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## Key indicators

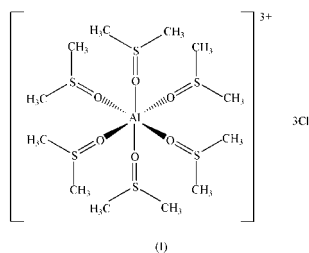
Single-crystal X-ray study  
T = 150 K  
Mean  $\sigma(\text{Al}-\text{O}) = 0.001 \text{ \AA}$   
R factor = 0.026  
wR factor = 0.068  
Data-to-parameter ratio = 30.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Hexakis(dimethyl sulfoxide- $\kappa\text{O}$ )aluminium(III)  
trichloride

The title compound,  $[\text{Al}\{(\text{CH}_3)_2\text{SO}\}_6]\text{Cl}_3$ , crystallizes in the trigonal space group  $R\bar{3}$ . In this structure, the O atoms of six dimethyl sulfoxide (DMSO) molecules are bonded to the  $\text{Al}^{3+}$  ion in the form of a trigonally distorted octahedron. The  $\text{Al}^{3+}$  ion is situated at special site  $3b$  (symmetry  $\bar{3}$ ), while the  $\text{Cl}^-$  ions are situated at special sites  $3a$  and  $6c$  (symmetries  $\bar{3}$  and  $3$ ). Considering only the  $\text{Al}^{3+}$  ions separately, they are arranged in a slightly distorted cubic close-packed arrangement. In this crystal structure, the  $\text{Cl}^-$  ions occupy both the tetrahedral sites and the octahedral sites, giving a  $\text{Cl}^-:\text{Al}^{3+}$  ratio of 3:1. This geometric condition results in a distorted rhombododecahedral arrangement of  $\text{Cl}^-$  ions around the  $\text{Al}^{3+}$  ions.

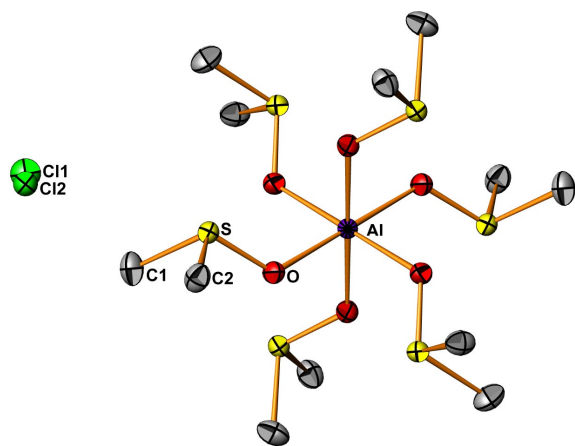
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## Comment

As part of a continuing research project, equilibria and speciation in the aqueous aluminium(III)/propionic system have been investigated. This system is dominated by one single complex, namely  $[\text{Al}_2(\text{OH})_2(\text{CH}_3\text{CH}_2\text{COO})]^{3+}$ , according to a potentiometric study by Marklund *et al.* (1989). Our original aim was to crystallize this complex and determine its structure. However, our efforts resulted in a crystal containing the title compound, (I). The structure is composed of discrete  $\text{Al}(\text{DMSO})_6^{3+}$  units and two structurally different chloride ions, and is isostructural with  $[\text{In}((\text{CH}_3)_2\text{SO})_6](\text{ClO}_4)_3$  (Harrowfield *et al.*, 1990).



Dimethyl sulfoxide (DMSO) is known to coordinate metal ions through either the O or S atom. As expected from the typically 'hard' character of the  $\text{Al}^{\text{III}}$  ion, in this case, the bonding is through oxygen. The coordination polyhedron of aluminium(III) is a trigonally distorted octahedron. In an extensive review of metal ion DMSO complexes, Calligaris & Carugo (1996) presented mean values for important bond distances and angles typical for the different coordination modes of DMSO. Distances and angles in (I) are in good agreement with what can be expected for a typical oxygen-coordinated DMSO-metal complex. Considering  $\text{Al}^{3+}$  separately, they are arranged in a slightly trigonally distorted cubic close-packed arrangement, at special site  $3b$ , with site symmetry  $\bar{3}$ . Within this arrangement, the  $\text{Cl}^-$  ions occupy



**Figure 1**

A view of the title cation and the two symmetry-independent chloride ions, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

both the tetrahedral sites and the octahedral sites ( $3a$  and  $6c$ , with site symmetries  $\bar{3}$  and  $3$ ), giving a  $\text{Cl}^-:\text{Al}^{3+}$  ratio of 3:1. This geometric condition results in a distorted rhombododecahedral arrangement of  $\text{Cl}^-$  ions around the  $\text{Al}^{3+}$  ions. The crystal structure is held together by electrostatic interactions between the  $[\text{Al}(\text{DMSO})_6]^{3+}$  complex and the  $\text{Cl}^-$  ions.

## Experimental

A solution with  $[\text{Al}^{\text{III}}]_{\text{tot}} = 0.6 \text{ M}$  and  $[\text{propionic acid}]_{\text{tot}} = 0.3 \text{ M}$ , at pH 3.7, was prepared; see Karlsson (1998) for further details. A tenfold excess of DMSO was added to this solution, which was put in a refrigerator at 277 K. After approximately three years of extremely slow evaporation, colourless crystals of appropriate dimensions had formed.

### Crystal data

$[\text{Al}(\text{C}_2\text{H}_6\text{OS})_6]\text{Cl}_3$   
 $M_r = 602.14$   
 Trigonal,  $R\bar{3}$   
 $a = 10.3760$  (6) Å  
 $c = 22.0210$  (12) Å  
 $V = 2053.2$  (2) Å<sup>3</sup>  
 $Z = 3$   
 $D_x = 1.461 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 1340 reflections  
 $\theta = 3.0\text{--}30.0^\circ$   
 $\mu = 0.85 \text{ mm}^{-1}$   
 $T = 150 \text{ K}$   
 Fragment, colourless  
 $0.25 \times 0.20 \times 0.15 \text{ mm}$

### Data collection

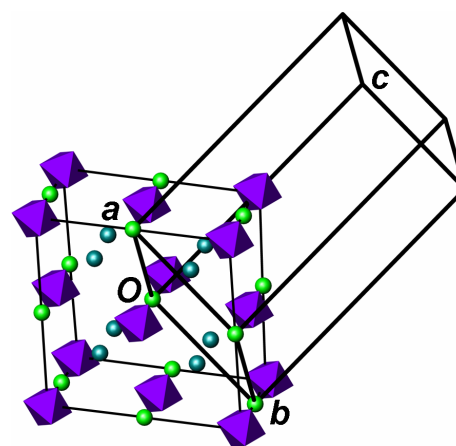
Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (HKL SCALEPACK; Otwinowski & Minor, 1997)  
 $T_{\text{min}} = 0.816$ ,  $T_{\text{max}} = 0.883$   
 2680 measured reflections

1340 independent reflections  
 1266 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.012$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -14 \rightarrow 14$   
 $l = -30 \rightarrow 30$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.068$   
 $S = 1.11$   
 1340 reflections  
 44 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 2.3297P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0018 (3)



**Figure 2**

A view of the packing of the structure, showing a face-centred pseudo-cube of octahedra, illustrating the presence of a trigonally distorted cubic closed-packed arrangement of the complexes. To facilitate the illustration of the packing, all atoms apart from Al and O in the complex (violet octahedra) and  $\text{Cl}^-$  ions (green spheres) have been omitted. The Cl ions occupy all the interstitial octahedral sites (light-green spheres), as well as the tetrahedral sites (dark-green spheres) in this distorted cubic close-packed arrangement, forming a 3:1 ratio of  $\text{Cl}^-$  to  $\text{Al}^{3+}$ .

**Table 1**

Selected geometric parameters (Å, °).

Cl—S	1.7751 (13)	S—O	1.5427 (8)
C2—S	1.7715 (12)	Al—O	1.8880 (8)
$\text{O}^i\text{—Al—O}$	88.48 (4)	$\text{O}^{ii}\text{—Al—O}$	91.52 (4)

Symmetry codes: (i)  $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$ ; (ii)  $1 - y, 1 + x - y, z$ .

The H atoms of the methyl groups were located in a difference Fourier map and were refined using a riding model, with  $U_{\text{(iso)}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , with C—H distances idealised to  $0.96 \text{ \AA}$ .

Data collection: COLLECT (Nonius, 1999); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Dowty, 2000); software used to prepare material for publication: SHELXL97 and local programs.

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