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Indium(I) tetrachloroaluminate

Tudor Timofte and Anja-Verena Mudring*

Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

Correspondence e-mail: a.mudring@uni-koeln.de

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(I–Al) = 0.003 Å
R factor = 0.051
wR factor = 0.174
Data-to-parameter ratio = 38.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

$InAlCl_4$ crystallizes in the baryte ($BaSO_4$) structure type. The structure is characterized by $AlCl_4$ tetrahedra and isolated In^I cations.

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Comment

In our ongoing studies to determine the origin of the stereochemical activity of lone pairs (Mudring & Rieger, 2005), we have attempted to synthesize monovalent indium compounds, since it has been well established that the $5s^2$ electron pair of In^I influences the sterochemistry of the simple monohalides InX (X = Cl, Br or I) (van den Berg, 1966; Meyer & Staffel, 1989; van der Vorst *et al.*, 1978) as well as of the ternary halides, such as InMBr$_4$ (M = Al, Ga or In) (Meyer & Staffel, 1990; Meyer, 1992).

The existence of $InAlCl_4$ was postulated in 1964 from phase analytical investigations of the InCl–$AlCl_3$ system (Levin *et al.*, 1964). The compound was synthesized in 1980 (Meyer & Schwan, 1980). From Guinier–Simon powder X-ray diffraction measurements, it was concluded that $InAlCl_4$ crystallizes like $InGaCl_4$ (Meyer *et al.*, 1990) in the baryte ($BaSO_4$) structure type, but, to date, no reliable X-ray structure determinations of $InAlCl_4$ have been available.

According to the synthetic procedure described here, we were able to obtain crystals of sufficient quality for single-crystal X-ray structure analysis (Fig. 1). As expected, $InAlCl_4$ crystallizes in the baryte structure type (Fig. 2). The main structural feature is the presence of isolated $AlCl_4^-$ tetrahedra, with a mean Al—Cl distance of about 2.12 Å. A noteworthy structural difference between $InAlCl_4$ and $BaSO_4$ occurs insofar as the coordination polyhedron spanned by the Cl^- ions around In^I in $InAlCl_4$ is better described as a strongly distorted octahedron (Fig. 3) compared with the tenfold coordination by O atoms surrounding Ba in $BaSO_4$. Thus, from the coordination of the Cl^- ions around In, a stereochemically active electron pair might be expected. (The mean In—Cl distance is 3.40 Å.) However, a similar coordination polyhedron is found in the isotypic ammonium tetrachloro-

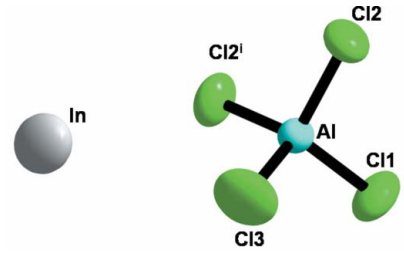

Figure 1
The asymmetric unit-cell contents of the crystal structure of $InAlCl_4$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $x, -y+\frac{3}{2}, z$.]

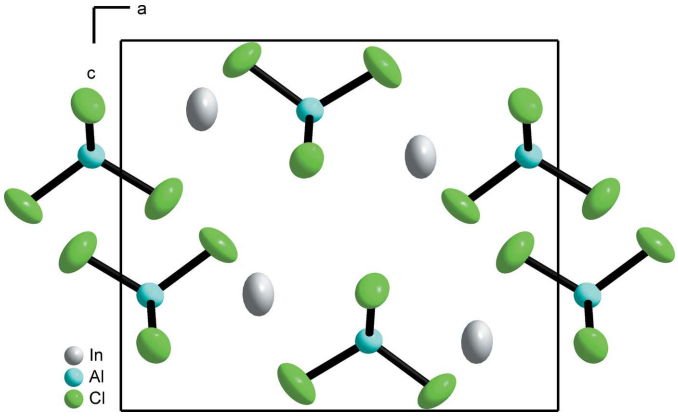

Figure 2
Projection of the unit cell of $InAlCl_4$ along the *b* axis.

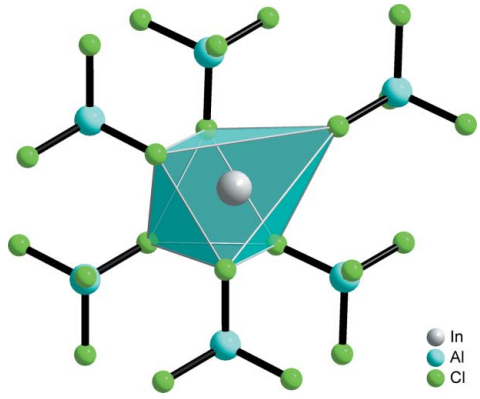

Figure 3
The coordination of In by Cl in $InAlCl_4$.

aluminate, NH_4AlCl_4 (Mairesse *et al.*, 1978). Thus, a stereochemically active electron pair is not likely to be the reason for the coordination environment around indium in $InAlCl_4$.

Experimental

Yellow transparent needle-shaped crystals of $InAlCl_4$ were obtained after reacting a mixture of indium shot (0.1298 g, 1.128 mmol; *ca* 4 mm, 99.99%, Alfa–Aesar), $InCl_3$ (0.125 g, 0.5643 mmol; 99.9%, Aldrich) and $AlCl_3$ (0.2259 g, 1.69 mmol; anhydrous, sublimed, 98%, Merck) in a vacuum-sealed Duran glass ampoule at 523 K (10 K h^{-1}, annealing at this temperature for 168 h) and subsequent slow cooling to room temperature (5 K h^{-1}). After initial inspection under an optical microscope, suitable crystals were sealed in glass capillaries (0.3 mm diameter) and checked by Laue photographs for their quality. All operations were carried out under an inert atmosphere (Ar, MBraun glove-box).

Crystal data

$InAlCl_4$
M_r = 283.60
Orthorhombic, *Pnma*
a = 10.937 (2) Å
b = 7.0519 (12) Å
c = 9.2671 (19) Å
V = 714.7 (2) Å^3
Z = 4
D_x = 2.636 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4273 reflections
θ = 2.8–28.3°
μ = 4.80 mm^{-1}
T = 298 (2) K
Needle, pale yellow
0.3 × 0.2 × 0.1 mm

Data collection

Stoe IPDS-II diffractometer
φ scans
Absorption correction: numerical [*X-RED* (Stoe & Cie, 2002) and *X-SHAPE* (Stoe & Cie, 1999)]
T_{min} = 0.353, T_{max} = 0.609
22140 measured reflections
1353 independent reflections
720 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 32.2°
$h = -16 \rightarrow 16$
$k = -8 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.174
S = 1.09
1353 reflections
35 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 0.8739P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.01 e Å^{-3}
$\Delta\rho_{min}$ = −0.95 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.017 (2)

Table 1
Selected geometric parameters (Å, °).

Al—Cl1	2.119 (3)	Al—Cl3	2.108 (3)
Al—Cl2	2.1256 (17)		
Cl3—Al—Cl1	112.59 (16)	Cl1—Al—Cl2	108.58 (9)
Cl3—Al—Cl2	109.58 (10)	Cl2^{i}—Al—Cl2	107.81 (12)

Symmetry code: (i) $x, -y+\frac{3}{2}, z$.

The highest residual electron-density peak is located 0.87 Å from the In atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXL97*.

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