

## References

- ANDERSEN, E. K. & ANDERSEN, I. G. K. (1975). *Acta Cryst.* **B31**, 387–390.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 73, 102. Birmingham: Kynoch Press.
- IWASAKI, F. (1973). *Chem. Lett.* pp. 227–228.
- IWASAKI, F., SATO, M. & AIHARA, A. (1973). *Chem. Lett.* pp. 249–250.
- SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKUHARA, M. (1967). *Rep. Inst. Phys. Chem. Res.* **43**, 62–69.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

*Acta Cryst.* (1977). **B33**, 1648–1650

## Trimethylammonium Hexachloroindate(III)

BY J. G. CONTRERAS,† F. W. B. EINSTEIN,‡ M. M. GILBERT AND D. G. TUCK§

*Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada V5A 1S6*

(Received 23 November 1976; accepted 5 February 1977)

**Abstract.**  $[(\text{CH}_3)_3\text{NH}]_3\text{InCl}_6$ ,  $M_r = 507.9$ , tetragonal,  $I4_1/acd$ ,  $a = 22.464$  (4),  $c = 17.551$  (3) Å,  $V = 8856.78$  Å<sup>3</sup>,  $\rho_o = 1.52$ ,  $\rho_c = 1.52$  g cm<sup>-3</sup>,  $Z = 16$ , Mo  $K\alpha_1$  radiation,  $\lambda = 0.70926$  Å,  $\mu(\text{Mo } K\alpha) = 17.68$  cm<sup>-1</sup>,  $R = 0.064$  for 722 observed reflexions,  $t = 25^\circ\text{C}$ . The structure is composed of  $\text{Me}_3\text{NH}^+$  and  $\text{InCl}_6^{3-}$  ions. The  $\text{InCl}_6^{3-}$  ions are octahedral (In–Cl 2.521 Å) and occupy crystallographic centres of symmetry. The  $\text{Me}_3\text{NH}^+$  ions are of two types; half are in general positions, while the remainder fill disordered positions near a crystallographic twofold axis.

**Introduction.** Crystals of the title compound are colourless parallelepipeds elongated along *c*. The space group was determined from Weissenberg photographs of layers  $hk0$ – $hk3$  and precession photographs of layers  $h0l$ – $h3l$  and  $hhl$  taken with Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å).

The space group  $I4_1/acd$  was determined from the systematic absences  $hkl$  when  $h + k + l = 2n + 1$ ,  $hk0$  when  $h = 2n + 1$ ,  $0kl$  when  $l = 2n + 1$ , and  $00l$  when  $2n + l \neq 4n$ . Reflexions for which  $hkl$  had  $h, k, l = 2n$  and  $h + k + l = 4n$  were, in general, very much stronger than the rest.

A crystal,  $0.20 \times 0.24 \times 0.40$  mm, sealed in a Lindemann-glass capillary was used for the determination of cell dimensions and for intensity collection (Mo  $K\alpha_1$ ,  $\lambda = 0.70926$  Å). To minimize multiple scattering,  $\mathbf{c}^*$  was offset approximately  $12^\circ$  from the  $\varphi$  axis of the diffractometer. Cell dimensions were determined from

† Present address: Instituto de Química, Universidad de Concepción, Casilla 3-C, Concepción, Chile.

‡ Author to whom correspondence should be addressed.

§ Present address: Department of Chemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4.

reflexions with  $2\theta > 31^\circ$ , with a take-off angle of  $1.2^\circ$ . For data collection the take-off angle was  $3.2^\circ$  and each reflexion was scanned in  $2\theta$  (base width  $1.4^\circ$  in  $2\theta$ ; extended for the  $\alpha_1\alpha_2$  splitting). The background was measured for 10 s at each end of the scan. Two standard reflexions were measured every 50 reflexions; the variation in their intensity was less than  $\pm 1\%$ .

From the alternation of strong and weak intensities, it was clear that the In atoms were located on the 16 centres of symmetry, while the Cl atoms were believed to be situated around In at approximately  $x, y, z_1; y, x, z_1$ ; and  $0, 0, z_2$ , resulting in a pseudosymmetry and reinforcing the strong–weak intensity pattern. Examination of the Patterson function confirmed this pseudosymmetry and led to the location of the Cl atoms.

Isotropic least-squares refinement gave  $R = 0.135$ ; a difference map showed some indication of  $\text{Me}_3\text{NH}^+$  groups, but had as its largest features peaks around the In and Cl atoms, indicating considerable anisotropic thermal motion. Successive difference maps and least-

Table 1. Atomic positions for  $(\text{Me}_3\text{NH})_3\text{InCl}_6$

|       | <i>x</i>    | <i>y</i>    | <i>z</i>   |
|-------|-------------|-------------|------------|
| In    | 0.00        | 0.00        | 0.00       |
| Cl(1) | 0.1074 (2)  | 0.0094 (2)  | 0.0382 (3) |
| Cl(2) | −0.0133 (2) | 0.1104 (2)  | 0.0258 (3) |
| Cl(3) | −0.0298 (2) | −0.0238 (3) | 0.1344 (3) |
| N(1)  | 0.380 (2)   | 0.165 (2)   | 0.017 (3)  |
| C(1)  | 0.337 (2)   | 0.167 (2)   | −0.030 (3) |
| C(2)  | 0.377 (2)   | 0.153 (2)   | 0.089 (3)  |
| C(3)  | 0.407 (2)   | 0.220 (2)   | 0.000 (2)  |
| N(2)  | 0.151 (2)   | 0.440 (2)   | 0.116 (2)  |
| C(4)  | 0.172 (3)   | 0.386 (3)   | 0.051 (4)  |
| C(5)  | 0.229 (2)   | 0.449 (2)   | 0.119 (4)  |
| C(6)  | 0.130 (3)   | 0.411 (3)   | 0.165 (4)  |

squares cycles led to the location of the C and N atoms. One cation was found to be disordered about the twofold axis at  $x, \frac{1}{4} + x, \frac{1}{2}$ ; the other fully occupied position was approximately at  $y, x, z$  to the first, thereby contributing, with the Cl atoms, to the pseudo-symmetry and making precise location of the cations difficult.

Further refinement yielded a final  $R = 0.064$  and  $R_w = 0.076$ . No attempt was made to refine the trimethylammonium groups with anisotropic temperature factors since they were too poorly defined. A final difference map showed no unusual peaks but had its largest features near the In atom.

The atomic coordinates with their standard deviations are given in Table 1,\* and the distances and angles within the  $\text{InCl}_6^{3-}$  anion in Table 2. Scattering factors (including the anomalous dispersion correction) were taken from Cromer & Waber (1965). The use of unit weights in the refinement proved satisfactory.

**Discussion.** The present paper completes a series of preparative, spectroscopic and crystallographic studies of a group of In compounds originally prepared by Ekeley & Potratz (1936), who obtained compounds which were formulated as the adducts  $\text{InCl}_3 \cdot nR_4\text{NCl}$  ( $n = 1, 2, 3$  or  $4$ ) from the reaction of  $\text{In}^{\text{III}}$  chloride with substituted ammonium chlorides. An extension of this work to include examination of the vibrational spectra showed that these substances are in fact salts containing the anions  $\text{InCl}_4^-$ ,  $\text{InCl}_5^{2-}$  or  $\text{InCl}_6^{3-}$  (Gislason, Lloyd & Tuck, 1971). Crystallographic studies confirmed these conclusions for  $\text{Et}_4\text{N}[\text{InCl}_4]$ , in which the anion is tetrahedral (Trotter, Einstein & Tuck, 1969) and  $(\text{Et}_4\text{N})_2[\text{InCl}_5]$ , where the anion has  $C_{4v}$  symmetry (Brown, Einstein & Tuck, 1969). Joy, Gaughan, Wharf, Shriver & Dougherty (1975) have proposed an alternative model of lower symmetry for  $\text{InCl}_5^{2-}$ , based on their isotropic refinement in space group  $P4$ , for which  $R$  is identical with that obtained in  $P4/n$ . The former requires almost twice as many variables as the latter, so that the X-ray data alone do not allow a decision as to the molecular symmetry. The bond lengths derived from this model do not differ substantially from those reported earlier by Brown, Einstein & Tuck (1969).

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32476 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Interatomic distances and angles in the  $\text{InCl}_6^{3-}$  anion

|          |             |                |           |
|----------|-------------|----------------|-----------|
| In—Cl(1) | 2.514 (5) Å | Cl(1)—In—Cl(2) | 89.1 (2)° |
| In—Cl(2) | 2.538 (5)   | Cl(1)—In—Cl(3) | 91.4 (2)  |
| In—Cl(3) | 2.510 (4)   | Cl(2)—In—Cl(3) | 90.5 (2)  |

One further piece of crystallographic evidence has confirmed the earlier spectroscopic arguments; the compounds  $(\text{MeNH}_2)_4\text{InCl}_7$  and  $(\text{Me}_2\text{NH}_2)_4\text{InCl}_7$  were formulated as lattices of four cations +  $\text{InCl}_6^{3-}$  +  $\text{Cl}^-$ , and this has been verified for the former by Schlimper & Ziegler (1972), whose structural parameters for the  $\text{InCl}_6^{3-}$  anion are in excellent agreement with those from the present work.

The range of coordination numbers demonstrated for  $\text{In}^{\text{III}}$ , and the importance of cation size, preparative conditions, *etc.* have been discussed elsewhere (Carty & Tuck, 1975). Table 3 shows that increasing coordination number is accompanied by a monotonic lengthening of the In—Cl bond in the series  $\text{InCl}_4^-$ — $\text{InCl}_5^{2-}$ — $\text{InCl}_6^{3-}$ . This relation is in keeping with (but does not of itself prove) the highly ionic character of the In—Cl bond, a property discussed earlier (Contreras & Tuck, 1972) in terms of the effect of coordination number upon the primary stretching force constant. The results in Table 3 establish that this latter argument can be more usefully restated as a dependence of the force constant upon bond length. Other  $d^{10}$  metal ions also give rise to neutral and covalent halides with a variety of coordination numbers, and  $\text{Sn}^{\text{IV}}$  ( $\text{SnCl}_4$ — $\text{SnCl}_6^{2-}$ ) and  $\text{Cd}^{\text{II}}$  ( $\text{CdCl}_2$ — $\text{CdCl}_4^{2-}$ ) are of special relevance in that they are isoelectronic with  $\text{In}^{\text{III}}$ . The values for the  $M$ —Cl length in the  $\text{SnCl}_6^{2-}$ — $\text{InCl}_6^{3-}$ — $\text{CdCl}_4^{2-}$  group show a strong dependence upon the oxidation state of the central metal atom, again in keeping with an ionic bonding model for these three anions. An extension of these investigations to the complexes of  $\text{Cd}^{\text{II}}$  is under way (Contreras & Tuck, 1975).

Finally, structural data are also available for aquachloro species  $[\text{InCl}_3(\text{H}_2\text{O})_3]$ ,  $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ , and  $[\text{InCl}_5(\text{H}_2\text{O})]^{2-}$ . The neutral trihydrate has been studied, as  $[\text{InCl}_3(\text{H}_2\text{O})]_3 \cdot (\text{dioxane})_3$ , by Whitlow & Gabe (1975). The existence of  $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ , originally postulated on the basis of solvent extraction (Tuck & Woodhouse, 1964a) and anion exchange (Dobud, Lee & Tuck, 1970) experiments, has been confirmed by the X-ray crystallographic work of Ziegler, Schlimper, Nuber, Weiss & Ertl (1975) who showed that the anion has the *cis*-stereochemistry proposed for  $[\text{InCl}_4(\text{urea})_2]^-$  from vibrational spectra (Tuck & Woodhouse, 1964b). The early study of  $[\text{InCl}_5(\text{H}_2\text{O})]^{2-}$ , as the ammonium salt, by Klug, Kummer & Alexander (1948) gave In—Cl distances (2.58 Å) which were substantially larger than those for any of the other compounds under discussion. More recent measurements by Wignacourt, Mairesse & Barbier (1976) yielded the values shown in Table 3.

The ionic model predicts that replacement of Cl ligands by neutral water molecules should lead to a shortening of the remaining In—Cl bonds, and the results for the series  $\text{InCl}_6^{3-}$ — $[\text{InCl}_3(\text{H}_2\text{O})_3]$  show that in general such is the case, although there are perturbations in the argument, due no doubt to the differing

Table 3. *Metal-chlorine bond lengths in indium(III) anions and related species*

| Anion   | M-Cl bond length (Å)                           | Reference                                  |
|---|--|--|
| $\text{InCl}_4^-$                                     | 2.33   | Trotter, Einstein & Tuck (1969)            |
| $\text{InCl}_5^{2-}$                                  | 2.42 (axial)                                   | Brown, Einstein & Tuck (1969)              |
|   | 2.46 (basal)                                   |  |
|   | 2.415 (axial)                                  |  |
|   | 2.495 (basal)                                  |  |
| $\text{InCl}_6^{3-}$                                  | 2.521  | Present work<br>Schlimper & Ziegler (1972) |
|   | 2.523  |  |
| $[\text{InCl}_3(\text{H}_2\text{O})_3]$               | 2.447, 2.420, 2.399<br>(all <i>trans</i> to O) | Whitlow & Gabe (1975)                      |
| $\text{cis-}[\text{InCl}_4(\text{H}_2\text{O})]^{2-}$ | 2.485 ( <i>cis</i> to O)                       | Ziegler <i>et al.</i> (1975)               |
|   | 2.425 ( <i>trans</i> to O)                     |  |
| $[\text{InCl}_5(\text{H}_2\text{O})]^{2-}$            | 2.474 ( <i>trans</i> to O)                     | Wignacourt, Mairesse & Barbier (1976)      |
|   | 2.463, 2.485, 2.486                            |  |
|   |  |  |
| $\text{SnCl}_6^{2-}$                                  | 2.43   | Awasthi & Mehta (1969)                     |
| $\text{CdCl}_6^{4-}$                                  | 2.63   | Bergerhoff & Schmitz-Dumart (1956)         |

values for In-Cl bonds *cis* and *trans* to In-OH<sub>2</sub>. We conclude that all the In-Cl bond distances in Table 3 are satisfactorily accounted for by an ionic model of bonding in these complexes.

This work was supported in part by Operating Grants from the National Research Council of Canada.

## References

- AWASTHI, M. N. & MEHTA, M. L. (1969). *Z. Naturforsch.* **24a**, 2029-2030.
- BERGERHOFF, G. & SCHMITZ-DUMART, O. (1956). *Z. anorg. allgem. Chem.* **284**, 10-19.
- BROWN, D. S., EINSTEIN, F. W. B. & TUCK, D. G. (1969). *Inorg. Chem.* **8**, 14-18.
- CARTY, A. J. & TUCK, D. G. (1975). *Progr. Inorg. Chem.* **19**, 343-337.
- CONTRERAS, J. G. & TUCK, D. G. (1972). *Inorg. Chem.* **11**, 2967-2971.
- CONTRERAS, J. G. & TUCK, D. G. (1975). *Canad. J. Chem.* **53**, 3487-3491.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104-109.
- DOBUD, P., LEE, H. M. & TUCK, D. G. (1970). *Inorg. Chem.* **9**, 1990-1997.
- EKELEY, J. B. & POTRATZ, H. A. (1936). *J. Amer. Chem. Soc.* **58**, 907-909.
- GISLASON, J., LLOYD, M. H. & TUCK, D. G. (1971). *Inorg. Chem.* **10**, 1907-1910.
- JOY, G., GAUGHAN, A. P., WHARF, I., SHRIVER, D. F. & DOUGHERTY, T. A. (1975). *Inorg. Chem.* **14**, 1795-1801.
- KLUG, H. P., KUMMER, E. & ALEXANDER, L. A. (1948). *J. Amer. Chem. Soc.* **70**, 3064-3068.
- SCHLIMPER, H. V. & ZIEGLER, M. L. (1972). *Z. Naturforsch.* **27b**, 377-379.
- TROTTER, J., EINSTEIN, F. W. B. & TUCK, D. G. (1969). *Acta Cryst.* **B25**, 603-604.
- TUCK, D. G. & WOODHOUSE, E. J. (1964a). *J. Chem. Soc.* pp. 6017-6022.
- TUCK, D. G. & WOODHOUSE, E. J. (1964b). *Chem. Ind.* pp. 1363-1364.
- WHITLOW, S. H. & GABE, E. J. (1975). *Acta Cryst.* **B31**, 2534-2536.
- WIGNACOURT, J. P., MAIRESSE, G. & BARBIER, P. (1976). *Cryst. Struct. Commun.* **5**, 293-296.
- ZIEGLER, M. L., SCHLIMPER, H. V., NUBER, B., WEISS, J. & ERTL, G. (1975). *Z. anorg. allgem. Chem.* **415**, 193-201.

*Acta Cryst.* (1977). **B33**, 1650-1653

## N-Acetyl-L-tryptophan

BY T. YAMANE, T. ANDOU AND T. ASHIDA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

(Received 25 December 1976; accepted 4 February 1977)

**Abstract.** C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>,  $M_r = 246.27$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.470$  (1),  $b = 25.912$  (4),  $c = 6.247$  (1) Å,  $Z = 4$ ,  $D_m = 1.35$ ,  $D_x = 1.353$  g cm<sup>-3</sup>,  $\mu = 8.17$  cm<sup>-1</sup> (for Cu K $\alpha$ ).  $R = 0.060$  for 626 non-zero reflexions. The molecular conformation shows good

agreement with those of glycyl-L-tryptophan dihydrate and acetyl-L-tryptophan methyl ester.

**Introduction.** N-Acetyl-L-tryptophan was supplied by Drs Y. Shimonishi and S. Aimoto of the Institute for