The Structure of the Tetraiodothallate(III) Ion in its Tetrabutylammonium Salt and in a Dichloromethane Solution

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The crystal structure of $[N(C_4H_9)_4][TlI_4]$ has been determined by single crystal X-ray diffraction methods. The orange-red compound crystallises in the monoclinic space group $P2_1$ (No. 4) with cell parameters $a = 11.746(2)$ Å, $b = 21.079(6$ Å, $c = 11.699(3)$ Å, $\beta = 98.23(2)°$, and $Z = 4$. The structure is built up of discrete tetrabutylammonium ions and almost regular tetrahedral tetraiodothallate(III) complex ions with Tl–I bond lengths between 2.723(4) and 2.840(5) Å.

A ruby-red 0.77 M solution of $[N(C_5H_{11})_4][TlI_4]$ in dichloromethane was investigated by X-ray diffraction. Tetrahedral TlI_4^- ions with a Tl–I bond length of 2.771(3) Å were found to occur in the solution.

Vibrational spectra of solid $[N(C_4H_9)_4][TlI_4]$ at both room temperature and liquid nitrogen temperature are reported and discussed.

A comparison is made of bond lengths of the d^{10} ions Tl(III), Hg(II), Cd(II), and Zn(II) in tetrahedral tetrahalide complexes and in their octahedrally hydrated cations.

The formation of Tl(III) halide complexes TlX_n^{3-n} (X = Cl, Br or I) has been extensively studied.[1] Although examples with Cl or Br have been reported where $n > 4^{(2-6)}$ there are none for iodides.

Crystalline $KTlBr_4 \cdot 2H_2O$, $RbTlBr_4 \cdot H_2O$, $CsTlBr_4$, $NH_4TlBr_4 \cdot 2H_2O$ and the corresponding tetraiodothallates(III) are all isomorphous and have been reported to contain planar TlX_4^- ions.[7] However, the validity of these early conclusions is doubtful because a recent single crystal X-ray study

has shown that in $KTlBr_4 \cdot 2H_2O$ the anion is tetrahedral.[8] Crystal structure determinations show tetrahedral TlX_4^- ions in $MTlCl_4$ (M = K, Tl(I), Rb, NH_4),[9] in $Tl(I)Tl(III)Br_4$ [10] and in $[C_5H_5NH]$-$[TlI_4]C_5H_5N$,[11*] and had been inferred from vibrational spectra of crystalline salts.[12]

Vibrational spectra of TlX_4^- salts in solution have also been interpreted on the basis of anions with T_d symmetry.[13,14]

As part of a structural study of thallium(III) halide complexes in crystalline solids [5,6,8,9c,15] and in solutions [16,17] the vibrational spectra of the TlI_4^- ion in dichloromethane solution and in $[NBu_4]TlI_4$-(s) have been re-examined. Since the stretching bands for the solid and for the solution showed some differences, as well as the Tl NMR chemical shifts,[17] it was decided to determine the structure of this anion in both phases by means of X-ray diffraction.

EXPERIMENTAL

Preparations. The compounds were prepared by stirring TlI (8.2g), I_2 (6.35g) and either $[N(C_4H_9)_4]I$ (9.2g) or $[N(C_5H_{11})_4]I$ (10.6g) with dichloromethane (100 cm³) for 2 h, during which time all but a little TlI dissolves to give a ruby red solution. The solution was filtered and diethylether was added to effect crystallization. Yields were practically quantitative. $[N(C_4H_9)_4][TlI_4]$ orange-red needles, m.p. 136–137 °C (lit. 117–118 °C);[18] found % C = 20.4, % H = 4.0, % N = 1.25: $C_{16}H_{36}NI_4Tl$ requires % C = 20.15, % H = 3.8, % N = 1.45. $[N(C_5H_{11})_4]$-$[TlI_4]$ orange-red needles, m.p. 138 °C; found %

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* A complete report of this determination has not, however, been published.

$C = 23.95$, % $H = 4.3$, % $N = 1.45$: $C_{20}H_{44}NI_4Tl$ requires % $C = 23.75$, % $H = 4.4$, % $N = 1.4$.

Vibrational Spectra. Infrared spectra were obtained with a Nicolet 7199 Fourier transform infrared spectrometer using a "Globar" source, 6.25 μm thick Mylar beam splitter and polyethylene-windowed triglycine sulphate detector. Spectra of the solid tetrabutylammonium salt, as a compressed pellet in polyethylene, were measured at ambient temperature and, using a Specac cryostat, at liquid nitrogen temperature. Data collection was sufficient for spectra to be computed at 2 cm^{-1} resolution, but somewhat degraded by use of a Happ-Genzel apodisation function.[19] The infrared spectrum of a dichloromethane solution was also recorded, using a cell with high density polyethylene windows and 0.2 mm spacer.

Raman spectra were excited with 647.1 nm radiation (0.4 W) from a Coherent Radiation Laboratories Model 52 krypton-ion laser and were measured with a Coderg T800 triple monochromator at 2 cm^{-1} resolution or better using photomultiplier (EMI 5998 A) detection and d.c. amplification. For measurement of the spectrum of the solid at liquid nitrogen temperature a Coderg Cryocirc cryostat was used.

The Crystal. A needle of $[N(C_4H_9)_4][TlI_4]$ was cut and ground to a sphere of diameter 0.20 mm and sealed into a thin-walled glass capillary. The crystal was found to have monoclinic symmetry by film methods. A least-squares refinement on 25 reflexions centered on the diffractometer gave the unit cell parameters $a = 11.746(2)$ Å, $b = 21.079(6)$ Å, $c = 11.699(3)$ Å, and $\beta = 98.23(2)°$. The density, estimated by flotation to 2.2(1) g cm^{-3}, corresponds to four formula units in the cell which gives a calculated density of 2.21 g cm^{-3}.

Intensity data were collected at room temperature on a Syntex $P2_1$ automatic four-circle diffractometer using the ω scan technique. All 2777 hkl and $hk\bar{l}$ reflexions up to $2\theta = 40°$ (MoKα radiation) were measured. Only $0k0$ reflexions with $k = 2n + 1$ were systematically absent.

The Solution. A ruby-red 0.767 M solution (density 1.582(4) g cm^3) of $[N(C_5H_{11})_4]$ TlI$_4$ in dichloromethane was prepared. The tetrapentylammonium salt was used due to its higher solubility in dichloromethane (about 1.0 M at 25 °C). The solution was contained in a sealed thin-walled spherical glass-bubble. The diffracted intensity of MoKα X-ray radiation was measured at 25 ± 1 °C from the surface of the solutions in the same way as described previously.[20]

No decomposition could be observed during the measurements, but a brown precipitate was slowly formed after a few weeks exposure to daylight.

DATA TREATMENT

The Crystal Data. The reduction to scaled F_o values was performed as described previously,[21]
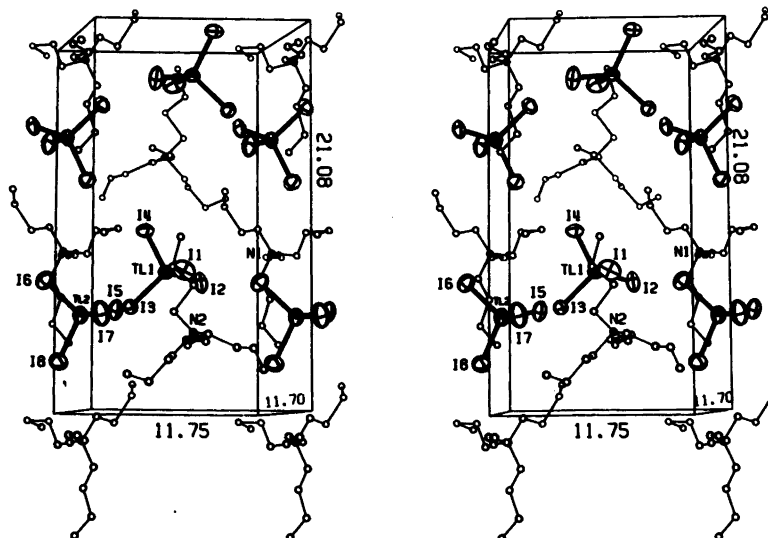

Fig. 1. A stereoscopic view of the monoclinic unit cell of $[N(C_4H_9)_4]$ $[TlI_4]$, showing the packing of the complex ions. The size of the thermal ellipsoids corresponds to 40 % probability, but all C and N atoms have for clarity been given the isotropic parameter value $U = 0.013$ Å^2. The lengths of the unit cell edges are given in Å.

Table 1. Final fractional atomic positional parameters for the heavy atoms. Estimated standard deviations are given in parentheses.

Atom	x	y	z
Tl1	0.4855(2)	0.6240(1)	0.7113(2)
I1	0.5216(4)	0.6280(2)	0.4834(3)
I2	0.6879(3)	0.6447(2)	0.8612(3)
I3	0.3188(3)	0.7164(2)	0.7328(3)
I4	0.3942(3)	0.5102(2)	0.7589(4)
Tl2	0.9841(2)	0.7574(1)	0.2111(2)
I5	0.1767(3)	0.7383(2)	0.3650(3)
I6	0.8232(3)	0.6680(2)	0.2424(3)
I7	0.0385(3)	0.7593(3)	0.9920(4)
I8	0.8931(3)	0.8763(2)	0.2606(4)

using computer programs and scattering factors from the same sources. The semi-empirical absorption correction method[22a] was applied, the linear

absorption coefficient was 100.3 cm^{-1}. The largest relative variation in the transmission factors was from 1 to 0.71.

The positions of the heavy atoms were found by direct methods applied on the non-centrosymmetrical space group $P2_1$. An isotropic least-squares refinement of their parameters gave $R = 0.14$ ($R_w = 0.20$).* Successive Fourier maps and refinements revealed possible positions of all nitrogen and carbon atoms. However, for some of the carbon atoms (mostly terminal ones) refinement of their parameters led to unreasonable bond lengths and angles to neighbouring atoms, and they were therefore kept constant ($U = 0.10$ Å^2) at the values obtained from the Fourier maps. The least-squares refinements were made using the Gauss-Seidel blocked method and were based on a minimization of

* Definitions in Ref. 21.

Table 2. Final anisotropic thermal parameters with estimated standard deviations in parentheses. The expression used is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl1	0.084(1)	0.061(1)	0.083(1)	0.000(1)	0.013(1)	0.005(1)
I1	0.183(4)	0.146(4)	0.056(2)	0.026(3)	0.009(2)	0.019(2)
I2	0.061(2)	0.176(4)	0.117(3)	0.008(2)	0.014(2)	−0.035(3)
I3	0.074(2)	0.078(2)	0.149(3)	0.005(2)	0.002(2)	−0.010(2)
I4	0.129(3)	0.069(2)	0.149(4)	−0.015(3)	0.015(3)	0.015(2)
Tl2	0.064(1)	0.099(1)	0.071(1)	−0.002(1)	0.005(1)	0.003(1)
I5	0.064(2)	0.142(3)	0.088(2)	−0.012(2)	0.001(2)	0.018(2)
I6	0.088(2)	0.104(3)	0.085(2)	−0.016(2)	−0.010(2)	0.013(2)
I7	0.102(3)	0.194(5)	0.110(3)	0.016(3)	0.035(2)	0.019(3)
I8	0.096(3)	0.093(3)	0.161(4)	0.001(2)	−0.009(2)	−0.043(3)

Table 3. Some interatomic distances in Å and angles in degrees. Estimated standard deviations are given in parentheses.

Tl1 − I1	2.760(4)[a]	2.791(4)[b]	I1 − Tl1 − I2	111.7(1)[a]
Tl1 − I2	2.779(4)	2.804(4)	I1 − Tl1 − I3	106.0(1)
Tl1 − I3	2.797(4)	2.811(4)	I1 − Tl1 − I4	110.2(1)
Tl1 − I4	2.718(4)	2.741(4)	I2 − Tl1 − I3	112.4(1)
			I2 − Tl1 − I4	109.6(1)
			I3 − Tl1 − I4	107.0(1)
Tl2 − I5	2.712(4)	2.723(4)	I5 − Tl2 − I6	109.6(1)
Tl2 − I6	2.730(4)	2.738(4)	I5 − Tl2 − I7	109.9(1)
Tl2 − I7	2.730(5)	2.757(5)	I5 − Tl2 − I8	107.5(1)
Tl2 − I8	2.818(4)	2.840(5)	I6 − Tl2 − I7	113.3(1)
			I6 − Tl2 − I8	107.3(1)
			I7 − Tl2 − I8	109.1(1)

[a] Non-corrected values. [b] Corrected for thermal motion assuming the I atom to ride on the Tl atom.

$\Sigma w\{|F_o|-|F_c|\}^2$, including reflexions with $|F_o|>$ 3.92 $\sigma(F_o)$. The weighting function used was $w=1/\{\sigma^2(F_o)+(0.03\ F_o)^2\}$ which gave $S=1.64$.*

The final cycle (187 parameters, the heavy atoms anisotropic, ten atoms not refined) led to $R=0.054$ ($R_w=0.071$) for 2046 independent reflexions. The largest shift for any parameter was less than 0.3 of its estimated standard deviation.

The probable absolute configuration was established by comparing the R_w values for the two possible enantiomers ($R_w=0.075$ for the other configuration) according to Hamilton.[22b] The two highest residual peaks in the final difference Fourier map were of height 1.0 e Å^{-3} and corresponded to alternative positions of two terminal carbon atoms. No hydrogen atoms were located.

The final parameter values of the heavy atoms are listed in Tables 1 and 2. Calculated bond lengths and angles in the two TlI$_4$ units are given in Table 3.** The thermal motion correction was performed using the algorithm described in Ref. 22c.

The Solution Data. The data treatment was essentially carried out as described before.[20] An additional empirical correction for the intensity loss in the glass bubble was made by measuring intensities from a standard solution within and without the glass bubble. The corrected experimental intensities were normalized to a stoichiometric unit of volume

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* Definitions in Ref. 21.
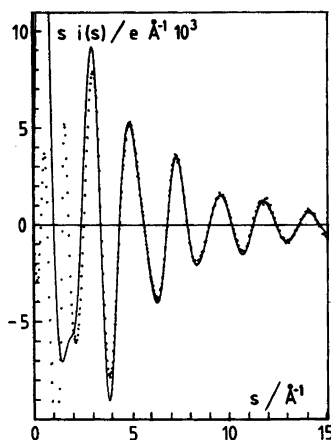** Full listings of parameter values and structure factors are available from the authors on request.

Fig. 2. A comparison (see text) of experimental (dots) and calculated (line) reduced intensities, multiplied by s, for the 0.77 M $[\mathrm{N(C_5H_{11})_4}]\mathrm{TlI_4}$ solution in dichloromethane.
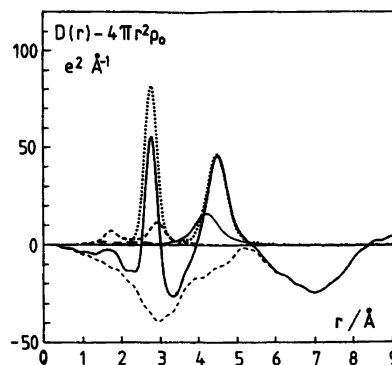

Fig. 3. The experimental difference distribution function, $D(r)-4\pi r^2\rho_o$, is represented by the heavy solid line. Calculated peak-shapes corresponding to interactions within TlI$_4^-$ (dotted line), CH$_2$Cl$_2$ molecules (short dashes), N(C$_5$H$_{11}$)$_4^+$ (long dashes), and to the estimated I$-$C interactions (solid line), are subtracted from the experimental curve to give the lower dashed line.

V containing one thallium atom. The reduced intensity curve, $i_{obs}(s)$ multiplied by s, is shown in Fig. 2. By a Fourier transformation the radial distribution curve was obtained, Fig. 3. The modification function used was $M(s)=\{f_{Tl}^2(0)/f_{Tl}^2(s)\}$ exp $\{-0.008\ s^2\}$ where f is the scattering factor and the scattering variable is $s=(4\pi/\lambda)\sin\theta$.

For each type of distinct intramolecular interaction between atoms p and q, its contribution to the reduced intensity was calculated according to eqn. (1), where the scattering factors have been corrected for anomalous dispersion effects.

$$i_{calc}(s)=$$
$$n_{pq}f_p(s)f_q(s)\ \frac{\sin sr_{pq}}{sr_{pq}}\ \exp\left(-\tfrac{1}{2}l_{pq}^2 s^2\right) \tag{1}$$

In the high-angle region where the intramolecular part of the scattered reduced intensity dominates,[20] least-squares refinements could be performed of the three parameters r_{pq} (the distance), n_{pq} (the number of distances per Tl atom), and l_{pq}^2 (the mean-square variation in the distance) within the Tl$-$I species. The intramolecular contributions from the solvent molecules CH$_2$Cl$_2$ and from the (C$_5$H$_{11}$)$_4$N$^+$ cations were calculated using values from crystal structures[23,24] and mean amplitudes from electron diffraction studies of related compounds.[25]
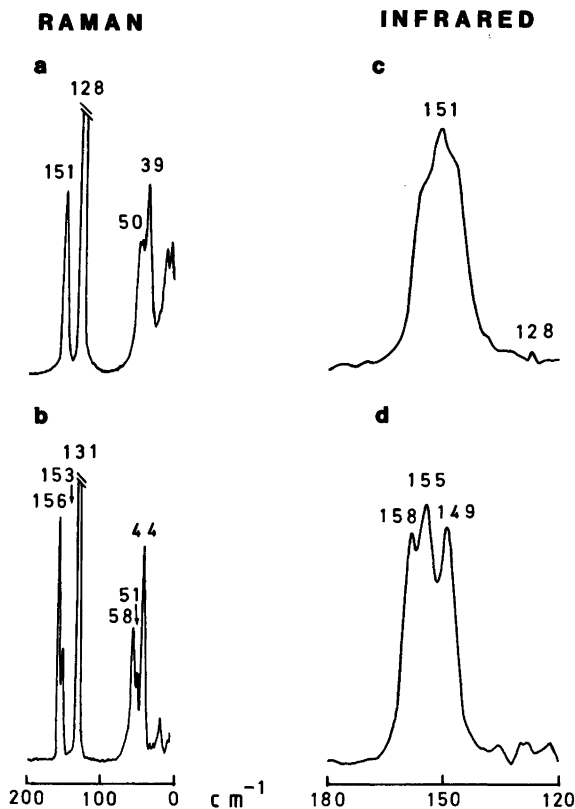
RAMAN   **INFRARED**

Fig. 4. IR and Raman spectra of solid $[N(C_4H_9)_4][TlI_4]$: (a) Raman at 293 K, (b) Raman at *ca.* 100 K, (c) IR at 293 K, (d) IR at *ca.* 100 K.

RESULTS AND DISCUSSION

The Crystal Structure. The two crystallographically independent TlI_4^--entities in the asymmetric part of the unit cell are in contact in the x-direction (Fig. 1) forming zig-zag chains surrounded by the tetrabutylammonium ions. The closest intermolecular contacts between the TlI_4 groups are I4−I8 4.379(5) Å (4.437)* and I3−I5 4.409(5) Å (4.455)*. Several I−C distances occur around 3.9 Å.

The Tl−I bond lengths range from 2.712 (2.723)** to 2.816 (2.840)** Å, Table 3, which agrees well with previously reported values, 2.734−2.774 Å.[11] The symmetry is approximately tetrahedral with I−Tl−I angles between 106.0(1) to 112.4(1)°.

The two different tetrabutylammonium ions show some signs of disorder, as mentioned above, and do

not give precise atomic positions. The average bond lengths obtained are C−N 1.57 and C−C 1.58 Å, and the average angles N−C−C, C−N−C, and C−C−C are all equal 109(3)°.

Vibrational Spectra of Solid $[N(C_4H_9)_4][TlI_4]$. Although spectra of this [12a] and some related solid salts [12b] have been reported previously, the Raman spectrum obtained at room temperature (Fig. 4a) shows low wavenumber features more clearly than hitherto. The spectrum appears to be in agreement with the predictions for an isolated regular tetrahedral ion with four fundamentals 151 (T_2), 128 (A_1), 50 (T_2) and 39 (E) cm^{-1}. However, the Tl−I stretching feature observed in the i.r. shows distinct shoulders (Fig. 4c) resulting from irregularity as observed in the crystal structure and consequent removal of degeneracy.

On cooling to liquid nitrogen temperature the effects of the asymmetry become much more distinct

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* Corrected for thermal motion assuming independent motion.
** Corrected for thermal motion assuming I to ride on Tl.

in the IR spectrum and are now clearly seen in the Raman spectrum (Figs. 4d and 4b).

Full factor group analysis for the $P2_1$ space-group[26] predicts there will be 16 Tl−I stretching modes active in both IR and Raman spectra. If correlation forces are negligible, the number might be expected to reduce to 8, four for each type of $[TlI_4]^-$ anion. Of course, because the distortions from tetrahedral regularity are not very large a relationship to the spectrum of a T_d anion is to be expected; thus the nature of the lowest wavenumber stretching co-ordinates will closely resemble that of the A_1 mode of the T_d system and although the Raman spectrum is dominated by a very intense band at 128 cm^{-1} (130.8 cm^{-1} in the low temperature spectrum) only a very weak infrared-active counterpart is detected (Figs. 4a−4c). Even at a resolution of 0.5 cm^{-1} no splitting of this Raman band into two features derived from the distinct types of $[TlI_4]^-$ is observed.

The three Tl−I stretching features in the IR spectrum are observed at 158.1, 154.6, and 149.3 cm^{-1}, but only two Raman bands are seen in the same region (at 156.5 and 153.0 cm^{-1}). Although the wavenumbers of the Raman bands do not coincide exactly with any of the IR bands they do presumably relate to similar normal co-ordinates. The point of particular interest is that the Raman feature relating to one of the components derived from the T_2 mode of the T_d ion is absent. In an ion of C_{2v} symmetry this effect could be rationalised in terms of a destructive Fermi resonance between the A_1 symmetric and asymmetric stretching modes if both have significant intrinsic intensity in both IR and Raman spectra.[27] This could result in the lower wavenumber A_1 feature having very high Raman intensity but very low i.r. intensity, with the high wavenumber A_1 mode showing the reverse intensity behaviour. In the present case, however, all modes are of the same symmetry species. Therefore, it is not clear to us why there should be such a marked intensity partitioning between two of the modes considering an individual $[TlI_4]^-$ ion. We note, however, that $[NBu_4][InI_4]$ shows identical behaviour.[28]

In the deformation region of the low-temperature Raman spectrum we presume that 57.8 and 51.2 cm^{-1} are deformations derived from T_2 and that 44.0 cm^{-1} is related to the E mode of a regular ion; unfortunately we were unable to obtain i.r. spectra of sufficient quality for meaningful comparison in this wavenumber range.

The Solution Structure. The radial distribution curve (*Fig. 3*) shows a minor peak at about 1.7 Å, mainly due to intramolecular C−Cl interactions in the CH_2Cl_2 molecules, and two major peaks at 2.78 and 4.5 Å. By comparison with the crystal structure, and in agreement with vibrational spectra[14] the latter are identified as being essentially due to Tl−I and I−I interactions, respectively. Their parameters have been refined by least-squares methods and a summary of the results is given in Table 4. In order to give a more realistic error estimate, including effects of systematic errors, the standard deviations given are increased to account also for the variation obtained in the parameter values when various s-intervals of the intensity data were used for the refinements.

Column A in *Table 4* gives the result from refinements without any intermolecular interactions included. The Tl−I distance obtained, 2.775(3) Å, corresponds closely to the average value from the crystal structure, 2.756[2.776]* Å. The number of Tl−I and I−I distances is also consistent with a tetrahedral structure. For regular tetrahedral symmetry, however, the expected I−I distance should be $\sqrt{8/3} \times r(Tl-I) = 4.532(5)$ Å. The value obtained for this refined model, 4.491(5) Å, is significantly shorter.

However, the non-coordinating solvent promotes the formation of ion-pairs. In the crystal structure,

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* Corrected for thermal motion assuming riding motion of I versus Tl. Note that an uncorrected distance r_{pq} is obtained as $|\langle \mathbf{r}_q \rangle - \langle \mathbf{r}_p \rangle|$ in a crystal structure determination, but as $|\langle \mathbf{r}_q - \mathbf{r}_p \rangle|$ for a solution (the brackets denote mean values and $\mathbf{r}$ denotes a vector). When comparing bond lengths from solution studies with interatomic distances from crystal structures, the latter should therefore be corrected for thermal motion effects.

Table 4. Parameter values (see text) obtained by least-squares refinement for the TlI_4^- complex ion in solution. The estimated standard deviations are given in parentheses.

Interaction	Parameter values	A	B
Tl−I	r (Å)	2.775(3)	2.771(3)
	n	3.9(1)	4.0(1)
	l^2 (Å^2)	0.0062(5)	0.0072(5)
I−I	r (Å)	4.491(5)	4.53(1)
	n	6.0(5)	6 (fixed)
	l^2 (Å^2)	0.040(4)	0.038(4)

Table 5. Bond lengths in Å for some d^{10} ions in octahedral hexaaqua complexes and in tetrahedral tetrahalocomplexes. The crystal structure values marked with (*) are corrected for thermal riding motion. The solvent is water except for TlI$_4^-$. Values for which references are not given are quoted from Ref. 32.

	[M(H$_2$O)$_6$]		[MCl$_4$]		[MBr$_4$]		[MI$_4$]	
	Crystal	Solution	Crystal	Solution	Crystal	Solution	Crystal	Solution
Tl(III)	*2.23(2)[33]	2.235(5)[16]	*2.433(3)[7]	2.43(1)[6]	*2.554(3)[8]	2.564(2)[16]	*2.776	2.771(3)
Hg(II)	*2.349(6)	2.41(1)	2.46$_4$	2.47(1)	2.58$_7$	2.610(5)	2.77 – 2.78	2.785(3)
Cd(II)	2.28[34]	2.292(5)[35]	2.45$_4$[36]	–	2.588(2)[45]	–	*2.790(3)[37]	2.790(3)[30]
Zn(II)	2.08[38]	2.093(15)[39]	2.25[40]	2.29(1)[41]	2.39[42]	2.40(1)[41]	2.60$_5$[43]	–

there are on the average six I – C distances shorter than 4.5 Å (13 less than 5 Å) for each iodine atom. Assuming six I – C distances at 4.5 Å with an estimated variation $l = 0.2$ Å, *cf.* eqn. (1), to occur in the solution, another set of refinements was performed (Table 4, column B). The ratio $r(I-I)/r(Tl-I) = 1.635$ (4) then obtained corresponds closely to the tetrahedral value 1.633. This is consistent with the vibrational spectra of [N(C$_5$H$_{11}$)$_4$]TlI$_4$ in dichloromethane solution, which displayed a single symmetrical stretching band: at 153 cm^{-1} in IR (after solvent subtraction) and at 130 cm^{-1} in Raman.[14]

The parameter values in Table 4, column B, have been used in a calculation of reduced intensities, $i_{calc}(s)$. Together with the constant contributions from the solvent as mentioned above, these values are compared with the experimental values in Fig. 2. The agreement is satisfactory in the high-angle regions ($s > 5$ Å) used in the refinements.

Peak shapes, calculated by Fourier transformation of the $i_{calc}(s)$ values, are subtracted from the distribution curve in Fig. 3. The difference curve is relatively smooth, without any sharp peaks. The broad feature remaining between 4 to 6 Å is mostly due to the solvent structure,[29] but probably also to distances from the ion-pair formation, not accounted for in the model.

Comparisons with other d^{10} *ions.* The root-mean-square variation in the distances (Table 4, column B) $l(Tl-I)$ 0.085(3) Å and $l(I-I)$ 0.20(1) Å, are comparable to the corresponding values obtained by X-ray diffraction for HgI$_4^{2-}$, 0.10(1) and 0.24(2) Å,[20] and for CdI$_4^{2-}$, 0.084(7) and 0.19(1) Å.[30] Calculated vibrational amplitudes from spectroscopic data are of the same magnitude, for HgI$_4^{2-}$ 0.070 and 0.195 Å, and for CdI$_4$ 0.075 and 0.190 Å,[31] respectively. In Table 5, a comparison is made of bond lengths in the tetrahalo complex ions of Tl(III), Hg(II), Cd(II), and Zn(II), and in their octahedral

hexaaqua complexes. It is interesting to note that the metal-ligand bond lengths for the tetraiodo complexes of Tl(III), Hg(II) and Cd(II) are virtually equal, although there is a marked difference in their hydrates, reflecting the different acceptor properties of the cations.[44] The very soft acceptor Hg^{2+} forms markedly longer bonds with the hard donor H$_2$O, than the less soft Tl^{3+} ion does. The Cd^{2+} ion has an intermediate character, which is discernible also for the tetrachloride complexes.

The relative decrease in bond length when the softness of the ligand decreases from the soft donor I$^-$ to the hard H$_2$O is, as expected, most pronounced for the hardest acceptor Zn^{2+}.

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