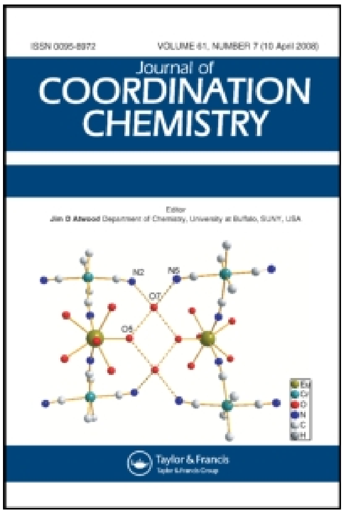

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The effect of MX anions (M = Al, Ga, In, Tl; X = Cl, Br, I) on the structures of their tetra-*N*-butylammonium salts

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THE EFFECT OF MX_4^- ANIONS (M = Al, Ga, In, Tl; X = Cl, Br, I) ON THE STRUCTURES OF THEIR TETRA-*N*-BUTYLAMMONIUM SALTS

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In order to study the effect of MX_4^- anions on the structures of $Bu_4N[MX_4]$ salts (M = Al, Ga, In, Tl; X = Cl, Br, I) the crystal structures of $Bu_4N[AlBr_4]$ (**1**), $Bu_4N[TlCl_4]$ (**2**) and $Bu_4N[TlBr_4]$ (**3**) have been determined by single-crystal X-ray diffraction. The three salts crystallize in the orthorhombic system, the space group *P*nna, $Z = 4$. The cell dimensions are: (**1**) $a = 18.624(11)$, $b = 11.724(8)$, $c = 11.679(7)$ Å, $V = 2549.9$ Å^3; (**2**) $a = 18.473(12)$, $b = 1.680(8)$, $c = 11.548(3)$Å, $V = 2491.6$ Å^3 and (**3**) $a = 18.656(7)$, $b = 11.918(8)$, $c = 11.804(5)$ Å, $V = 2624.5$ Å^3. The structures consist of distorted tetrahedral MX_4^- anions and Bu_4N^+ cations. In the tetrahedral $AlBr_4^-$, $TlCl_4^-$ and $TlBr_4^-$ anions there are always two pairs of M–X distances: 2.25(1), 2.29(1); 2.391(4), 2.395(5); and 2.531(2), 2.537(3) Å, respectively. Comparison of the existing data on the structures of $Bu_4N[MX_4]$ salts shows that: (1) for each group 13 element from Al to Tl the significantly greater increase in M–X distance on passing from Br to I than from Cl to Br results in a change of symmetry from *Pnna* to $P2_1/n$ and in a greater distortion of the tetrahedron; (2) the increase in the M–X distance when Br is substituted for Cl, or I for Br, is independent of M, which suggests that for a given X atom the character of the M–X bond is the same, irrespective of the central M atom.

Keywords: Tetra-*n*-butylammonium salts; Tetrabromoaluminate(III); Tetrachlorothallate(III), Tetrabromothallate(III); X-ray crystal structure analysis

INTRODUCTION

In our previous papers the salts $Bu_4N[InI_4]$ [1], $Bu_4N[GaCl_4]$, $Bu_4N[GaBr_4]$ and $Bu_4N[GaI_4]$ [2] were structurally characterized and compared with the tetra-*n*-butylammonium salts of $InCl_4^-$, $InBr_4^-$ [3] and TlI_4^- [4]. The comparison of the data has shown that when iodide is substituted for bromide or for chloride in the MX_4^- anion the symmetry of the space group decreases from *Pnna* to $P2_1/n$. We have also found that the decrease in symmetry is accompanied by a greater distortion of the $[MX_4]$ tetrahedron. Therefore, the major objective in this study was to examine whether the correlation between the size of the MX_4^- anion, space group and distortion is generally valid, and can also be observed for the $Bu_4N[TlX_4]$ and $Bu_4N[AlX_4]$ salts. It was also important to know whether the change in the M–X distance on substituting Br for Cl,

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or I for Br, depended on M, which could provide information on a possible effect of the central metal atom on the bond character. Another objective was to collect more data on the M–X distances in the MX_4^- complexes formed by the group 13 elements. The whole of the data will make it possible to check whether the M–X distances show the so-called secondary periodicity, which is an important feature of p-block elements [5]. To achieve these goals in this paper we have studied the structures of the $Bu_4N[AlBr_4]$, $Bu_4N[TlCl_4]$ and $Bu_4N[TlBr_4]$ salts. The X-ray data on the tetra-*n*-butylammonium salts of $TlCl_4^-$ and $TlBr_4^-$ reported in ref. [6] contain only information on the space group and cell dimensions but not on the Tl–X distances.

EXPERIMENTAL

Preparation of $Bu_4N[TlCl_4]$, $Bu_4N[TlBr_4]$ and $Bu_4N[AlBr_4]$

The $Bu_4N[TlCl_4]$ and $Bu_4N[TlBr_4]$ salts were prepared from trihalides and Bu_4NX ($X = Cl$, Br) [6]. The trihalides were obtained in reactions between the respective thallous salt and an excess of chlorine or bromine in acetonitrile. To a solution of TlX_3 in acetonitrile a stoichiometric amount of tetra-*n*-butylammonium chloride or bromide was added. To induce crystallization a 1:1 mixture of acetone and ethanol was added, which after two weeks yielded prismatic crystals. Like $Bu_4N[TlI_4]$ crystals [4], they were stable in air. The $Bu_4N[AlBr_4]$ salt was prepared by sintering stoichiometric amounts of $Bu_4N[GaBr_4]$ and Al at 150°C for three days. After cooling in a desiccator, the reaction product was dissolved in a 1:1 mixture of dichloromethane and methanol. The solution, left to crystallize for one day, yielded light-orange prismatic crystals, stable in air.

X-ray Studies

The reflections for all compounds were measured at room temperature on a KUMA KM4 (Mo Kα radiation) four-circle diffractometer operating in the ω–2θ mode. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections (average $18 < 2\theta < 30$). Two standard reflections monitored every 200 reflections remained constant throughout every data collection process. All reflections were processed using profile analysis and were corrected for Lorentz and polarization effects. An absorption correction based on a ψ-scan was applied. In the case of each salt two atoms in the anion were located by the Patterson method. The two atoms in the TlX_4^- salts were thallium and chlorine or bromine and in the $AlBr_4^-$ salt aluminum and bromine. The remaining atoms were found by successive Fourier syntheses. However, using difference Fourier maps we could not determine the positions of all hydrogen atoms. Therefore, the hydrogen atoms were located using standard geometrical criteria and were restrained to be bound to C-atoms with the C–H distance of 0.97 Å in the CH_2 group and 0.96 Å in the CH_3 group. Final refinement was carried out on positional parameters of all atoms, with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. The structure was refined by the full-matrix least-squares method on F^2. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (\mathrm{Max}(F_o^2) + 2F_c^2)/3$ and A, B are the refined parameters listed in Table I. Calculations were carried out using the

TABLE I Crystal data and structure refinement details for $Bu_4N[TlCl_4]$ and $Bu_4N[TlBr_4]$

Empirical formula	$C_{16}H_{36}NCl_4Tl$	$C_{16}H_{36}NBr_4Tl$
Formula weight	588.54	766.13
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorombic	orthorombic
Space group	*Pnna*	*Pnna*
Unit cell dimensions (Å)	$a = 18.473(12)$ $b = 11.680(8)$ $c = 11.548(3)$	$a = 18.656(7)$ $b = 11.918(8)$ $c = 11.804(5)$
Volume (Å^3)	$V = 2491.61$	$V = 2624.53$
Z	4	4
Calculated density (g cm^{-3})	1.569	1.94
μ (MoKα) (mm^{-1})	6.91	12.24
F(000)	1152	1440
Crystal dimensions (mm)	0.5 × 0.4 × 0.35	0.45 × 0.3 × 0.3
Max 2θ for data collection (°)	53.34	49.97
Index range	$0 \leq h \leq 22$ $0 \leq k \leq 14$ $0 \leq l \leq 14$	$0 \leq h \leq 21$ $0 \leq k \leq 14$ $0 \leq l \leq 14$
No. of measured reflections	889	924
No. of unique reflections	876	920
No. of reflections with $F_o > 4\sigma(F_o)$	876	562
R_{int}	0.017	0.0892
Method of structure solution and refinement	Patterson method and least squares on F^2	
No. of parameters refined	103	103
Goodness-of-fit on F^2	1.128	1.099
Final $R1$ [$F_o > 4\sigma(F_o)$]	0.0396	0.0295
Final $wR2$ index (for all unique reflections)	0.1069	0.0931
Absorption correction	experimental ψ-scan	
Largest diff. peak and hole (e Å^{-3})	0.96 and −0.47	0.22 and −0.23
Weight parameters (A, B)	0.0687, 5.3757	0.0458, 0.0664
Mean shift/esd	0.015	0.004

SHELXL97 program [7]. The crystal structure of $Bu_4N[AlBr_4]$ could not be satisfactorily solved, because we were not able to attain the final $wR2$ index smaller than 0.2554, hindering exact location of C, N and H atoms but with less influence on the location of atoms in the tetrahedron, which show an average Br–Al–Br angle of 109.67°. However, we found that the compound crystallizes in the orthorhombic space group *Pnna*, $Z = 4$ and the a, b, c parameters are: 18.624(11), 11.724(8), 11.679(7) Å and $V = 2549.9$ Å^3. The Al–Br distances are discussed below. Listings of observed and calculated structure factors and anisotropic thermal parameters are available from the authors on request.

Table I shows crystal and refinement data for tetra-*n*-butylammonium salts of $TlCl_4^-$ and $TlBr_4^-$. Table II shows the positional and equivalent isotropic displacements, while interatomic distances and bond angles are shown in Tables III and IV. Figure 1 shows the $Bu_4N[TlCl_4]$ molecule (which is isostructural with the $Bu_4N[TlBr_4]$ molecule) with the atom numbering scheme.

DISCUSSION

The X-ray crystal structure analysis shows that the $Bu_4N[TlCl_4]$ and $Bu_4N[TlBr_4]$ salts crystallize in the same orthorhombic system, space group *Pnna*. The unit cell a, b, c parameters of these two compounds reported in ref. [3] from oscillation and precession

TABLE II Fractional atomic coordinates and equivalent isotropic displacement (Å^2) for Bu$_4$N[TlCl$_4$] and Bu$_4$N[TlBr$_4$]

Atom	x	y	z	U_{eq}
T(1)	0.59323(4)	0.75(0)	0.75(0)	0.0980(4)
Cl(1)	0.6654(2)	0.9036(3)	0.6764(4)	0.124(1)
Cl(2)	0.5209(4)	0.8296(6)	0.9021(5)	0.217(3)
N	0.5629(7)	0.25(0)	0.75(0)	0.071(3)
C(11)	0.6117(7)	0.1737(9)	0.824(1)	0.077(3)
C(12)	0.6613(7)	0.231(1)	0.908(1)	0.090(4)
C(13)	0.7051(9)	0.147(1)	0.975(1)	0.116(5)
C(14)	0.754(1)	0.189(2)	1.062(2)	0.15(1)
C(21)	0.5174(7)	0.176(1)	0.675(1)	0.085(4)
C(22)	0.4591(8)	0.102(1)	0.733(1)	0.103(4)
C(23)	0.4193(9)	0.032(1)	0.642(2)	0.126(6)
C(24)	0.359(1)	−0.032(2)	0.687(2)	0.19(1)
Tl	0.5944(1)	0.25(0)	0.25(0)	0.1105(4)
Br(1)	0.6699(1)	0.4062(1)	0.3328(2)	0.1339(7)
Br(2)	0.5214(2)	0.3422(3)	0.0944(3)	0.242(2)
N	0.5602(8)	0.75(0)	0.25(0)	0.092(4)
C(11)	0.6082(9)	0.672(1)	0.176(2)	0.107(5)
C(12)	0.6549(9)	0.732(1)	0.089(1)	0.108(5)
C(13)	0.701(1)	0.645(2)	0.026(2)	0.156(8)
C(14)	0.750(1)	0.692(3)	−0.054(3)	0.19(1)
C(21)	0.5165(9)	0.676(1)	0.325(1)	0.095(4)
C(22)	0.4587(8)	0.610 (1)	0.268(2)	0.115(5)
C(23)	0.413(1)	0.545(2)	0.358(2)	0.18(1)
C(24)	0.354(1)	0.479(3)	0.297(3)	0.22(1)

TABLE III Bond lengths (Å) and bond angles (°) for Bu$_4$N[TlCl$_4$]

Tl–Cl(1)	2.391(4)	Cl(1)–Tl–C1(2)	106.3(2)
Tl–Cl(2)	2.395(5)	Cl(1)–Tl–C1(2)^{I}	110(1)
N–C(11)	1.53(1)	Cl(1)–Tl–C1(1)^{I}	112.2(2)
N–C(21)	1.49(2)	Cl(2)–Tl–C1(2)^{I}	112.1(4)
C(11)–C(12)	1.49(2)	Cl(1)–N–C(21)	109(1)
C(12)–C(13)	1.48(2)	Cl(1)–N–C(21)^{II}	110(1)
C(13)–C(14)	1.45(2)	C(11)–N–C(11)^{II}	108(1)
C(21)–C(22)	1.54(2)	C(21)–N–C(21)^{II}	111(1)
C(22)–C(23)	1.53(2)	N–C(11)–C(12)	118(1)
C(23)–C(24)	1.43(2)	N–C(21)–C(22)	118(1)
		C(11)–C(12)–C(13)	112(1)
		C(12)–C(13)–C(14)	119(2)
		C(21)–C(22)–C(23)	109(1)
		C(22)–C(23)–C(24)	113(2)

Symmetry codes: $^{I}x, -y+3/2, -z+3/2$; $^{II}x, -y+1/2, -z+3/2$.

photographs are, within the reported error of 0.1%, equal to ours, and the space group is the same. Comparison of our data for the orthorhombic Bu$_4$N[TlCl$_4$] and Bu$_4$N[TlBr$_4$] salts with those reported for the monoclinic Bu$_4$N[TlI$_4$] [4] salt shows that the unit cell volume increases from 2491.6 Å^3 for TlCl$_4^-$ to 2624.5 Å^3 for TlBr$_4^-$ and then to 2866.8 Å^3 for the TlI$_4^-$ salt. The much greater increase in the volume difference between the iodide and bromide than between the bromide and chloride salts results in a change from the orthorhombic *Pnna* to the monoclinic $P2_1/n$ space group. The same correlation between symmetry and the volume occupied by the Bu$_4$N[MX$_4$] molecule, equal to V/Z, has also been observed for the respective gallium

TABLE IV Bond lengths (Å) and bond angles (°) for Bu$_4$N[TlBr$_4$]

Tl–Br(1)	2.531(2)	Br(1)–Tl–Br(2)	105.1(1)
Tl–Br(2)	2.537(3)	Br(1)–Tl–Br(2)^{I}	109.8(1)
N–C(11)	1.56(2)	Br(1)–Tl–Br(1)^{I}	112.3(1)
N–C(21)	1.49(2)	Br(2)–Tl–Br(2)^{I}	115.0(2)
C(11)–C(12)	1.52(2)	C(11)–N–C(21)	107(1)
C(12)–C(13)	1.54(2)	C(11)–N–C(21)^{II}	109(1)
C(13)–C(14)	1.42(3)	C(11)–N–C(11)^{II}	110(2)
C(21)–C(22)	1.49(2)	C(21)–N–C(21)^{II}	114(2)
C(22)–C(23)	1.57(3)	N–C(11)–C(12)	115(1)
C(23)–C(24)	1.53(3)	N–C(21)–C(22)	116(1)
		C(11)–C(12)–C(13)	110(1)
		C(12)–C(13)–C(14)	114(2)
		C(21)–C(22)–C(23)	110(2)
		C(22)–C(23)–C(24)	109(2)

Symmetry codes: $^{I}x,\ -y+1/2,\ -z+1/2$; $^{II}x,\ -y+3/2,\ -z+1/2$.

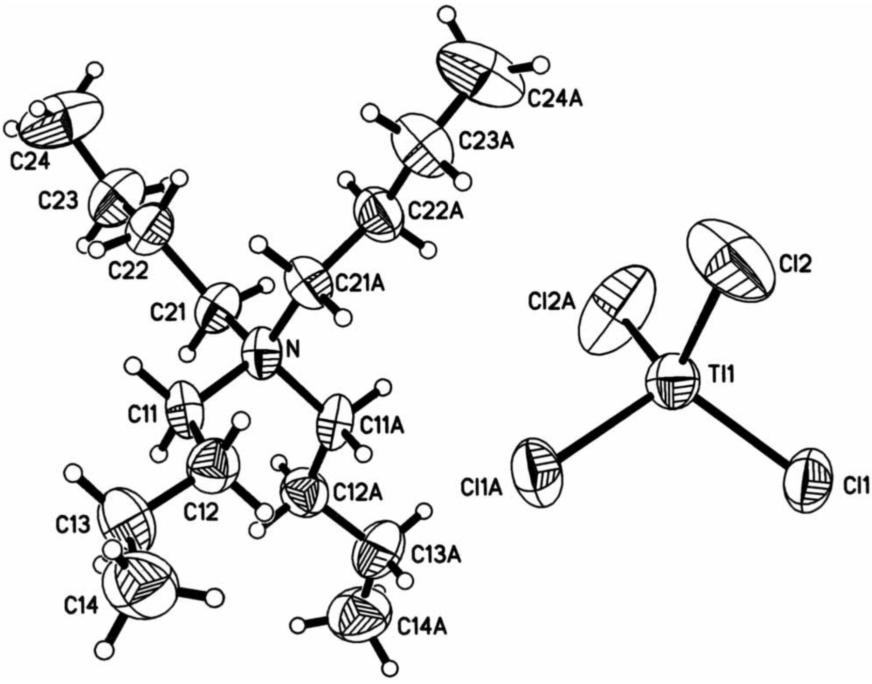

FIGURE 1 The molecular structure of Bu$_4$N[TlCl$_4$] with the atom numbering scheme.

[2] and indium [1,3] salts. As pointed out in the previous paragraph the refinement of the structure of Bu$_4$N[AlBr$_4$] was not satisfactory. However, the cell volume of 2549.9 Å^3 is correct and there is no doubt that Bu$_4$N[AlBr$_4$] crystallizes in the orthorhombic *Pnna* space group. This result and the data for the monoclinic Bu$_4$N[AlI$_4$] salt [8] show that, as for gallium, indium and thallium salts, substitution of the larger iodide for bromide in the AlX$_4^-$ ion results in a change from orthorhombic *Pnna* to monoclinic $P2_1/n$ space group.

The structures of the $Bu_4N[TlCl_4]$, $Bu_4N[TlBr_4]$, $Bu_4N[TlI_4]$ and $Bu_4N[AlBr_4]$ salts consist of tetrahedral Bu_4N^+ cations and more or less distorted tetrahedral MX_4^- anions. The cations in the first three salts have almost the same structures. The average C–C and N–C distances in the chloride and bromide salts are equal to 1.50 and 1.52 Å, respectively. The corresponding distances in the iodide salt are 1.58 and 1.57 Å. In the first two salts the average C–C–C, N–C–C and C–N–C angles are equal to 111.5, 117 and 110°, respectively. In the iodide salt all three angles are equal to 109°.

The anions in the $Bu_4N[TlX_4]$ and $Bu_4N[AlX_4]$ salts show more significant differences. In the orthorhombic $Bu_4N[TlCl_4]$ and $Bu_4N[TlBr_4]$ salts there are two pairs of identical distances: 2.391(4), 2.395(5) Å and 2.531(2), 2.537(3) Å, respectively. On the other hand, in the monoclinic $Bu_4N[TlI_4]$ salt the larger complex anion displays four different M–I distances: 2.748(2), 2.752(2), 2.764(1) and 2.770(2) Å [4]. As expected for the *Pnna* group the $AlBr_4^-$ anion shows two pairs of identical distances 2.25(1) and 2.29(1) Å, whereas in the monoclinic $Bu_4N[AlI_4]$ salt there are four different Al–I distances equal to 2.506(8), 2.523(8), 2.528(7) and 2.532(7) Å. In spite of poor refinement, the Al–Br distances seem to be reliable within the reported accuracy. It can be concluded from the data shown in Table V that when bromine is substituted for chlorine, and iodine for bromine the increase in the average M–X distance is 0.138 and 0.234 Å, respectively. For each substitution the increase is independent of the metal atom within ±0.01 Å, which suggests that in the range from Al to Tl the character of the M–X bond remains essentially the same. In spite of many attempts we were not able to synthesize the tetrabutylammonium salt of $AlCl_4^-$. However, the known structure of the monoclinic $H_2PMe_2[AlCl_4]$ salt shows two sets of four different Al–Cl distances [9], with the average Al–Cl distance equal to 2.127 Å. When the average difference between the M–Br and M–Cl distances (0.138 Å) is added to this value one gets for the average Al–Br distance 2.265 Å, which is almost the same as that obtained from direct measurements. It should be noted that the average Al–Cl distance in the $AlCl_4^-$ salts of Li^+, Na^+, K^+, Cs^+, NO^+ and $NH_4{}^+$, equal to 2.126 Å [10], does not significantly differ from that in $H_2PMe_2[AlCl_4]$, showing that the effect of the cation, at least in the $AlCl_4^-$ salts, is negligible. The comparison of the M–X distances in the $Bu_4N[MX_4]$ salts (Table V) shows that the difference between the longest and the shortest M–X distance is, in general, greater in the iodide salts than in the chloride and bromide salts. The large, in comparison with other orthorhombic salts, difference between the two pairs of distances in $AlBr_4^-$ may be the result of poor refinement. The average X–X distance in the $[TlX_4]$ tetrahedron increases from 3.906 to 4.136 and to 4.505 Å for the chloride, bromide and iodide salts, respectively. In each case it differs only slightly from the distance calculated for a regular tetrahedron with the center-to-vertex distance equal to the average M–X distance.

The crystal data show that the anions are surrounded by five nearest Bu_4N^+ cations, which occupy the corners of a distorted trigonal bipyramid. In the orthorhombic $TlCl_4^-$ and $TlBr_4^-$ salts there are two pairs of M–N distances equal to 5.867(2), 6.454(6) and to 5.993(2), 6.568(7) Å, respectively. The fifth distance is equal to 6.352(13) and 6.445(15) Å, and the average distance is equal to 6.199 Å for the tetrachloride and 6.313 Å for the tetrabromide salt. In the monoclinic TlI_4^- salt all Tl–N distances are different, ranging from 5.973 to 8.001 Å. These results show that, as in the case of gallium [2] and indium salts [1,3], the arrangement of the Bu_4N^+ cations in the iodide salt differs from that in the chloride and bromide salts. They also confirm our previous conclusion

TABLE V Crystal data for Bu_4N [MX_4] salts

MX_4^-	*Space group*	V (Å^3)	M–X (Å)^a	M–N (Å)^{a,b}	*Ref.*
$AlCl_4^{-c}$	$P2_1/c$	2031.0	2.127(3) (av.)		[9]
$AlBr_4^-$	*Pnna*	2549.9	2.25(1) 2.29(1)		This work
AlI_4^-	$P2_1/n$	2805.0	2.506(8) 2.523(8) 2.528(7) 2.532(7)	5.957(24) 7.970(24)	[8]
$GaCl_4^-$	*Pnna*	2445.2	2.163(2) 2.174(2)	5.795(5) 6.370(7)* 6.409(5)	[2]
$GaBr_4^-$	*Pnna*	2565.0	2.297(2) 2.316(3)	5.925(3) 6.362(17)* 6.550(8)	[2]
GaI_4^-	$P2_1/n$	2803.3	2.537(2) 2.539(2) 2.549(2) 2.554(2)	5.990(8) 7.943(9)	[2]
$InCl_4^-$	*Pnna*	2483	2.345(3) 2.355(3)	5.854(2) 6.380(9)* 6.433(4)	[3]
$InBr_4^-$	*Pnna*	2621	2.479(2) 2.479(2)	5.981(2) 6.425(17)* 6.574(8)	[3]
InI_4^-	$P2_1/n$	2854.7	2.695(2) 2.699(2) 2.704(1) 2.709(1)	6.008(9) 7.988(10)	[1]
$TlCl_4^-$	*Pnna*	2491.6	2.391(4) 2.395(5)	5.867(2) 6.352(14)* 6.455(6)	This work
$TlBr_4^-$	*Pnna*	2624.5	2.531(2) 2.537(3)	5.993(2) 6.445(15)* 6.569(7)	This work
TlI_4^-	$P2_1/n$	2866.8	2.748(2) 2.752(2) 2.764(1) 2.770(2)	5.973(12) 8.001(13)	[4]

For all tetra-*n*-butylammonium salts there are four moieties per unit cell.

[a] In the orthorhombic salts there are two pairs of identical M–X and two pairs of identical M–N distances; *denotes the fifth M–N distance.

[b] In the monoclinic salts there are five different M–N distances. Only the shortest and the longest distance are presented in the table.

[c] H_2PMe_2 [$AlCl_4$].

that lower symmetry of the salt and greater distortion of the tetrahedron are accompanied by a much larger range of the M–N distances and vice versa.

Comparison of all available data on the structures of the $Bu_4N[MX_4]$ salts where M is a group 13 element from Al to Tl and X = Cl, Br, I (see Table V), leads to the following conclusions:

1. The tetrachloride and tetrabromide salts crystallize in the orthorhombic space group *Pnna*, whereas the tetraiodide salts crystallize in the monoclinic $P2_1/n$ space group.

The main reason for the change in the symmetry is the considerably greater increase in the volume of the MX_4^- anion when iodide is substituted for bromide, than when bromide is substituted for chloride. The increase in the volume of the anion is accompanied by an almost twice as large (average) increment in the unit cell volumes of the $Bu_4N[MX_4]$ salts on passing from Br to I ($\Delta V = 238\,\text{Å}^3$) than on passing from Cl to Br ($\Delta V = 130\,\text{Å}^3$).

2. In each salt the MX_4^- anion is surrounded by five nearest Bu_4N^+ cations, which occupy corners of a distorted trigonal bipyramid. In the orthorhombic salts there are two pairs of identical distances and one different distance. In the monoclinic salts all five distances are different and show significantly greater dispersion.
3. In the MCl_4^- and MBr_4^- anions there are always two statistically different pairs of identical M–X distances. On the other hand, in the MI_4^- anions there are four different M–I distances. Greater distortion of the tetrahedron is accompanied by a much larger range of M–N distances. That is because the positive charge located mainly on the central nitrogen atom in the Bu_4N^+ cation acts on the positively charged M atom and on the negatively charged X atom in the MX_4^- anion, the stronger interaction gives a smaller M–N distance and vice versa.
4. The increase in the M–X distance when bromide is substituted for chloride or iodide for bromide is almost independent of the central metal atom, in spite of the increase in electronegativity and size of M from Al to Tl. This suggests that for a given X the character of the M–X bond in the MX_4^- complexes is the same for each M atom.

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