The electron-density peaks $\Delta\rho_{max}$ and $\Delta\rho_{min}$ are at 0.82 and 0.79 Å from Cd4 and Cd3, respectively.

Data collection: *DIF*4 (Stoe & Cie, 1987). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1995).

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fac-Triaquatrichloroindium(III)

Damian R. Aris, William Errington and Gerald R. Willey

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England. E-mail: w.errington@warwick.ac.uk

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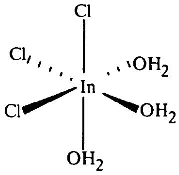
Abstract

The structure of the title compound, $[InCl_3(H_2O)_3]$, features In atoms in a distorted *fac*-octahedral geometry and involves a three-dimensional network of intermolecular hydrogen bonding. It is the first structurally characterized example of a discrete tris-hydrate of a Group 13 M^{III} halide (*M* = B, Al, Ga or In).

Comment

The title compound, (I), was obtained as a side-product from an anaerobic study of indium trichloride with *n*-butyl acetate (3 equivalents) in hexane. This solution was stored at 278 K for several days, resulting in the slow deposition of colourless block-shaped crystals which were stable within the reaction mixture. On removal, the crystals rapidly decomposed (hydrolysis), even under an atmosphere of dry argon. The crystal for the present X-ray study was obtained by manipulating the crystals under a layer of sodium-dried nujol. The trace of water required in the formation of compound (I) was probably derived from the commercial sample of *n*-butyl acetate.



(I)

Although several stable hydrates of the Group 13 trihalides MX_3 (*M* = B, Al, Ga or In; *X* = halogen) are known, structural reports are restricted to anionic forms such as $K[InBr_4(H_2O)_2]$ (Wignacourt *et al.*, 1980) and $Cs_2[InCl_5(H_2O)]$ (Atkinson & Field, 1970). The $InCl_3(H_2O)_3$ moieties in $[fac\text{-}InCl_3(H_2O)_3]\cdot 18\text{-crown-}6$ (Streltsova *et al.*, 1991) and $[fac\text{-}InCl_3(H_2O)_3]\cdot 3(\text{dioxane})$ (Whitlow & Gabe, 1975) feature an extensive network of hydrogen bonding between the coordinated water molecules and the organic ligands which serves to stabilize each complex. Similarly, for $InCl_3\cdot 4H_2O$, it was concluded that an $[InCl_3(H_2O)_2]$ unit was enmeshed in a network of hydrogen bonding incorporating solvate water molecules (Wignacourt *et al.*, 1982).

In the title compound, which contains two molecules in the asymmetric unit (Fig. 1), each six-coordinate metal centre exhibits a distorted *fac*-octahedral geometry, with interligand angle ranges Cl—In—Cl 95.29 (3)–103.65 (3)° and O—In—O 77.71 (9)–83.96 (10)° (Table 1); these values are consistent with a steric effect opening up the angles between the larger ligand atoms. A survey of complexes of indium(III) halides (Knop *et al.*, 1987) predicts the In—Cl bond distance for an $InCl_3$ fragment in a neutral six-coordinate environment to be 2.432 (17) Å, based upon a linear function of the coordination number and the charge. The observed In—Cl bond lengths in the title compound range from 2.4203 (8) to 2.4662 (7) Å; these are within the predicted range, but are perceptibly longer than those reported for the corresponding O-donor complex $[(InCl_3)_2(DME)_3]$ (DME is $CH_3OCH_2CH_2OCH_3$), for which the range is 2.391 (1)–2.404 (2) Å (Carta *et al.*, 1995). The In—O bond distances in (I) are in the range 2.191 (2)–2.224 (2) Å and may be compared with those in similar octahedral In^{III} hydrate systems, *e.g.* 2.313 (8) Å for $[InCl_3(H_2O)(Me_3AsS)_2]$ (Robinson *et al.*, 1988), 2.239 (8) Å for $[InCl_3(bipy)(H_2O)]$ (Malyarick *et al.*, 1992), 2.231 (4) Å for $[InCl_3(Me_3PO)_2(H_2O)]\cdot H_2O$ (Robinson *et al.*, 1990), 2.201 (5) Å for $[In(L^1)Cl(ox)(H_2O)]\cdot 2H_2O$ [L^1 is pyridine-2,6-bis(acetyloxime) and ox is oxalate; Abram *et al.*, 1997] and 2.199–2.283 Å for [*fac*-$InCl_3(H_2O)_3$]·3(dioxane) (Whitlow & Gabe, 1975).

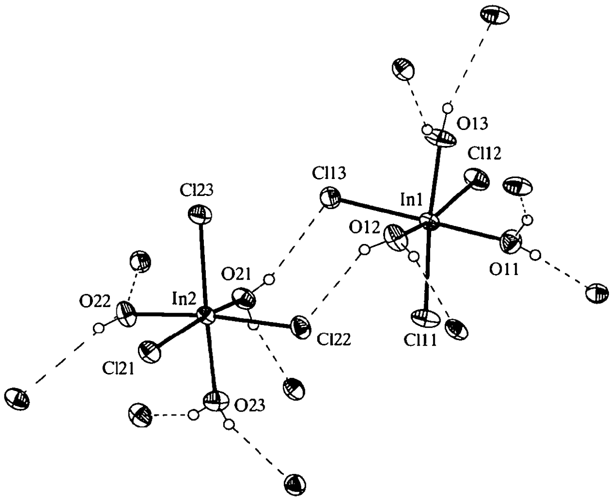


Fig. 1. View of the structure of (I) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Interestingly, the tris-solvate $[InCl_3(thf)_3]$ (thf is tetrahydrofuran) exhibits a six-coordinate *mer*-octahedral geometry (Wells *et al.*, 1994), with a mean In—Cl distance of 2.422 Å. The variation in geometry from *fac*- to *mer*- (in changing the ligand from water to thf) is presumably due to the increased steric demands of the thf ligands. However, this must be a borderline situation because, under less forcing conditions, the $InCl_3$–thf system also forms the bis-adduct, which exhibits five-coordinate trigonal bipyramidal geometry, with the two *trans*-thf ligands in axial positions (Self *et al.*, 1993) and a mean In—Cl distance of 2.321 Å. With more bulky ligands, such as Me_3N, only five-coordinate adducts are known, *e.g.* $[InCl_3(Me_3N)_2]$ is identified as trigonal bipyramidal with *trans*-trimethylamine groups (Karia *et al.*, 1986) and a mean In—Cl distance of 2.360 Å.

Unexpectedly, all the H atoms were located from electron-density maps; during refinement they were restrained to give common O—H and H···H distances. Each water molecule is hydrogen bonded to two Cl atoms, thereby producing an infinite three-dimensional structure. The O···Cl hydrogen-bonded distances (Table 2) are comparable with or less than the sum of the van der Waals radii (2.27 Å; Bondi, 1964). The O—H···Cl angles are in the range 134 (4)–171 (3)°, but these are unlikely to be accurate in such a system.

Experimental

n-Butyl acetate (0.90 ml, 6.8 mmol) was added to a suspension of $InCl_3$ (0.50 g, 2.26 mmol) in hexane (30 ml) under argon, and the reaction mixture was heated at 333 K for 12 h. The resulting colourless solution was concentrated and stored at 278 K for several days, yielding crystals of the title compound (approximate yield of 7%). Satisfactory microanalytical data could not be obtained.

Crystal data

$[InCl_3(H_2O)_3]$
$M_r = 275.22$
Monoclinic
$P2_1/n$
$a = 12.0332 (6)$ Å
$b = 10.5925 (6)$ Å
$c = 12.1984 (7)$ Å
$\beta = 107.432 (3)^\circ$
$V = 1483.42 (14)$ Å^3
$Z = 8$
$D_x = 2.465$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6887 reflections
$\theta = 2.09$–25.99°
$\mu = 4.188$ mm^{-1}
$T = 200 (2)$ K
Block
0.38 × 0.36 × 0.26 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.226$, $T_{max} = 0.337$
7552 measured reflections
2871 independent reflections

2443 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 26^\circ$
$h = -14 \rightarrow 14$
$k = -13 \rightarrow 12$
$l = -15 \rightarrow 10$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.048$
$S = 0.977$
2871 reflections
175 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.682$ e Å^{-3}
$\Delta\rho_{min} = -0.993$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

In1—O12	2.191 (2)	In2—O22	2.205 (2)
In1—O11	2.207 (2)	In2—O21	2.223 (2)
In1—O13	2.217 (2)	In2—O23	2.224 (2)
In1—Cl12	2.4232 (8)	In2—Cl23	2.4203 (8)
In1—Cl11	2.4358 (8)	In2—Cl22	2.4403 (7)
In1—Cl13	2.4662 (7)	In2—Cl21	2.4568 (7)

O12—In1—O11	81.26 (10)	O22—In2—O21	81.08 (9)
O12—In1—O13	77.72 (9)	O22—In2—O23	83.96 (10)
O11—In1—O13	83.13 (10)	O21—In2—O23	77.71 (9)
O12—In1—Cl12	163.54 (7)	O22—In2—Cl23	90.42 (7)
O11—In1—Cl12	93.16 (7)	O21—In2—Cl23	87.34 (7)
O13—In1—Cl12	86.27 (7)	O23—In2—Cl23	164.66 (7)
O12—In1—Cl11	95.81 (7)	O22—In2—Cl22	170.13 (7)
O11—In1—Cl11	88.22 (7)	O21—In2—Cl22	92.55 (6)
O13—In1—Cl11	169.86 (7)	O23—In2—Cl22	87.32 (7)
Cl12—In1—Cl11	99.50 (3)	Cl23—In2—Cl22	96.85 (3)
O12—In1—Cl13	87.82 (7)	O22—In2—Cl21	87.52 (7)
O11—In1—Cl13	168.82 (7)	O21—In2—Cl21	164.26 (7)
O13—In1—Cl13	92.27 (7)	O23—In2—Cl21	90.39 (7)
Cl12—In1—Cl13	96.71 (3)	Cl23—In2—Cl21	103.65 (3)
Cl11—In1—Cl13	95.29 (3)	Cl22—In2—Cl21	97.20 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11*A*···Cl23^{i}	0.785 (18)	2.379 (19)	3.157 (3)	171 (3)
O11—H11*B*···Cl11^{ii}	0.779 (19)	2.67 (3)	3.260 (3)	134 (4)
O12—H12*A*···Cl22	0.786 (19)	2.42 (3)	3.129 (3)	150 (4)
O12—H12*B*···Cl12^{ii}	0.79 (2)	2.43 (2)	3.210 (3)	167 (4)
O13—H13*A*···Cl21^{iii}	0.795 (18)	2.46 (2)	3.208 (2)	158 (3)
O13—H13*B*···Cl11^{iv}	0.781 (18)	2.48 (2)	3.214 (3)	158 (3)
O21—H21*A*···Cl13	0.75 (2)	2.42 (2)	3.149 (3)	164 (5)
O21—H21*B*···Cl21^{v}	0.762 (19)	2.48 (2)	3.220 (2)	164 (5)
O22—H22*A*···Cl13^{vi}	0.750 (19)	2.56 (2)	3.285 (3)	164 (4)
O22—H22*B*···Cl12^{vii}	0.751 (19)	2.56 (2)	3.283 (3)	161 (4)
O23—H23*A*···Cl13^{viii}	0.765 (19)	2.50 (2)	3.242 (3)	165 (4)
O23—H23*B*···Cl22^{v}	0.75 (2)	2.58 (3)	3.236 (3)	147 (4)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, 1-y, 1-z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (vi) $1-x, -y, 1-z$; (vii) $x, y, 1+z$; (viii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

H atoms were located from electron-density maps and refined using restraints to equalize the O—H distances. They were given isotropic displacement parameters and allowed to refine.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* . Software used to prepare material for publication: *SHELXTL/PC*.

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Rb_2MoS_4

Jan Ellermeier, Christian Näther and Wolfgang Bensch

Institut für Anorganische Chemie, Christian-Albrechts Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany. E-mail: wbensch@ac.uni-kiel.de

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Abstract

The reaction of $(NH_4)_2MoS_4$, AgI, RbI and S in 1,2-ethanediamine under solvothermal conditions yields red crystals of Rb_2MoS_4, dirubidium tetrasulfidomolybdate(2−), as a minor phase and black powdered Ag_2S as the main product. Rb_2MoS_4 crystallizes like Cs_2MoS_4 and $(NH_4)_2MoS_4$ in the β-K_2SO_4 type. The structure contains tetrahedral $[MoS_4]^{2-}$ anions which are connected *via* Rb^+ cations.

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