text{C}$ ).

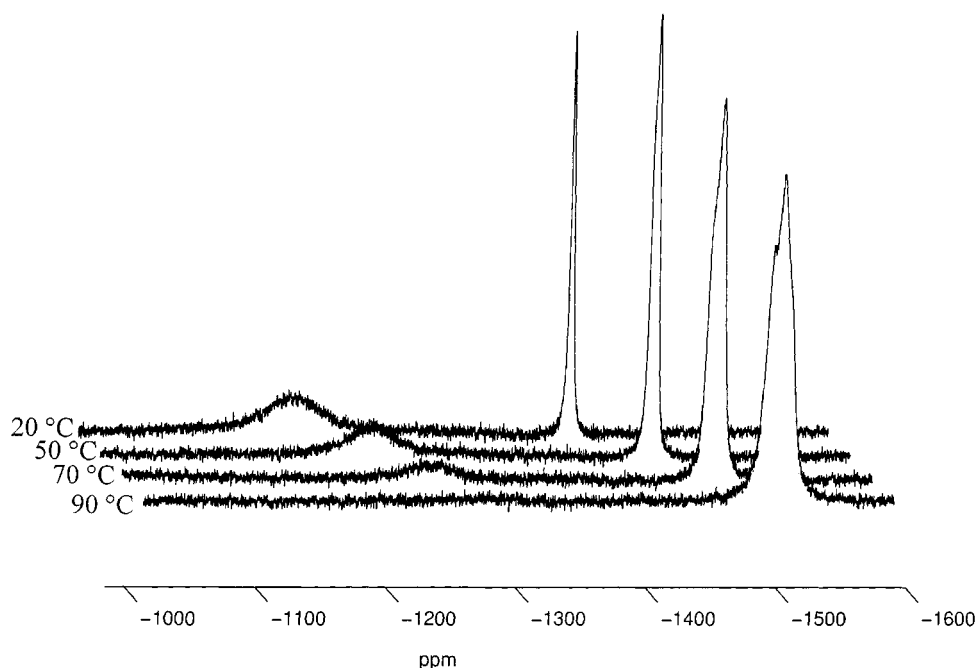
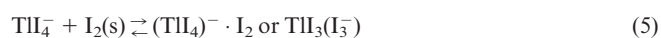


Figure 10. The <sup>205</sup>Tl NMR spectra of  $\text{TII}-(\text{Et}_3\text{S})\text{I}_7$  with increasing temperature

(3) The peak assigned to  $\text{TlI}_4^-$  splits at higher temperatures; the new component appearing at an about 12 ppm more positive shift. This effect is reversed upon cooling, indicating a temperature-dependent equilibrium between two very similar  $\text{Tl}^{\text{III}}-\text{I}^-$  species. The small difference in chemical shift and the vibrational spectroscopic data invariably infer a  $\text{Tl}^{\text{III}}$  species of tetrahedral  $\text{TlI}_4^-$  character. The equilibrium in Equation (4) thus seems to be a logical assumption. However, recent spectroscopic and theoretical work show that the corresponding  $\text{Ga}_2\text{I}_7^-$  and  $\text{In}_2\text{I}_7^-$  ions only seem to be stable in solid state because of a strong tendency towards reduction of  $\text{M}^{\text{III}}$  to  $\text{M}^{\text{I}}$ .<sup>[33]</sup> Keeping in mind the easier reduction of  $\text{Tl}^{\text{III}}$  to  $\text{Tl}^{\text{I}}$ ,  $\text{Tl}_2\text{I}_7^-$  is a less likely species in solution. An equilibrium of the type of Equation (5) can possibly be suggested.<sup>[34]</sup>



A gradual increase in temperature up to 90 °C of a  $\text{TlI}-(\text{Me}_3\text{S})\text{I}_7$  melt not preheated to 90 °C shows the features (1) and (2) (about  $-1 \text{ ppm}/^\circ\text{C}$ ); however, the peak assigned to  $\text{TlI}_4^-$  surprisingly does not split at higher temperatures.

## Conclusion

This work has shown that thallium does not have the same ability to be incorporated into polyiodide networks as the late transition metals (e.g. Au, Hg and Cd). A  $\text{Tl}[(\text{Me}/\text{Et})_3\text{S}]\text{I}_x$  polyiodide compound is probably formed but it is very unstable under ambient conditions and could not be detected or isolated with the methods applied. However, the polyiodide  $(\text{Me}_3\text{S})_3\text{I}_{26}$  could be isolated; which is surprising considering the small cation used. Consequently, the  $\text{TlI}/(\text{R}_3\text{S})\text{I}_x$  system indicates that it is possible to synthesise large polyiodides, even though a small cation is used, by supplying a strong Lewis acid which is not necessarily incorporated in the produced polyiodide compounds.

The  $\text{Tl}[(\text{Me}/\text{Et})_3\text{S}]\text{I}_x$  system is very complicated and the small change from  $\text{Me}_3\text{S}^+$  to  $\text{Et}_3\text{S}^+$  cations generate clear differences in the chemistry. In order to obtain a further understanding of which Tl species are present in the  $\text{Tl}/(\text{R}_3\text{S})\text{I}_x$  system other polyiodides with larger cations need to be investigated.

## Experimental Section

**Vibrational Spectroscopy:** The far-infrared (far-IR) spectra were recorded with a Bio-Rad FTS 6000 FT-IR spectrometer using a resolution of  $8 \text{ cm}^{-1}$ . A globular light source was used, and a 6.25-mm Mylar beamsplitter in combination with a PE-DTGS detector produce an effective spectrum range of  $50-550 \text{ cm}^{-1}$ . The window material of the sample cells was of spectroscopic-quality polyethylene (Merck). The backscattering of the compounds was recorded using the 1064-nm radiation from an Nd:YAG laser in a Bio-Rad FT-Raman spectrometer. The radiation was recorded using a nitrogen-cooled, Ge-diode detector and  $4\text{-cm}^{-1}$  resolution.

**$^{205}\text{Tl}$  NMR Spectroscopy:** The  $^{205}\text{Tl}$  NMR spectra of the  $\text{TlI}-(\text{R}_3\text{S})\text{I}_7$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) reaction media (1:5 to 1:40 ratios and  $20-90^\circ\text{C}$ ) were recorded with a Varian Unity 300-MHz spectrometer operating at 172.925 MHz. A solution of  $0.3 \text{ M TINO}_3$  in water was used as standard and assigned a shift of  $\delta = -7$ .<sup>[35]</sup>

**Synthesis of 1 and 2:** The syntheses of compounds **1** and **2** were performed by direct reaction of  $\text{TlI}$  and the  $(\text{R}_3\text{S})\text{I}_7$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) melts at  $90^\circ\text{C}$ . Both reactions were performed with a molar ratio of 1:3. A metal iodide/trialkylsulfonium hepta-iodide ratio was chosen so that all metal iodide was dissolved in the reaction step with enough liquid polyiodide remaining to solvate the crystals produced. The latter condition is a necessary requirement for growing single crystals and for the survival of the otherwise air- and moisture-sensitive product **1**. The solid products were also examined after a few days of exposure to light and air, separated from the stabilising polyiodide melt, in order to determine the products after decomposition. A similar experiment was performed avoiding the contact with air and humidity, by sealing a tube containing the crystals and slightly heating the sample ( $T = 323 \text{ K}$ ) for 72 h.

Analogous syntheses starting from pure thallium metal were also performed. The products obtained were identical to those of using the  $\text{TlI}$ -based routes.

The crystalline products from the syntheses described above were recrystallised from methanol, ethanol, acetonitrile, acetone and *N,N*-dimethylthioformamide. In all cases, the resulting crystals observed after slow evaporation of the solvent apparently contain less iodine, i.e. they become lighter in colour than their precursors. This behaviour has previously been observed for similar compounds, most likely arising because of the effective and undesired solvation of  $\text{I}_2$  by the solvents used. In order to minimise the loss of iodine we also recrystallised the solid compounds **1** and **2** from iodine-saturated ethanol. The latter resulted in darker crystals with a more porous habit as compared to the crystals obtained from other solvents.

**X-ray Crystallographic Study:** Single crystals of **1** and **2** were obtained from the reaction mixture at room temperature. The crystal data for the structures are presented in Table 2. The data for **1** were collected at 150 K, because of the tendency to lose iodine, while the data for **2** were collected at room temperature. All data were corrected for Lorentz-polarisation effects and an empirical absorption correction was applied using the Difabs (compound **1**) and  $\psi$ -scan (compound **2**) methods.<sup>[36,37]</sup> The structures were solved by the direct methods of SIR92 (**1**) and SHELXTL-PLUS (**2**) program packages.<sup>[38,39]</sup> The structure of **1** was refined on  $F$ , while the structure of **2** was refined on  $F^2$ .<sup>[40,39]</sup> The carbon and sulfur atoms of **1** were refined isotropically due to the high thermal displacement. One of the cations in **1** has the sulfur [S(1)] atom disordered in two positions. The cation of **2** is highly disordered and only the positions of the sulfur atoms were located (refined isotropically). Hydrogen atoms were placed in calculated positions for **1** (except for the disordered cation), and completely omitted in **2** because of the cation disorder. – Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-134329 [for  $(\text{Me}_3\text{S})_3\text{I}_{26}$ ] and CCDC-34330 [for  $(\text{Et}_3\text{S})\text{TlI}_4$ ]. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>9</sub> H <sub>27</sub> I <sub>26</sub> S <sub>3</sub>	C <sub>6</sub> H <sub>15</sub> I <sub>4</sub> STl
<i>M</i>	3531.01	799.19
Crystal size [mm]	0.10×0.08×0.08	0.17×0.15×0.10
<i>a</i> [Å]	10.833(4)	8.680(1)
<i>b</i> [Å]	13.10(1)	8.680(1)
<i>c</i> [Å]	23.64(1)	12.294(3)
$\alpha$ [°]	97.77(7)	90
$\beta$ [°]	97.51(5)	90
$\gamma$ [°]	109.50(5)	90
<i>V</i> [Å <sup>3</sup> ]	3076(4)	926.3(2)
Space group	<i>P</i> 1	<i>I</i> 4
<i>Z</i>	2	2
<i>D<sub>c</sub></i> [gcm <sup>−3</sup> ]	3.811	2.870
$\mu$ [mm <sup>−1</sup> ]	13.18	15.47
Diffractometer	CAD4	CAD4
Radiation	Mo- <i>K</i> $\alpha$	Mo- <i>K</i> $\alpha$
Scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
2 $\theta_{\max}$	52	50
<i>T</i> [K]	150	293
Total data collected	12682	786
Unique data	12367	719
<i>R</i> <sub>int</sub>	0.076	0.047
Observed data	6672 [ $> 3\sigma(I)$ ]	631 [ $> 2\sigma(I)$ ]
Data/variables	287/6672	23/719
Goodness of fit	2.26	1.16
Final difference map	−3.82, 3.27	−3.04, 1.39
<i>R</i>	0.065	0.0543 <sup>[a]</sup>
<i>R<sub>w</sub></i>	0.097	0.136 <sup>[b]</sup>

<sup>[a]</sup>  $R(F^2)_{\text{obs}} - \text{[b]} R_w(F^2)_{\text{obs}}$

## Acknowledgments

The Swedish Natural Science Research Council and the Wenner–Gren Foundation are gratefully acknowledged for their financial support.

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Received September 20, 1999  
[199333]