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The Structures of Tetra-*n*-butylammonium Salts of $InCl_4^-$, $InBr_4^-$, $InBrCl_3^-$ and $InBr_3Cl^-$

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Abstract

The crystal structures of $[N(n\text{-}C_4H_9)_4][InCl_4]$ (I), $[N(n\text{-}C_4H_9)_4][InBrCl_3]$ (II), $[N(n\text{-}C_4H_9)_4][InBr_3Cl]$ (III), and $[N(n\text{-}C_4H_9)_4][InBr_4]$ (IV) have been determined by X-ray analysis which showed that the four structures are isomorphous, with the orthorhombic space group *Pnna* and $Z = 4$. The cell dimensions are: (I) $a = 18{\cdot}479$ (5), $b = 11{\cdot}657$ (3), $c = 11{\cdot}525$ (3) Å, $V = 2483$ (1) Å^3; (II) $a = 18{\cdot}524$ (5), $b = 11{\cdot}715$ (4), $c = 11{\cdot}575$ (4) Å, $V = 2512$ (1) Å^3; (III) $a = 18{\cdot}650$ (4), $b = 11{\cdot}860$ (3), $c = 11{\cdot}745$ (2) Å, $V = 2598$ (1) Å^3; (IV) $a = 18{\cdot}676$ (3), $b = 11{\cdot}905$ (2), $c = 11{\cdot}787$ (3) Å, $V = 2621$ (1) Å^3. (Final $R = 0{\cdot}057$, $0{\cdot}060$, $0{\cdot}049$ and $0{\cdot}053$ for 1165, 768, 711 and 691 observed reflections respectively.) Each structure consists of four-coordinate InX_4^- or InX_3Y^- anions ($X \neq Y =$ Cl, Br) which have distorted-tetrahedral or C_{2v} symmetry, and $[N(n\text{-}C_4H_9)_4]^+$ cations. The InX_3Y^- anions are disordered and the odd halogen atom is assumed to have 25% occupancy on all four coordination sites.

Introduction

A recent paper from this laboratory (Drake, Hencher, Khasrou, Tuck & Victoriano, 1980) described the preparation of tetra-*n*-butylammonium salts of InX_3Y^- and $InX_2Y_2^-$ anions ($X \neq Y =$ Cl, Br, I) by the oxidation of the appropriate salts of $In_2X_6^{2-}$ or InX_2^- with halogen (Y_2). Vibrational spectra served to identify the products as individual complexes, rather than the appropriate mixture of InX_4^- and InY_4^- complexes, and also permitted the calculation of force constants for the various vibrational modes. A later study of the solution chemistry of these and related anionic complexes by ^{115}In NMR spectroscopy (McGarvey, Trudell, Tuck & Victoriano, 1980) showed that rapid ligand-redistribution reactions occur in non-aqueous solutions, although the parent $InX_nY_{4-n}^-$ salt is again obtained on crystallization.

These mixed-halide complexes are unusual in that they give rise to stable crystalline solids, and a series of single-crystal structure determinations has now been carried out with the aim of obtaining the bond lengths and angles. The only directly comparable analogues are the corresponding thallium(III) complexes, for which X-ray powder experiments were reported for the series $TlBr_nI_{4-n}^-$ (n = 0–4) (Matthews & Walton, 1968), and a study of $[N(n\text{-}C_4H_9)_4][GaBrCl_3]$, which on the basis of cell volume is said to be structurally similar to $[N(n\text{-}C_4H_9)_4][TlCl_4]$ (Efremov, Grigor'ev, Spiridonov & Mikheeva, 1974). In the event, the present work gave the desired structural details for the $InCl_4^-$ and $InBr_4^-$ salts, but disorder prevented the measurement of the individual In—X and In—Y bond lengths for $InBrCl_3^-$ and $InBr_3Cl^-$.

Experimental

Preparative

The tetra-*n*-butylammonium salts of $InCl_4^-$ and $InBr_4^-$ were prepared by crystallizing ethanol solutions of InX_3 + $[N(n\text{-}C_4H_9)_4]X$ (Gislason, Lloyd & Tuck, 1971). The mixed-halide species were obtained by oxidizing indium(II) complexes (Drake *et al.*, 1980).

X-ray studies

Additional crystal data (see also *Abstract*) and refinement data for the compounds, labelled (I)–(IV), are summarized in Table 1, from which it is clear that all four compounds display similar crystal morphologies.

In each determination, a colourless acicular crystal was mounted along the largest dimension, which was subsequently shown to be the *b* axis, and data were collected with a Syntex $P2_1$ diffractometer following the procedure described previously (Khan, Steevensz, Tuck, Noltes & Corfield, 1980). The intensities of three monitor reflections did not change significantly during the data-collection process for compounds (I), (III), and (IV), and decreased by 5% for (II). In each case, the appropriate scaling factor was applied during the data reduction. The space group *Pnna* (No. 52) was determined from the systematic absences ($0kl$, $k + l = 2n + 1$; $h0l$, $l + h = 2n + 1$; $hk0$, $h = 2n + 1$). The data were corrected for Lorentz and polarization effects, and analytical absorption corrections were applied.

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The similar crystal morphologies and cell dimensions, and the identity of the space group suggested that all four compounds have isomorphous crystal structures, and this was confirmed by the final refinements.

Table 1. *Summary of crystal data, intensity collections and structural refinement for* $N(C_4H_9)_4^+$ *salts of* $InCl_4^-$, $InBr_4^-$, $InBrCl_3^-$ *and* $InBr_3Cl^-$

	$InCl_4^-$ (I)	$InBrCl_3^-$ (II)	$InBr_3Cl^-$ (III)	$InBr_4^-$ (IV)
M_r	499·1	543·6	632·5	676·9
D_o (g cm^{-3})	1·34	1·42	1·62	1·71
D_c (g cm^{-3})	1·335	1·437	1·617	1·716
$F(000)$	1024	1096	1240	1312
Crystal dimensions (mm)	0·42 × 0·24 × 0·22	0·49 × 0·13 × 0·14	0·49 × 0·26 × 0·23	0·51 × 0·22 × 0·17
μ (cm^{-1})	13·7	28·2	55·7	69·3
Min./max. absorption correction	1·31/1·35	1·28/1·46	2·82/3·43	2·58/3·24
Radiation (λ = 0·71069 Å)		Mo $K\alpha$		
Number of reflections measured ($2\theta_{max.}$ = 50°)	2520	2550	3296	2653
Number observed [$I > 3\sigma(I)$]	1165	768	711	691
$R = (\sum\Delta/\sum\lvert F_o\rvert)$	0·057	0·060	0·049	0·053
$R_w = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$	0·069	0·069	0·054	0·057
(Shift/e.s.d.)$_{max}$	0·02	0·03	0·06	0·04
$\Delta\rho_{max}$ (e Å^{-3})	0·39	0·59	0·45	0·52

The cell dimensions for $[N(n\text{-}C_4H_9)_4][InBrCl_3]$ are similar to those reported for the analogous gallium compound (Efremov, Grigor'ev, Spiridonov & Mikheeva, 1974).

The first structure to be solved was that of $[N(n\text{-}C_4H_9)_4][InBr_3Cl]$ (III). A three-dimensional Patterson map revealed that the In position is on a twofold axis, which requires Br and Cl to be symmetrically equivalent and hence means that the orientations of the $InBr_3Cl^-$ ions are disordered. In the Patterson map, two peaks initially attributed to In—X vectors differed in height by approximately 40%, and we therefore tentatively identified the higher peak as being from sites of pure In—Br vector, and the lower peaks as arising from the disordered sites. In fact, the Patterson maps for compounds (I) and (IV) also showed this same pattern of differing peak heights, so that this explanation was rejected. Further analysis centred on three models: (i) 50% Br, 50% Cl for $X(1)$; (ii) 50% Br, 50% Cl for $X(2)$; (iii) 75% Br, 25% Cl; of these, model (iii) gave significantly the best refinement. Similarly, the best refinement for the $InBrCl_3^-$ salt (II) was obtained with a 75% Cl, 25% Br model. We therefore conclude that for (II) and (III) the disorder in

Table 2. *Final fractional coordinates* (×10^4) *and* U_{eq} *values* (Å^2 ×10^3)

Standard deviations are in parentheses. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	(I)				(II)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
In	920·3 (5)	2500	2500	84 (1)	927 (1)	2500	2500	86 (1)
$X(1)$*	1636 (2)	996 (2)	1788 (3)	113 (2)	1647 (2)	988 (3)	1757 (3)	117 (3)
$X(2)$*	207 (3)	1731 (4)	4004 (3)	194 (3)	218 (3)	1691 (5)	4004 (5)	207 (4)
N	4373 (5)	2500	2500	60 (3)	4386 (9)	2500	2500	63 (6)
C(11)	3899 (5)	1728 (6)	3278 (6)	75 (3)	3891 (7)	1696 (11)	3295 (11)	68 (7)
C(12)	3393 (5)	2344 (7)	4089 (8)	85 (4)	3385 (9)	2314 (15)	4104 (12)	98 (7)
C(13)	2954 (6)	1434 (8)	4774 (9)	113 (4)	2972 (10)	1386 (13)	4753 (14)	105 (8)
C(14)	2451 (7)	1946 (11)	5636 (10)	121 (4)	2462 (11)	1837 (19)	5614 (15)	129 (9)
C(21)	4826 (4)	3255 (6)	3280 (7)	76 (4)	4831 (8)	3285 (11)	3302 (11)	70 (8)
C(22)	5404 (5)	3960 (8)	2635 (8)	94 (4)	5411 (9)	3942 (14)	2684 (15)	97 (8)
C(23)	5817 (6)	4701 (10)	3561 (9)	125 (4)	5808 (10)	4625 (18)	3640 (18)	121 (9)
C(24)	6438 (7)	5292 (12)	3106 (14)	154 (4)	6400 12)	5304 (27)	3185 (21)	178 (10)

	(III)				(IV)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
In	935 (1)	2500	2500	88 (1)	936 (1)	2500	2500	81 (1)
$X(1)$	1677 (1)	971 (2)	1704 (2)	102 (2)	1677 (1)	968 (2)	1692 (2)	103 (2)
$X(2)$	207 (2)	1642 (3)	4014 (3)	204 (4)	200 (2)	1634 (3)	4016 (3)	213 (3)
N	4387 (9)	2500	2500	69 (8)	4376 (9)	2500	2500	54 (8)
C(11)	3923 (8)	1715 (12)	3256 (12)	77 (8)	3935 (8)	1724 (15)	3259 (13)	76 (9)
C(12)	3450 (8)	2343 (15)	4115 (14)	93 (9)	3442 (9)	2319 (16)	4117 (15)	83 (9)
C(13)	3002 (10)	1403 (14)	4754 (16)	110 (10)	2993 (10)	1413 (15)	4724 (16)	97 (9)
C(14)	2517 (11)	1922 (21)	5672 (16)	141 (11)	2515 (13)	1917 (25)	5673 (18)	133 (10)
C(21)	4842 (8)	3260 (12)	3305 (11)	73 (8)	4836 (8)	3283 (12)	3296 (13)	70 (8)
C(22)	5427 (9)	3931 (14)	2648 (18)	104 (9)	5410 (8)	3944 (16)	2636 (18)	95 (9)
C(23)	5816 (10)	4630 (18)	3612 (17)	127 (10)	5816 (11)	4630 (20)	3624 (18)	120 (11)
C(24)	6435 (13)	5232 (22)	3159 (24)	168 (11)	6410 (14)	5270 (23)	3162 (27)	151 (11)

* X is Cl for (I), 75% Cl, 25% Br for (II), 75% Br, 25% Cl for (III), and Br for (IV).

Table 3. *Interatomic distances* (Å) *with e.s.d.'s in parentheses*

	(I)	(II)	(III)	(IV)
In—X(1)*	2·345 (3)	2·378 (3)	2·465 (2)	2·479 (2)
In—X(2)*	2·355 (3)	2·377 (5)	2·458 (3)	2·479 (3)
N—C(11)	1·54 (1)	1·61 (2)	1·55 (2)	1·53 (2)
N—C(21)	1·51 (1)	1·55 (2)	1·56 (2)	1·58 (2)
C(11)—C(12)	1·51 (1)	1·51 (2)	1·53 (2)	1·54 (2)
C(12)—C(13)	1·55 (1)	1·53 (2)	1·58 (2)	1·54 (2)
C(13)—C(14)	1·49 (2)	1·47 (2)	1·54 (2)	1·55 (3)
C(21)—C(22)	1·54 (1)	1·50 (2)	1·56 (2)	1·54 (2)
C(22)—C(23)	1·57 (1)	1·55 (2)	1·58 (3)	1·61 (3)
C(23)—C(24)	1·44 (2)	1·45 (3)	1·46 (3)	1·45 (3)

* X is Cl for (I), 75% Cl, 25% Br for (II), 75% Br, 25% Cl for (III), and Br for (IV).

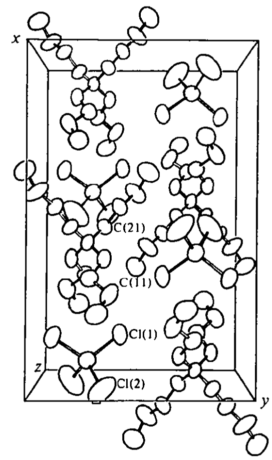

Fig. 1. Packing of $N(n\text{-}C_4H_9)_4^+$ and InX_4^- ions.

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II)	(III)	(IV)
X(1)—In—X(2)	106·8 (1)	106·1 (2)	106·3 (1)	106·3 (1)
X(1)—In—X(2)*	110·1 (2)	110·0 (2)	109·9 (2)	109·8 (2)
X(1)—In—X(1)*	111·3 (2)	111·8 (2)	111·7 (1)	112·2 (1)
X(2)—In—X(2)*	111·9 (3)	113·0 (4)	112·9 (2)	112·6 (2)
C(11)—N—C(21)	108·0 (4)	108·0 (7)	107·7 (7)	107·6 (8)
C(11)—N—C(11)*	110·9 (9)	110·3 (13)	112·1 (16)	114·8 (16)
C(11)—N—C(21)*	108·7 (9)	107·5 (15)	107·7 (15)	106·5 (15)
C(21)—N—C(21)*	112·7 (9)	115·5 (15)	114·1 (15)	114·0 (15)
N—C(11)—C(12)	115·8 (6)	115·4 (11)	114·0 (12)	115·4 (13)
C(11)—C(12)—C(13)	108·4 (7)	106·0 (14)	105·9 (14)	107·9 (16)
C(12)—C(13)—C(14)	113·1 (8)	113·6 (15)	111·2 (16)	112·1 (18)
N—C(21)—C(22)	114·1 (6)	113·6 (10)	112·2 (12)	112·3 (12)
C(21)—C(22)—C(23)	107·6 (7)	105·3 (14)	103·6 (15)	102·8 (14)
C(22)—C(23)—C(24)	113·8 (10)	112·4 (17)	111·0 (19)	110·8 (19)

* Atoms at positions x, $0{\cdot}5 - y$, $0{\cdot}5 - z$.

the anions is at all four sites, and that the lower peaks in the Patterson map are due to the unusually large thermal motion of those atoms. Scattering factors (including the anomalous-dispersion terms for the heavy atoms) were taken from Ibers & Hamilton (1974).

Each structure was refined anisotropically by full-matrix least-squares methods, the function $\sum w(|F_o| - |F_c|)^2$ being minimized. Unit weights were used in the initial stages of refinement, while in the final cycles of calculation a weighting scheme of the form $w = \{1/[\sigma^2(F) + pF^2]\}$ was employed, with a final p value of 0·01 in each case. Convergence to the final R values was achieved in six to ten cycles. H atoms were not visible in the final difference maps and no attempt was made to include them. The refinement data for compounds (I)–(IV) are summarized in Table 1. The final coordinates and the standard deviations are given in Table 2* and the important interatomic distances and angles are in Tables 3 and 4. Fig. 1 shows the packing.

All calculations were made on the Amdhal computer at the Wayne State University or the IBM 3031 computer at the University of Windsor. Programs used include *ORFLS* [structure factor calculations and full-matrix least-squares refinement by Busing, Martin & Levy (1962)], *ABSORB* (analytical absorption correction by D. Templeton and L. Templeton), *ORTEP* (Johnson, 1965), and *SHELX*77 [full-matrix least-squares refinement and Fourier synthesis by Sheldrick (1977)].

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36440 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

Structures of $InCl_4^-$ *and* $InBr_4^-$

The most directly comparable previous work is that on $[NEt_4][InCl_4]$ (Trotter, Einstein & Tuck, 1969) in which the anion has C_{3v} symmetry with reported In—Cl bond lengths of 2·30 (2) and 2·36 (3) Å, in good agreement with the more accurate values of 2·345 (3) and 2·355 (3) Å now found for compound (I). The Cl—In—Cl angles also agree within experimental error. The only other comparable indium(III) anionic species is $CH_3InCl_3^-$, in which the In—Cl bond lengths are 2·409 (3), 2·394 (3) and 2·397 (4) Å (Guder, Schwartz, Weidlein, Widler & Hausen, 1976), demonstrating a significant lengthening (~0·05 Å) consequent upon the substitution of a methyl group for one chloride.

The structure of $InBr_4^-$ confirms previous spectroscopic work which identified this as a tetrahedral ion in solution (Woodward & Bill, 1955) and solid (Gislason, Lloyd & Tuck, 1971). Taken together with an earlier determination of the structure of InI_4^- (Einstein & Tuck, 1970), the results give a reliable set of In—X bond lengths for the three InX_4^- anions: $InCl_4^-$

2·350 (2) (present work), $InBr_4^-$ 2·479 (2) (present work),* InI_4^- 2·71 (1) Å (Einstein & Tuck, 1970). As might be expected, these values show a monotonic relation with such parameters as ligand electronegativity, stretching force constant, *etc.*

Structures of $InBrCl_3^-$ *and* $InBr_3Cl^-$

It is unfortunate that the disorder problem noted above prevented the measurement of the individual In—Br and In—Cl bond lengths in these complexes. The bond lengths in Table 3 do not permit any analysis of possible changes in the In—Cl or In—Br bonds between (say) $InCl_4^-$ and $InBrCl_3^-$. From the average values for the In—Cl bond distance in (I) [2·350 (2) Å] and the In—Br bond in (IV) [2·479 (2) Å], the weighted mean distances for $InBrCl_3^-$ and $InBr_3Cl^-$ are calculated as 2·382 and 2·447 Å respectively, values which are not significantly different from the observed In—X distances in these ions. There are no significant changes in bond angles within the series of anions studied. In addition to the disorder problem the large thermal parameters noted earlier must serve to obscure any structural differences which might exist.

Tetra-n-butylammonium cations

Given the large estimated standard deviations in bond lengths and angles (Tables 3 and 4), there are no significant differences in corresponding C—C or C—N bonds in the cations in the four compounds studied, and we conclude that the cations are essentially identical in structure in each of the salts. The thermal parameters are again large, and the whole structure is clearly undergoing considerable vibrational motion at the temperature of the study (~298 K).

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* This value supersedes the preliminary figure of 2·442 Å quoted in a previous publication (Khan & Tuck, 1981).

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