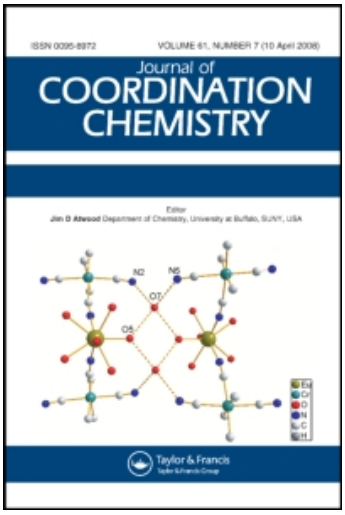

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THE CRYSTAL STRUCTURE OF TETRA-n-BUTYLAMMONIUM TETRAIODOINDATE(III)

K. RUDAWSKA, H. PTASIEWICZ-BĄK* and S. SIEKIERSKI

Institute of Nuclear Chemistry and Technology, ul. Dorodna 16, 03-195 Warszawa, Poland

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The crystal structure of tetra-n-butylammonium tetraiodoindate(III) $Bu_4N[InI_4]$ has been determined by x-ray diffraction. The crystal is monoclinic, the space group $P2_1/n$, $Z=4$ and the cell dimensions are: $a=11.699(2)$, $b=20.994(4)$, $c=11.745(2)$ Å, $V=2854.7$ Å^3. Final $R1=0.0338$ for 1673 observed reflections. The structure consists of distorted tetrahedral InI_4^- anions and Bu_4N^+ cations. In the tetrahedral anion there are four In–I distances: 2.695(2), 2.699(2), 2.704(1) and 2.709(1) Å. Comparison with published data on other tetrahaloindates has shown that the average In–X distance increases with decreasing size of the cation, and that distortion of the tetrahedron in the $Bu_4N[InX_4]$ salts is accompanied by decreasing symmetry of the space group from Pnna to $P2_1/n$.

Keywords: Tetra-n-butylammonium tetraiodoindate(III); X-ray crystal structure; Ligand effect

INTRODUCTION

In 1982 Khan and Tuck [1] described structures of tetra-n-butylammonium salts of $InCl_4^-$, $InBrCl_3^-$, $InBr_3Cl^-$ and $InBr_4^-$. In spite of increasing size of the anion all compounds crystallize in the orthorhombic space group Pnna. The calculated In–X distance in the anion increases from an average of 2.350 in $InCl_4^-$ to 2.479 Å in $InBr_4^-$. In the $InCl_4^-$ anion there are two pairs of distances differing by 0.01 Å, while the four In–Br distances were found to be equal. The In–I distance in the tetrahedral InI_4^- anion is known from

*Corresponding author. Tel.: 4822 811 0656, Fax: 4822 811 1532, e-mail: bptas@orange. ichtj. waw.pl

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measurements on $In[InI_4]$ salt (space group Pnna). In this compound there are two distances of 2.711(1) and 2.717(1) Å [2]. A similar distance of 2.71 Å was found for the monoclinic space group C2/c $[InI_2(Me_2SO)_4]$ $[InI_4]$ salt [3]. Comparison of the two salts of InI_4^- suggests that a change from orthorhombic to monoclinic may be related to increasing size of the cation. Therefore, it was interesting to know whether further increase in the size of the InX_4^- anion when iodine is substituted for bromine would also result in decreased symmetry, and whether such a decrease would be accompanied by distortion of the $[InI_4]$ tetrahedron. To answer these questions we have studied the structure of the tetra-n-butylamonium salt of InI_4^- and compared it with the structure of tetra-n-butylamonium salts of $InCl_4^-$ and $InBr_4^-$.

EXPERIMENTAL

Preparation of $Bu_4N[InI_4]$

In the first stage indium(III) iodide was prepared by reaction of indium foil with stoichiometric amounts of iodine in xylene [4]. To a xylene solution of InI_3 a stoichiometric amount of tetra-n-butylammonium iodide was added. The suspension was warmed with stirring till the formation of a yellow oil. After the reaction mixture was allowed to cool to room temperature the oil yielded a yellow solid which according to analysis was $Bu_4N[InI_4]$. In order to get crystals suitable for x-ray analysis the suspension in xylene was warmed to about 60°C and a small amount of chloroform was added. The solution was then left for crystallization that yielded prismatic crystals stable in air.

X-ray Studies

The reflections were collected at room temperature on a KUMA KM4 (MoK_α radiation) four-circle diffractometer operating in $\omega - 2\theta$ mode. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections ($15 < 2\theta < 25$). Two standard reflections were monitored every 200 reflections. The intensities of the two monitored reflections did not change during data-collection. Reflections were processed using profile analysis and were corrected for Lorentz and polarization effects. Absorption correction based on ψ-scan was applied. Most non-hydrogen atoms *i.e.*, the anion atoms, the nitrogen atom and almost all carbon atoms in the cation were found by the Patterson method. The few remaining carbon atoms were found by successive Fourier syntheses. However, using difference Fourier maps we could not determine positions of all hydrogen atoms. Therefore,

hydrogen atoms were located using standard geometrical criteria and restrained to be bound to C-atoms with the C—H distance of 0.97 Å. Final refinement was carried out on positional parameters of all atoms, 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: $w = I/[\sigma^2(F_o^2) + (A * P)^2 + B * P]$, where $P = (Max(F_o^2) + 2F_c^2)/3$ and A, B are refined parameters listed in Table I. Calculations were carried out using the SHELXL97 program [5]. Listings of observed and anisotropic thermal parameters are available from the authors on request.

Table I shows crystal and refinement data, Table II the positional and thermal parameters, while interatomic distances and bond angels are shown in Table III. Figure 1 shows the molecule with the atom number and Figure 2 gives the stereoscopic view of the crystal structure.

TABLE I Crystal data and structure refinement details for $Bu_4N[InI_4]$

Empirical formula	$C_{16}H_{36}NI_4In$
Formula weight	864.4
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	$a = 11.699(2)$ (Å) $b = 20.994(4)$ (Å) $c = 11.745(2)$ (Å) $\beta = 98.27(3)(^\circ)$
Volume	$V = 2854.7(Å^3)$
Z	4
Calculated density	2.012 g cm^{-3}
μ (MoKα)	5.15 mm^{-1}
F(000)	1600
Crystal dimensions (mm)	$0.1 \times 0.5 \times 0.5$
Max 2θ for data collection	50.02(°)
Index range	$-13 \leq h \leq 13,\ -24 \leq k \leq 0,\ 0 \leq 1 \leq 13$
No. of measured reflections	2638
No. of reflections with $F_o > 4\sigma(F_o)$	1673
R_{int}	0.0168
Method of structure solution	Patterson method
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	203
Goodness-of-fit on F^2	1.113
Final R1 [$F_o > 4\sigma(F_o)$]	0.0338
Final wR2 index [for all 2514 unique reflections]	0.1052
Absorption correction	experimental ψ-scan
Min. and max. transmission factors	0.639, 0.867
Largest diff. peak and hole	0.66e/$Å^3$ and -0.72e/$Å^3$
Weight parameters (A, B)	0.0596, 0.00
Mean shift/esd	0.022

TABLE II Fractional atomic coordinates and equivalent isotropic displacement ($Å^2$) for $Bu_4N[InI_4]$

Atom	*x*	*y*	*z*	*Ueq*
In	0.46333(8)	0.81737(5)	1.23497(7)	0.0751(3)
I2	0.48997(9)	0.72743(5)	1.07549(8)	0.0977(4)
I3	0.61159(9)	0.79780(6)	1.42962(8)	0.1070(4)
I4	0.24364(9)	0.81550(7)	1.2803(1)	0.1328(5)
I1	0.5114(1)	0.93140(5)	1.1459(1)	0.1197(4)
N	0.3614(8)	0.8636(5)	0.7256(8)	0.074(3)
C32	0.583(1)	0.8708(6)	0.759(1)	0.099(4)
C33	0.685(1)	0.8780(9)	0.846(2)	0.127(6)
C21	0.351(1)	0.9200(6)	0.645(1)	0.098(4)
C31	0.476(1)	0.8696(7)	0.808(1)	0.084(4)
C11	0.264(1)	0.8627(7)	0.799(1)	0.098(4)
C22	0.232(2)	0.927(1)	0.571(1)	0.141(7)
C12	0.242(2)	0.9202(9)	0.864(2)	0.129(6)
C13	0.146(2)	0.909(1)	0.935(2)	0.18(1)
C34	0.800(2)	0.882(1)	0.809(2)	0.20(1)
C23	0.243(3)	0.988(2)	0.493(3)	0.28(2)
C41	0.362(1)	0.8028(7)	0.660(1)	0.088(4)
C42	0.383(1)	0.7430(7)	0.725(1)	0.095(4)
C43	0.366(2)	0.6844(8)	0.650(2)	0.126(6)
C44	0.386(2)	0.6231(9)	0.710(2)	0.162(9)
C14	0.138(2)	0.958(1)	1.016(3)	0.22(1)
C24	0.150(6)	1.011(2)	0.455(4)	0.46(5)

TABLE III Bond lengths (Å) and bond angles (°) for $Bu_4N[InI_4]$

In-I3	2.695(2)	13-In-I4	110.22(5)
In-I4	2.699(2)	13-In-I1	108.61(5)
In-I1	2.704(1)	14-In-I1	110.25(5)
In-I2	2.709(1)	13-In-I2	110.87(4)
N-C41	1.49(2)	14-In-I2	109.49(5)
N-C21	1.52(1)	I1-In-I2	107.36(5)
N-C11	1.51(2)	C41-N-C21	110(1)
N-C31	1.54(2)	C41-N-C11	110(1)
C31-C32	1.45(2)	C41-N-C31	109(1)
C32-C33	1.47(2)	C21-N-C11	111(1)
C33-C34	1.47(2)	C21-N-C31	108(1)
C21-C22	1.53(2)	C11-N-C31	107(1)
C22-C23	1.58(3)	C22-C21-N	115(1)
C23-C24	1.22(6)	C32-C31-N	118(1)
C11-C12	1.47(2)	C12-C11-N	119(1)
C12-C13	1.51(2)	C42-C41-N	118(1)
C13-C14	1.42(3)	C31-C32-C33	112(1)
C41-C42	1.47(2)	C21-C22-C23	105(2)
C42-C43	1.51(2)	C11-C12-C13	111(2)
C43-C44	1.47(2)	C14-C13-C12	113(2)
		C24-C23-C22	112(4)
		C41-C42-C43	113(1)
		C44-C43-C42	116(2)

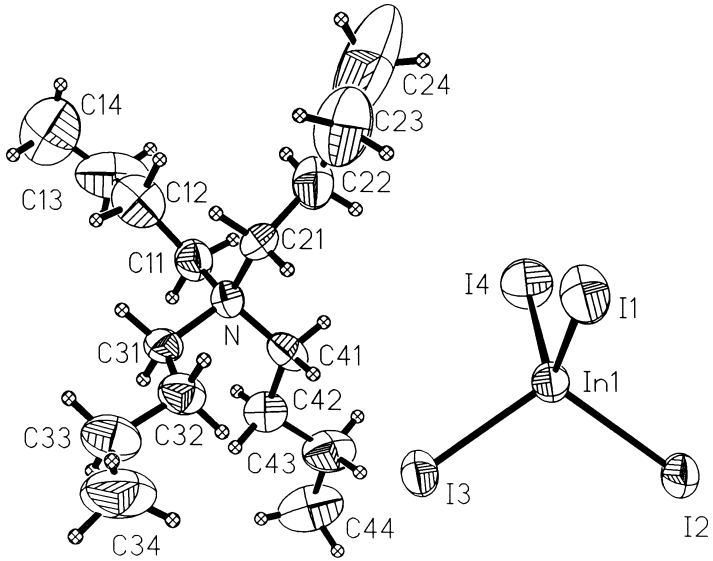

FIGURE 1 The molecular structure of $Bu_4N[InI_4]$ with the atomic numbering scheme.

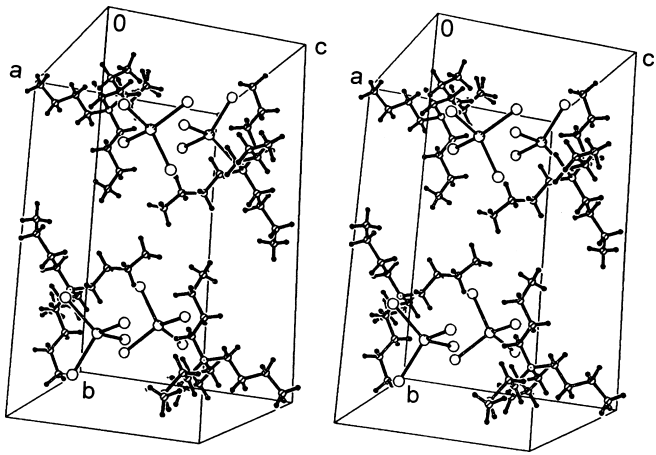

FIGURE 2 Stereoscopic picture of crystal structure of $Bu_4N[InI_4]$.

DISCUSSION

The results show that the $Bu_4N[InI_4]$ salt crystallizes in the monoclinic space group $P2_1/n$, in contrast to $Bu_4N[InCl_4]$ and $Bu_4N[InBr_4]$ which crystallize

in the orthorhombic Pnna space group. However, in each case there are four moieties per unit cell. Comparison with the published data [1] shows that the unit cell volume increases from 2483 Å^3 for $InCl_4^-$ to 2621 Å^3 for $InBr_4^-$ and then to 2855 Å^3 for the InI_4^- salt. The almost twice as big increase in the volume difference between the I and Br than that between the Br and Cl salts results, as expected, in lower symmetry. However, it should be noted that the unit cell of the InI_4^- salt is smaller than expected from a linear correlation between unit cell volume and anion volume. This is shown by the decrease in the $\Delta V(cell)/\Delta V(anion)$ ratio from 1.90 for the Br/Cl pair to only 1.69 for the I/Br pair. As the anion volume we have adopted the volume of a sphere with radius equal to the sum of indium(III) radius and twice the halide radius.

The structures of the three $Bu_4N[InCl_4]$, $Bu_4N[InBr_4]$ and $Bu_4N[InI_4]$ salts are similar. In each the InX_4^- anion is surrounded by five nearest Bu_4N^+ cations which occupy corners of a distorted trigonal bipyramid. The Bu_4N^+ cation shows essentially the same structure and in each salt the C—C distance is in the range from 1.45(2) to 1.58(3) (average 1.46) Å. An exception is the C23-C24 distance in $Bu_4N[InI_4]$, which is equal to only 1.22(6) Å. The C24 atom which is the terminal atom in the chain, has the biggest equivalent isotropic displacement. In the chloride and bromide salts the carbon atom which shows the shortest distance to its nearest neighbour also has the biggest equivalent isotropic displacement.

Contrary to cations, the structure of anions in the $Bu_4N[InX_4]$ salts shows much larger differences. In the monoclinic iodide salt the InI_4^- anion displays four different metal-to-ligand distances equal to 2.695(2), 2.699(2), 2.704(1) and 2.709(1) Å, while in the orthorhombic chloride and bromide salts there are either two pairs of distances, 2.345(3) and 2.355(3) Å, or only one distance equal to 2.479(2) Å, respectively. Two pairs of M(III)–X distances are also shown by the $In[InI_4]$ [2], $In[InBr_4]$ [6], $Ga[GaCl_4]$ and α-$Ga[GaBr_4]$ [7] salts which all crystallize in the orthorhombic system. On the other hand, when the $Bu_4N[InX_4]$ salt crystallizes in the monoclinic system all four distances are different, which is shown by both the title compound and $Bu_4N[TlI_4]$. The latter shows four Tl–I distances equal to 2.782(3), 2.766(2), 2.775(3), 2.791(2) Å [8]. From this comparison one can conclude that distortion of the $[MX_4]$ tetrahedron is sensitive to the whole crystalline environment. The effect of environment appears to be greater for heavier atoms in the tetrahedron. This is reflected in the decrease of the symmetry from Pnna for $Bu_4N[InCl_4]$ and $Bu_4N[InBr_4]$ to $P2_1/n$ for $Bu_4N[InI_4]$ and $Bu_4N[TlI_4]$.

It seems obvious that both the average In–X distance and distortion of the tetrahedron should depend on the interaction between cations and the In(III) bonded halide anions. Thus, one can presume that the average In–X distance in the tetrahedron should be longer the shorter is the distance between the X ligands and the centers of the positive charge. This presumption is confirmed by the increase in the average In–X distance in the tetrahedron from 2.702 to 2.714 Å and from 2.479 to 2.503 Å when the large Bu_4N^+ cation is replaced by the small In^+ cation in the respective iodide and bromide $M[InX_4]$ salts.

From distortion of the $[InX_4]$ tetrahedron in the tetra-n-butylamonium salts one could expect a correlation between the specific In–X distance and the X–N or the X-(nearest C) distance. We indeed found that in the case of the $InCl_4^-$ anion the In–Cl distance increases from 2.345 to 2.355 Å with decreasing average Cl–N distance from 4.986 to 4.846 Å (nearest two N atoms) and average Cl–C distance decreasing from 3.933 to 3.901 Å (nearest four C atoms). The Cl–N and Cl–C distances have been calculated from published data [1]. For the title anion there is also a general trend of increasing In–I distance with decreasing average I–N distance (two nearest N atoms) and decreasing average I–C distance (five nearest C atoms). However, the relationships are non-monotonic and in each of the two plots a different In–I distance deviates from the monotonic dependence. On the other hand, in the $InBr_4^-$ anion all In–Br distances are equal, in spite of two different Br–N and two different Br–C distances. Apparently, the problem of distortion of the tetrahedron requires further studies.

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