The crystal structure of tetraethylammonium tetrachloroindate (III)

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Crystals of Et_4NInCl_4 are hexagonal, $a = 8.30$, $c = 13.31$ Å, $Z = 2$, space group $P6_3mc$. The structure was determined by three-dimensional Patterson and least-squares methods, using Mo $K\alpha$ scintillation-counter data. The crystal contains Et_4N^+ and $InCl_4^-$ ions with a nickel arsenide arrangement. In the tetrahedral $InCl_4^-$ anion, In–Cl = 2.33 Å.

Some years ago, Ekeley & Potratz (1936) reported that the reaction of indium halides and the corresponding substituted alkylammonium and alkylsulphonium halides in non-aqueous media gives rise to a series of colourless crystalline compounds. These species were originally formulated as simple adducts, with stoichiometries ranging from $InX_3.CX$ to $InX_3.4CX$ ($X = Cl$, Br or I; $C = $ substituted ammonium or sulphonium cation), but an alternative formulation would obviously be in terms of complex indium(III) anions $C[InX_4]$, $C_2[InX_5]$, *etc.*, in keeping with the known solution properties of indium(III) – halide systems (Tuck & Woodhouse, 1964). The only haloindium(III) anion whose crystal structure in the solid state was established is that of the compound $(NH_4)_2[InCl_5(H_2O)]$, in which the anion has a C_{4v} structure (Klug, Kummer & Alexander, 1948). Recently the vibrational spectrum of the $InCl_6^{3-}$ anion has been reported (Barrowcliffe, Beattie, Day & Livingston, 1967); the Raman spectra of InX_4^- species ($X = Cl$, Br, I) in non-aqueous solution have been studied by Woodward and his co-workers (Woodward & Bill, 1955; Woodward & Singer, 1958; Woodward & Taylor, 1960).

We now report the structure of Et_4NInCl_4. In addition to confirming the formulation of the compound, we have obtained indium(III) – chlorine bond lengths which can be compared with those reported for $(NH_4)_2[InCl_5(H_2O)]$ and In_2Cl_6.

Crystals of Et_4NInCl_4 are colourless needles. Crystal data were measured from Weissenberg and precession films and on the General Electric XRD 5 Spectrogoniometer. The crystals are hexagonal, $a = 8.30$, $c = 13.31$ Å, $c/a = 1.60$, $Z = 2$. The diffraction pattern showed $6/mmm$ symmetry, and the systematically absent reflexions were $hh2\bar{h}l$, $l = 2n + 1$, so that the space group could be $P\bar{6}2c$ (D_{3h}^4), $P6_3mc$ (C_{6v}^4) or $P6_3/mmc$ (D_{6h}^4); $P6_3mc$ was selected, and was confirmed by the subsequent analysis. The crystal used had dimensions $0.07 \times 0.08 \times 0.21$ mm. The intensities were measured on the Spectrogoniometer using approximately monochromatic Mo $K\alpha$ radiation (zirconium filter and pulse height analyser) and a θ–2θ scan. Background corrections (approximately a function of θ only) were made, Lorentz and polarization factors were applied, and struc-

ture amplitudes were derived for a total of 259 reflexions, of which 89 were insignificantly above background, and were treated as unobserved.

The indium and chlorine positions were readily obtained from the three-dimensional Patterson function, and were refined by block-diagonal least-squares techniques. Thomas–Fermi–Dirac scattering factors were used for the indium atom (corrected for the real phase component of the anomalous scattering), and self-consistent field values for all other atoms (*International Tables for X-ray Crystallography*, 1962). The structure refined satisfactorily, and after 6 cycles R had decreased from 0.43 to 0.16.

The interpretation of the Patterson function required the tetrahedral $InCl_4^-$ anion to have exact C_{3v} symmetry (with one unique chlorine atom). Since there are only two formula units in the unit cell and both twofold positions have the symmetry $3m$, the tetraethylammonium group must be disordered in some way so that it also would have the minimum required crystallographic C_{3v} symmetry.

No difficulty was found in locating the nitrogen atom from a three-dimensional electron density difference map. Further refinement of the In, Cl, and N parameters reduced R to 0.135. At several stages in the refinement three-dimensional electron density difference maps were constructed and examined in an attempt to locate the position of the carbon atoms. Basically two alternatives were considered:

(*a*) Either one CH_2 or one CH_3 group on the threefold axis. This would allow (but not require) either $3CH_2$ groups or $3CH_3$ groups to fall on the mirror planes, permitting the maximum degree or ordering consistent with an Et_4N^+ ion occupying a position of $3m$ symmetry.

(*b*) Disorder in which 3 tetrahedral sets of four positions are randomly occupied by each of the two types of carbon atoms.

In both cases the possible positions were restricted by the known bond length and angle requirements. The first model was excluded since no significant peaks could be found at or near the threefold axis. Inclusion of the methylene carbon atoms in an arrangement of the second type did not improve the structure factor agreement; since each atomic position would only be associated with one third of a carbon atom it is hardly surprising that this could not be

Table 1. *Final positional (fractional) and thermal* (Å²) *parameters, with their standard deviations in parentheses*

	Position	x	y	z	B
In(1)	2 (*a*)	0	0	0.0000 (12)	5.53 (10)
Cl(2)	6 (*c*)	0.1527 (12)	−0.1527 (12)	0.0511 (18)	7.25 (33)
Cl(3)	2 (*a*)	0	0	−0.1775 (23)	6.56 (61)
N(4)	2 (*b*)	$\frac{2}{3}$	$\frac{1}{3}$	0.2633 (56)	2.97 (99)
C(5)			not located		
C(6)			not located		

detected in the presence of the heavier indium and chlorine atoms. In addition to (b) it is possible that full rotational disorder might occur.

The atomic coordinates and thermal parameters with their least-squares standard deviations are given in Table 1. Since the electron density associated with the carbon atoms has not been accounted for, the values of the standard deviations may not be reliable. A list of the structure factors and details of the weighting scheme used may be obtained from the authors.

The structure of Et_4NInCl_4 is based on the well known nickel arsenide structure, which, unlike some of the other arrangements related to closest packed structures, has different anion and cation environments. Since the $InCl_4^-$ anion occupies the Ni position of NiAs, the crystal has the anti-NiAs structure (Wyckoff, 1963), but unlike the classic examples of this type of structure (e.g. FeS) the compound has constant composition, and there appears to be little or no covalent interaction between anion and cation. Furthermore the c/a ratio (1·60) is close to that expected for a closest-packed arrangement characteristic of ionic solids. The interatomic distances and angles are given in Table 2; the $InCl_4^-$ ion is a regular tetrahedron within experimental error.

Table 2. *Interatomic distances and angles, and standard deviations*

In(1)–Cl(2)	2·30 ± 0·02 Å	Cl(2)–In(1)–Cl(3)	107 ± 1°
In(1)–Cl(3)	2·36 ± 0·03	Cl(2)–In(1)–Cl(2)	111 ± 1

The packing of ions in the structure is such that each cation is trigonal-prismatically surrounded by six equidistant adjacent anions. The anion is surrounded by eight near neighbours, six of which are cations, and the remaining two nearby anions, these latter contacts consisting of the tetrahedral $InCl_4^-$ ions stacked one on top of another, with the unique chlorine atom 4·29 Å from the next indium atom. The unique indium–chlorine bond is slightly, but not significantly, longer than the other three (2·36 compared to 2·30 Å, average 2·33 Å). These values are shorter than those reported (*Tables of Interatomic Distances*, 1958, 1965) for In_2Cl_6 (2·46 Å average) and $(NH_4)_2[InCl_5(H_2O)]$ (2·58 Å average).

It is interesting to compare the bond length in $InCl_4^-$ with that for the isoelectronic molecule $SnCl_4$ (Sn–Cl 2·33 Å; *Tables of Interatomic Distances*, 1958, 1965). Despite the similarities, the force constants for these two species are markedly different, being $2·16 \times 10^5$ dynes.cm^{-1} for $InCl_4^-$ and $2·80 \times 10^5$ dynes.cm^{-1} for $SnCl_4$ (Woodward & Taylor, 1960). If this represents a difference in bond energies, rather than a difference in the potential well, the Sn–Cl bond is clearly much the stronger. The most obvious source of the extra bond energy resides in the higher formal charge of +4 on the central atom in $SnCl_4$ compared with $InCl_4^-$. This charge effect is probably best regarded as operating by increasing the acidic (acceptor) property of the central atom for ligand electrons. In terms of this electrostatic model, Blake & Cotton (1963) obtained a reasonable estimate of the total bond energy in $CoCl_4^{2-}$ from a model of a point charge of +2, tetrahedrally surrounded by four −1 point charges at the appropriate internuclear distance. Application of this model to the isoelectronic pair $SnCl_4$ and $InCl_4^-$ obviously requires a stronger bond energy in the former, as indicated by the force constants.

References

BARROWCLIFFE, T., BEATTIE, I. R., DAY, P. & LIVINGSTON, K. (1967). *J. Chem. Soc.* A, p. 1810.

BLAKE, A. B. & COTTON, F. A. (1963). *Inorg. Chem.* **2**, 906.

EKELEY, J. B. & POTRATZ, H. A. (1936). *J. Amer. Chem. Soc.* **58**, 907.

International Tables for X-ray Crystallography (1962). Vol. II. Birmingham: Kynoch Press.

KLUG, H. P., KUMMER, E. & ALEXANDER, L. A. (1948). *J. Amer. Chem. Soc.* **70**, 3064.

Tables of Interatomic Distances and Configuration in Molecules and Ions (1958, 1965). Special Publications Nos. 11 and 18. London: The Chemical Society.

TUCK, D. G. & WOODHOUSE, E. J. (1964). *J. Chem. Soc.* p. 6017.

WOODWARD, L. A. & BILL, P. T. (1955). *J. Chem. Soc.* p. 1699.

WOODWARD, L. A. & SINGER, G. H. (1958). *J. Chem. Soc.* p. 716.

WOODWARD, L. A. & TAYLOR, M. J. (1960). *J. Chem. Soc.* p. 4473.

WYCKOFF, R. W. G. (1963). *Crystal Structures* Vol. I, p. 122. New York: Interscience.