

Tetraphenylarsenic Hexakis(isothiocyanato)indate(III)

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Abstract. $[\text{As}(\text{C}_6\text{H}_5)_4][\text{In}(\text{NCS})_6]$, $M=1613$, monoclinic, $C2/c$, $a=47.696$ (9), $b=20.069$ (7), $c=16.382$ (3) Å, $\beta=103.04$ (1)°, $V=15274$ Å³; $\rho_o=1.43$ (3) (floatation in chloroform-*n*-butyl bromide), $Z=8$, $\rho_c=1.40$ g cm⁻³. Mo $K\alpha_1$ radiation, $\lambda=0.70926$ Å, $F(000)=6512$, $T=22 \pm 2$ °C. Final $R=0.072$ for 2792 observed reflexions. There are eight $\text{In}(\text{NCS})_6^{3-}$ ions in the unit cell; half of these are situated on centres of symmetry, the other half on twofold axes. Coordination of the thiocyanate ligand is through N (average In-N=2.12 Å) and, within error limits, the coordination about each In atom is octahedral.

Introduction. The reaction of In^{III} isothiocyanate with various thiocyanate salts of organic cations in ethanol gives rise to two series of anionic In^{III} isothiocyanato complexes, involving $[\text{In}(\text{NCS})_5]^{2-}$ and $[\text{In}(\text{NCS})_6]^{3-}$, respectively (Habeeb & Tuck, 1973). Vibrational spectroscopy served to establish that in each case bonding to the metal is through the N atom. In view of the current interest in five-coordinate complexes, it seemed appropriate to investigate the structure of the compound $(\text{Ph}_4\text{As})_2[\text{In}(\text{NCS})_5]$; in fact, the present study shows that the material obtained by recrystallization from acetone is $(\text{Ph}_4\text{As})_3[\text{In}(\text{NCS})_6]$. We return to this point below.

Intensities and cell dimensions were obtained from an approximately spherical specimen with a diameter varying from 0.27 to 0.30 mm. Systematic absences hkl , $h+k \neq 2n$ and $h0l$, $l \neq 2n$ indicate the space groups $C2/c$ or Cc ; intensity statistics and successful structure determination confirm $C2/c$. Accurate cell dimensions were determined from least-squares refinement of the 2θ values ($2\theta > 30^\circ$) for 16 strong reflexions centred on the Mo $K\alpha_1$ ($\lambda=0.70926$ Å) peak on a Picker FACS-1 automated diffractometer. Data were collected to a maximum 2θ value of 35° with Nb-filtered Mo $K\alpha$ radiation ($\lambda=0.7107$ Å; $\theta-2\theta$ scan, scan width = 1.2° , scan speed = 2° min^{-1}). Background counts of 10 s were measured at each of the scan limits. Variation in the intensity of either of two standard reflexions measured after every 70 reflexions was less than 1% during the data collection.

Intensity measurements were obtained for 4872 unique reflexions of which 2792 (57.3%) were treated

as observed with $I/\sigma(I) > 2.3$ where $\sigma(I) = [T + (t_s/t_b)^2 (B_1 + B_2) + (kI)^2]^{1/2}$ and T = total count, B_1 and B_2 are the background counts, t_s = scan time, t_b = total background count time, k is constant at 0.03 and I is the net count. Lorentz and polarization effects were corrected for but no correction for absorption was deemed necessary, the maximum error in F being $< 5\%$.

Heavy atoms were located from a Patterson synthesis. Refinement of positional and thermal parameters by full-matrix least squares and subsequent difference maps served to locate all non-hydrogen atoms. In addition, the difference maps indicated the presence of a molecule of acetone (apparently with reduced occupancy) on the twofold axis. Two final cycles of refinement (the function minimized was $\sum w(|F_o| - |F_c|)^2$) in which In, As and S were treated anisotropically gave a final $R=0.072$ ($R_w=0.076$) where $R = \sum(|F_o| - |F_c|) / \sum|F_o|$.

Unobserved reflexions were excluded from all stages of the least-squares refinement. For the initial refinement, constant (unit) weights were used but, in the final two cycles, weights ($=1/\sigma^2 F$) were given in terms of $\sigma F = \sigma I / (Lp) 2F_o$. Scattering factors were those of Cromer & Waber (1965); anomalous dispersion corrections for In and As were taken from Cromer (1965). Crystallographic computer programs have been described (Einstein & Jones, 1972).

Table 1. Bond lengths and angles

(a) Interatomic distances (Å)

In(1)—N(1)	2.16 (2)	In(2)—N(4)	2.16 (1)
In(1)—N(2)	2.12 (2)	In(2)—N(5)	2.15 (2)
In(1)—N(3)	2.06 (2)	In(2)—N(6)	2.12 (2)
N(1)—C(1)	1.10 (3)	N(4)—C(4)	1.18 (2)
N(2)—C(2)	1.15 (3)	N(5)—C(5)	1.16 (2)
N(3)—C(3)	1.10 (4)	N(6)—C(6)	1.12 (3)
C(1)—S(1)	1.66 (2)	C(4)—S(4)	1.63 (2)
C(2)—S(2)	1.65 (3)	C(5)—S(5)	1.65 (2)
C(3)—S(3)	1.72 (3)	C(6)—S(6)	1.68 (2)

Average C—C distance 1.41 [72 C—C bonds (12 phenyl rings)]

Average As—C distance 1.91

(b) Interatomic angles (°)

In(1)—N(1)—C(1)	162 (2)	In(2)—N(4)—C(4)	171 (1)
In(1)—N(2)—C(2)	166 (2)	In(2)—N(5)—C(5)	171 (2)
In(1)—N(3)—C(3)	153 (2)	In(2)—N(6)—C(6)	167 (1)
N(1)—C(1)—S(1)	173 (2)	N(4)—C(4)—S(4)	177 (2)
N(2)—C(2)—S(2)	174 (2)	N(5)—C(5)—S(5)	178 (2)
N(3)—C(3)—S(3)	176 (2)	N(6)—C(6)—S(6)	177 (1)

Average In—N—C 165 ± 5

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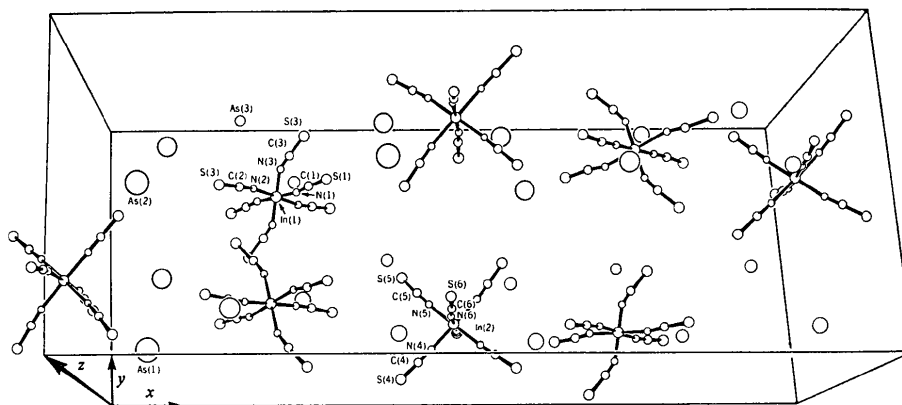


Fig. 1. View illustrating the ionic packing of $[\text{In}(\text{NCS})_6]^{3-} [\text{AsPh}_4]_3^+$.

Bond lengths and angles relevant to the discussion are given in Table 1.* Fig. 1 illustrates the ionic packing (phenyl rings have been omitted for clarity).

Discussion Crystallization of the compound studied here occurs with eight formula units per unit cell. Half of the $[\text{In}(\text{NCS})_6]^{3-}$ ions occupy centres of symmetry, the others are on twofold axes. Within experimental error, the coordination shell about both In atoms is a regular octahedron and, as might be expected, the ligand bonds to In through the hard, electronegative N atom. This result confirms the earlier conclusion, based on vibrational spectroscopy (Habeeb & Tuck, 1973). Such techniques have also established this mode of bonding for the neutral compounds $\text{M}(\text{NCS})_3$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) and their adducts (Patel, Sowerby & Tuck, 1967; Goggin, McColm & Shore, 1966; Patel & Tuck, 1969). Double-bond character is not expected in the In–N bonds; this is reflected in the fact that the N=C=S groups show no significant departures from linearity. Variations in the In–N–C angle are interpreted here as arising from packing considerations.

The change of stoichiometry from $(\text{Ph}_4\text{As})_2[\text{In}(\text{NCS})_5]$ to $(\text{Ph}_4\text{As})_3[\text{In}(\text{NCS})_6]$ on recrystallization is interesting in the light of earlier work on the anionic halogeno complexes of In^{III} , some of which are known to undergo similar rearrangements. A striking example is $(\text{Et}_4\text{N})_2\text{InCl}_5$, which can be recrystallized unchanged from dichloromethane (Brown, Einstein & Tuck, 1969), but which yields $\text{Et}_4\text{N} \cdot \text{InCl}_4$ on recrystallization from ethanol (Gislason, Lloyd & Tuck, 1971). These redistribution reactions and the concomitant preparation of anionic complexes of different stoichiometry and coordination number, are

an important feature of In^{III} chemistry (Tuck, 1970; Carty & Tuck, 1975), and one which obviously extends to complexes involving the isothiocyanate ligand.

Our results also show that the packing arrangement is such that each In has nine nearby As (shortest distance = 6.7 Å) and that each As is surrounded by three In atoms in an approximately trigonal environment. During refinement, S(3) appeared to have unusually large anisotropic thermal motion parameters. [The alternative interpretation in terms of two 'half atoms' in adjacent disordered positions (~0.5 Å apart) did not behave well.] C(3) and N(3) also exhibit larger isotropic thermal parameters than comparable atoms.

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* A list of structure factors and the final positional and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31731 (28 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.