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The Crystal Structure of Indium Diiodide, Indium(I) Tetraiodoindate(III), $In[InI_4]$

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Abstract

The crystal structure of the title compound has been determined by the heavy atom method. The crystals are orthorhombic, space group *Pnna*, with unit cell dimensions a = 8.525(5) Å, b = 10.969(9) Å, c = 11.162(8) Å, Z = 4; R = 0.043 for 807 unique 'observed' reflections. The structure consists of InI_4^- anions (r(In–I) = 2.714 Å (av.)) and In^+ cations. A value is derived for the ionic radius of In^+. Indium dichloride is not isomorphous with $In[InI_4]$.

Introduction

The structure of the dihalides of the heavier elements of Group IIIA has been the subject of both investigation and speculation, with gallium and indium species receiving most attention. The compounds are diamagnetic, which eliminates structures based on M^{2+} ions, and the two formulae proposed then involve either M–M species, or the mixed oxidation state ionic dimer $M^I[M^{III}X_4]$.

For gallium, magnetic, vibrational spectra and X-ray investigations [1–4] have established that $Ga[GaX_4]$ (X = Cl, Br, I) is the correct structure in the solid, solution and molten phases. At the same time, the existence of M–M bonded derivatives has also been demonstrated [5–8], notably for $Ga_2Cl_6^{2-}$ and the neutral adducts $Ga_2Cl_4 \cdot L_2$ (L = pyridine, 1,4-dioxane). For indium dibromide and diiodide, the vibrational spectra [9] have been interpreted in terms of the $In[InX_4]$ formula, but the structure of solid indium dichloride remained in doubt (see below). For this element too, M–M bonding has been confirmed for $In_2X_6^{2-}$ anions [10] and for neutral adducts [11–13] of In_2X_4 and In_2X_3Y (X = Y ≠ Cl, Br, I). We now report an X-ray crystallographic study of indium diiodide, which is shown to consist of In^+ and InI_4^- ions.

Experimental

Indium diiodide was prepared by the method described by Freeland and Tuck [14]; crystals suitable for X-ray crystallography were obtained by slowly cooling a solution in mixed xylenes. A small pale yellow prismatic crystal (see Table I for dimensions, and other relevant data) was sealed in a capillary and mounted on a Syntex $P2_1$ diffractometer for X-ray data collection. Details on the data collection procedures have been given previously [15, 16]. The intensity of three monitor reflections did not change significantly during data collection. The data were corrected for Lorentz and polarization effects, and analytical absorption corrections were applied. The systematic absences (okl, k + l = 2n + 1; hol, l + n = 2n + 1; hko, h = 2n + 1) indicated the space group *Pnna*.

The structure was solved by the heavy atom method, and refined anisotropically by the full-matrix least-squares method. The refinement converged at R = 0.043 and R_w = 0.057 for 807 unique 'observed' reflections. In the final cycle of refinement, the largest shift: error ratio was 0.1. The final difference map showed no features of any chemical significance.

Positional and thermal parameters are given in Table II and interatomic distances bond angles in Table III. Figure 1 shows the cell packing and the atomic numbering scheme. Tables of structure factors are available as Supplementary Data.

Results and Discussion

General

The results confirm unequivocally that the structure of crystalline indium diiodide is that of an ionic dimer $In[InI_4]$, as proposed earlier [9]. The InI_4^- anion shows only slight deviations from tetrahedral symmetry (see Table III) and the In–I bond distances are in good agreement with an earlier determination [17] of 2.71(1) Å. The average In–I distances in In_2I_6, which consists of two InI_4 tetrahedron joined along one edge [18], are $In–I_{ter}$ = 2.642 Å and $In–I_{br}$ = 2.839 Å, whose average is also close to the present values.

The indium(I) cation is surrounded by eight iodine atoms at distances ranging from 3.588(2) Å to 3.673(2) Å, all considerably greater than the sum of the covalent radii. The arrangement of

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TABLE I. Summary of Crystal Data, Intensity Collection and Structural Refinement for In_2I_4.

Cell constants	a = 8.425(5) Å b = 10.969(9) Å c = 11.162(8) Å
Cell volume (Å^3)	1031(1)
Space group	*Pnna*
Z	4
M_r	737.3
ρ(calc) (g cm^{-3})	4.749
Absorption coefficient (cm^{-1})	153.1
Min/max absorption correction	5.7/46.8
Crystal dimensions (mm)	0.135 × 0.192 × 0.346
Radiation	MoK$_\alpha$ (λ = 0.71069 Å)
Temp. (°C)	22
2θ angle (°)	20–30 (cell refinement); 4–50 (data collection)
Scan type	coupled θ(crystal)/2θ(counter)
Scan width	$K_{\alpha 1} - 1°$ to $K_{\alpha 2} + 1°$
Scan speed (° min^{-1})	2.0–5.0
Background time/scan time	0.5
Total reflections measured	1093
Unique data used (m)	807 ($F_o^2 > 2\sigma(F_o)^2$)
No. of parameters (n)	30
$R = (\Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert)$	0.043
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma_w F_o^2]^{1/2}$	0.057
$\Delta\rho_{max}$ (e Å^{-3})	1.1
Shift: error (max)	0.1

TABLE II. Atomic Coordinates and Anisotropic Thermal Parameters[a] for In[InI$_4$].

Atomic coordinates

Atom	x	y	z
In(1)	0.2500	0.0	0.6783(1)
In(2)	0.6615(3)	0.2500	0.7500
I(1)	0.5054(2)	−0.0480(1)	0.8193(1)
I(2)	0.3431(2)	0.1931(1)	0.5439(1)

Thermal parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In(1)	40(2)	36(1)	34(1)	−2(1)	0	0
In(2)	54(2)	58(1)	57(1)	0	0	0(1)
I(1)	48(2)	43(1)	52(1)	6(1)	−11(1)	3(1)
I(2)	52(2)	56(1)	48(1)	13(1)	7(1)	21(1)

[a] Anisotropic Temperature Factors of the Form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

TABLE III. Interatomic Distances (Å) and Angles (°), with e.s.d.s in Parentheses, for In[InI$_4$].

Distances

In(1)–I(1)	2.717(1)	In(1)–I(2)	2.711(1)
In(2)–I(1)	3.607(1)	In(2)–I(2)	3.588(2)
In(2)–I(1)^a	3.659	In(2)–I(2)^b	3.673(2)

Angles

I(1)–In(1)–I(2)	104.0(1)	I(1)–In(1)–I(1)^c	109.2(1)
I(1)–In(1)–I(2)^c	113.5(1)	I(2)–In(1)–I(2)^c	112.8(1)
I(1)–In(2)–I(2)	73.0(1)	I(1)–In(2)–I(1)^d	137.2(1)
I(1)–In(2)–I(1)^a	150.9(1)	I(1)–In(2)–I(2)^b	100.9(1)
I(1)–In(2)–I(2)^d	75.4(1)	I(1)–In(2)–I(2)^e	96.6(1)
I(2)–In(2)–I(1)^a	122.9(1)	I(2)–In(2)–I(2)^b	73.1(1)
I(2)–In(2)–I(2)^d	83.3(1)	I(2)–In(2)–I(2)^e	156.0(1)

Symmetry equivalent positions

^{a}1.5 − x, 0.5 + y, 1.5 − z
0.5 + x, y, 1.0 − z
^{c}0.5 − x, −y, z
^{d}x, 0.5 − y, 1.5 − z
^{e}0.5 + x, 0.5 − y, 0.5 + z

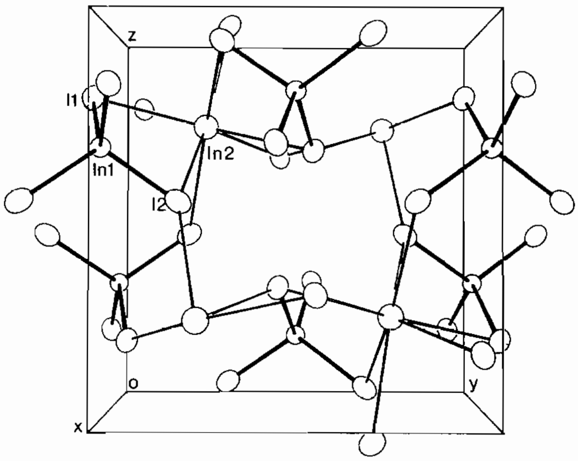

Fig. 1. Cell packing and atomic numbering scheme for In[$\mathrm{InI_4}$].

these iodine atoms does not conform to any simple geometrical shape, and it appears that the packing of the $\mathrm{InI_4}^-$ anions determines the overall geometry around what is essentiallly a bare In^+ cation. There is no evidence for the presence of a stereochemically active lone pair of electrons on this cation.

There are a number of interesting comparisons between the present results and the structure of gallium dichloride [4], Ga[$\mathrm{GaCl_4}$], beginning with the identity of the space groups. The M^+ cation is eight-coordinate in both cases, being surrounded by halide ions from six different $\mathrm{MX_4}^-$ tetrahedra. Garton and Powell found the average $\mathrm{M^+–X^-}$ distance to be 3.22 Å, from which the ionic radius of Ga^+ is 1.41 Å (r(Cl^-) = 1.81 Å (Goldschmidt)) [19]. A similar treatment of the present results, taking r($\mathrm{In^+–I}$) (av.) as 3.63 Å and r(I^-) = 2.20 Å, gives r(In^+) = 1.43 Å. These results compare reasonably with r(Tl^+) = 1.49 Å found by Goldschmidt. If one uses the ionic radii proposed by Ladd [20], the corresponding values for r(Ga^+, In^+, Tl^+) are 1.52, 1.51 and 1.54 Å, respectively. In either case, the general conclusion, that the Ga^+ and InX^+ ions are of similar size, and slightly smaller than Tl^+, seems well-founded. Both of the values derived for r(In^+) are considerably larger than that deduced [21] from the structure of indium(I) iodide.

A recent structural determination [22] of the complex ($\mathrm{Sn^{2+}}$)($\mathrm{AsF_6}^-$)$_2$($\mathrm{SbF_3}$)$_2$ shows that in this lattice the bare $\mathrm{Sn^{2+}}$ ion is coordinated by nine fluoride ions. The range of Sn–F distances (2.31(2)–3.02(2) Å is again larger than the sum of the covalent radii (2.12 Å). In this structure, as in In[$\mathrm{InI_4}$], the arrangement of the $\mathrm{AsF_6}^-$ and $\mathrm{SbF_3}$ units appears to be more important than are the $\mathrm{Sn^{2+}–F}$ interactions.

Indium Dibromide and Dichloride

The spectroscopic studies discussed earlier [9] established that both indium dibromide and diiodide lattices can be formulated as In[$\mathrm{InX_4}$]. Given that this conclusion is now fully confirmed for X = I, it seems reasonable to accept that indium dibromide is isostructural, with a lattice of In^+ and $\mathrm{InBr_4}^-$ ions.

The structure of indium dichloride presents a more difficult problem. Vibrational spectra have demonstrated the presence of the $\mathrm{InCl_4}^-$ anion in molten [23–25] indium dichloride, but the analogous studies of the room temperature phase are variously interpreted as confirming [26] or denying [24–26] the presence of the tetrahedral anion in the lattice. X-ray powder studies of the solid are also claimed to support the presence of $\mathrm{InCl_4}^-$ in both of two different phases of indium dichloride [27, 28]. Attempts in the course of the present work to determine the structure of indium dichloride were frustrated by the poor quality of the crystals obtained by sublimation in a Carius tube. Preliminary results indicate that the structure is not isomorphous with indium diiodide; the parameters of the rhombohedral cell include a = 7.750(9) Å, α = 67.05(5) Å. Given the known tendency of indium(III) to form six-coordinate rather than four-coordinate anionic complexes with chloride ion [29], differences between the present structure and the presumed ionic lattice of indium dichloride are not surprising.

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Note added in proof

Since submitting this paper, we have bcome aware of a prior determination of the structure of In[$\mathrm{InI_4}$] by H. P. Beck (*Z. Naturforsch., Teil B:*, 39, 310, (1984)). The present results are in good agreement with those reported by Beck, although the methods of crystal preparation were different.

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