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Pentaamminechlorogallium(III) dichloride

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean *σ*(a–N) = 0.003 Å
R factor = 0.022
wR factor = 0.053
Data-to-parameter ratio = 14.1

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

Crystals of the title compound, $[Ga(NH_3)_5Cl]Cl_2$, were prepared from 1-butyl-3-methylimidazolium chloride and $GaCl_3$. The crystal structure is isotypic with $[Al(NH_3)_5Cl]Cl_2$ and other members of the series $[M(NH_3)_5Cl]Cl_2$, with M = Cr, Co, Rh, Ir, Ru or Os. It consists of discrete cationic $[Ga(NH_3)_5Cl]^{2+}$ octahedra and Cl^- anions arranged in motifs related to the K_2PtCl_6 structure type. In the cation, the Ga atom, one Cl atom and three N atoms are located on a mirror plane.

Comment

We have synthesized the new gallium(III) complex $[Ga(NH_3)_5Cl]Cl_2$. This compound is expected to be an effective inorganic precursor for the preparation of the (III,V) semiconductor GaN by thermal decomposition under specific conditions. The crystal structure analysis may also give details to enable the derivation of the structure of the soluble species or the local coordination around the Ga atom in supercritical ammonia fluid, which is curently used for the single-crystal growth of GaN by the ammonothermal method with the base mineralizer NH_4Cl (Yoshikawa *et al.*, 2004).

The crystal structure of the title compound is isotypic with $[Al(NH_3)_5X]X_2$ (X = Cl or Br; Jacobs & Schröder, 2002) and with other members of the series $[M(NH_3)_5Cl]Cl_2$ (M = Cr, Co, Rh, Ir, Ru or Os; Hambley & Lay, 1986). Fig. 1 illustrates the arrangement around the Ga atom. It is octahedrally coordinated by one Cl atom and five NH_3 molecules, with Ga—N distances ranging from 2.055 (2) to 2.076 (3) Å (Table 1). These values are close to the Ga—N distance of 2.006 (5) Å

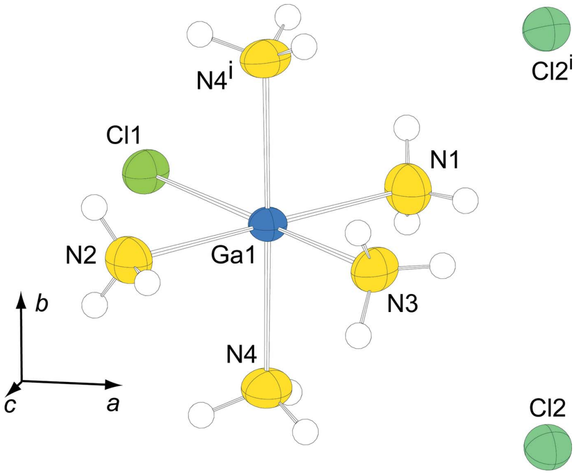

Figure 1
The structure and the atom labelling of the $[Ga(NH_3)_5Cl]^{2+}$ octahedron and the anions in the $[Ga(NH_3)_5Cl]Cl_2$ structure. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes as in Table 1.

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reported for $Ga(NH_3)_2F_3$, where the Ga atoms are octahedrally coordinated by two NH_3 molecules and four F atoms (Roos & Meyer, 1999). Covalent bonds between *M* and Cl atoms, with *M*—Cl bond lengths of 2.286–2.371 Å, were discussed for $[M(NH_3)_5Cl]Cl_2$ compounds (*M* = Cr, Co, Rh, Ir, Ru or Os; Hambley & Lay, 1986). The Ga—Cl distance in $[Ga(NH_3)_5Cl]^{2+}$ of 2.3840 (11) Å is somewhat longer than these values, but significantly longer than the Ga^{III}—Cl distances of 2.159 (2) and 2.184 (2) Å reported for $Ga^{I}Ga^{III}Cl_4$ (Wilkinson *et al.*, 1991). The Ga and Cl atoms, together with three ammine ligands, lie on a mirror plane.

As shown in Fig. 2, the cationic $[Ga(NH_3)_5Cl]^{2+}$ octahedra are surrounded by distorted cubes of Cl^- anions at the Cl2 sites, resembling the structural motifs of the K_2PtCl_6 structure type (Jacobs & Schröder, 2002). Each facet of one octahedron is capped with a Cl2 atom, and one of the rectangular faces of the Cl2 cube is larger than the others, due to the presence of atom Cl1 near its centre.

The ionic bonding interaction between the $[Ga(NH_3)_5Cl]^{2+}$ octahedra and the Cl^- anions is complemented by N—H···Cl hydrogen bonds (Table 2). Atom Cl2 is surrounded by ten NH_3 molecules, with N—Cl2 donor–acceptor distances ranging from 3.353 (2) to 3.683 (3) Å. These values are in accordance with the N—Cl distances reported for $[Al(NH_3)_5Cl]Cl_2$ [3.382 (2)–3.703 (4) Å] and for the series $[M(NH_3)_5Cl]Cl_2$ (3.433–3.457 Å) with *M* = Cr, Co, Rh, Ir, Ru or Os.

Experimental

1-Butyl-3-methylimidazolium chloride, [bmim]Cl, was dissolved in water to prepare an approximately 80% wt solution, to which $GaCl_3$ (9 g) was slowly added. In the course of dissolving $GaCl_3$, it reacted with [bmim]Cl and formed 1-butyl-3-methylimidazolium tetrachlorogallate, $[bmim]GaCl_4$. As the reaction proceeded, a liquid–liquid phase separation occurred. The upper liquid phase, containing the [bmim]Cl aqueous solution, was separated by decantation from the lower phase, containing $[bmim]GaCl_4$ and [bmim]Cl. An amount (10 g) of the lower phase was mixed with NH_4Cl (10 g) and sealed in a stainless steel tube (2.5 cm diameter, 27 cm long) with stainless steel caps. The sealed tube was then heated to 840 K, while the temperature of the top seal cap was held at about 640 K. These temperatures were maintained for 6 h before the tube was cooled to room temperature. Transparent triangular crystals with a size between 0.1 and 1.0 mm, and yellow crystals with a size less than 50 µm, were obtained on the inside of the top cap. The two types of single crystals were selected in a glove box and sealed in argon-filled glass capillaries. Whereas the diffraction data obtained from the colourless crystals of the title compound were of satisfactory quality, diffraction data of the yellow crystals were not of sufficient quality to identify the compound or to refine its crystal structure.

Crystal data

$[Ga(NH_3)_5Cl]Cl_2$
$M_r = 261.24$
Orthorhombic, *Pnma*
$a = 13.448\ (6)$ Å
$b = 10.518\ (5)$ Å
$c = 6.750\ (4)$ Å
$V = 954.8\ (8)$ Å^3
$Z = 4$
$D_x = 1.817$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 3.66$ mm^{-1}
$T = 295\ (2)$ K
Block, colourless
0.18 × 0.17 × 0.10 mm

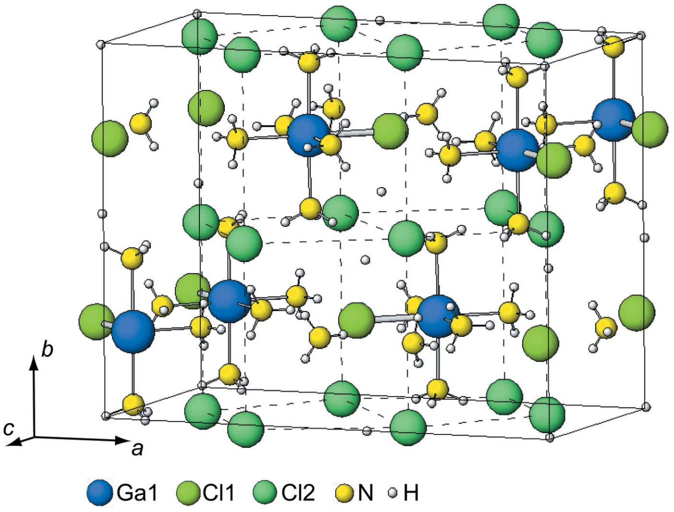

Figure 2
The arrangement of the cationic $[Ga(NH_3)_5Cl]^{2+}$ octahedra and of the distorted cubes of Cl^- cubes (dotted lines) in the crystal structure of $[Ga(NH_3)_5Cl]Cl_2$. All atoms are drawn as spheres of arbitrary radii.

Data collection

Rigaku R-AXIS RAPID-II IP camera
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
$T_{min} = 0.476$, $T_{max} = 0.577$
8938 measured reflections
1157 independent reflections
1041 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.053$
$S = 1.07$
1157 reflections
82 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.3606P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—Ga1	2.3840 (11)	Ga1—N1	2.073 (3)
Ga1—N4	2.055 (2)	Ga1—N3	2.076 (3)
Ga1—N2	2.072 (3)		
N1—Ga1—N3	89.73 (13)	N4—Ga1—N4^{i}	177.91 (12)
N1—Ga1—Cl1	89.89 (10)	N4—Ga1—N2	90.10 (6)
N2—Ga1—N3	89.57 (13)	N4—Ga1—N1	89.91 (6)
N2—Ga1—N1	179.30 (13)	N4—Ga1—N3	91.04 (6)
N2—Ga1—Cl1	90.80 (10)	N4—Ga1—Cl1	88.96 (6)
N3—Ga1—Cl1	179.63 (9)		

Symmetry code: (i) $x, -y + \frac{1}{2}, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl2	0.79 (6)	3.10 (4)	3.561 (3)	120.0 (16)
N1—H2···Cl2^{ii}	0.77 (4)	2.62 (4)	3.385 (2)	172 (4)
N2—H3···Cl2^{iii}	0.85 (6)	3.20 (3)	3.683 (3)	118.2 (17)
N2—H4···Cl2^{iv}	0.74 (3)	2.61 (3)	3.353 (2)	172 (3)
N3—H5···Cl2	0.81 (6)	3.04 (3)	3.486 (2)	116.9 (16)
N3—H6···Cl2^{iii}	0.85 (4)	2.58 (4)	3.398 (2)	164 (3)

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{N4-H7}\cdots\mathrm{Cl2^{iv}}$	0.83 (4)	2.77 (4)	3.575 (3)	162 (3)
$\mathrm{N4-H8}\cdots\mathrm{Cl2^{ii}}$	0.77 (4)	2.83 (4)	3.578 (3)	164 (3)
$\mathrm{N4-H9}\cdots\mathrm{Cl2^{iii}}$	0.81 (5)	2.81 (5)	3.383 (3)	129 (4)
$\mathrm{N4-H9}\cdots\mathrm{Cl2}$	0.81 (5)	2.86 (4)	3.405 (3)	126 (4)

Symmetry codes: (ii) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, y, -z+\frac{1}{2}$.

The structure was refined using the coordinates of the isotypic compound $[\mathrm{Al(NH_3)_5Cl}]\mathrm{Cl_2}$ (Jacobs & Schröder, 2002) as starting parameters. For the final model, some of these coordinates were then transformed to create a set with connected atoms. The positions of the H atoms of the $\mathrm{NH_3}$ ligands were refined freely except for the constraints of the mirror plane.

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2005); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); method used to solve structure: coordinates taken from an isotypic structure (Jacobs & Schröder, 2002); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2005); software used to prepare material for publication: *SHELXL97*.

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