

# Dichlorotetrakis(tetrahydrofuran)aluminium trichloroethylaluminate

Radek Sluka,<sup>a</sup> Marek Nečas<sup>b\*</sup>  
and Pavel Šindelář<sup>a</sup>

<sup>a</sup>Polymer Institute Brno, Tkalcovská 36/2, 656 49 Brno, Czech Republic, and <sup>b</sup>Department of Inorganic Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Correspondence e-mail: man@chemi.muni.cz

## Key indicators

Single-crystal X-ray study

$T = 120\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

$R$  factor = 0.036

$wR$  factor = 0.096

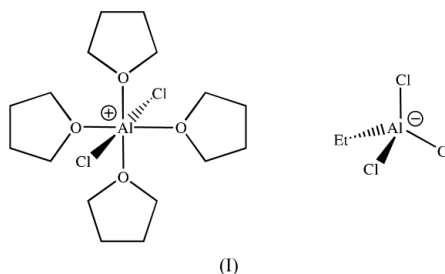
Data-to-parameter ratio = 17.1

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

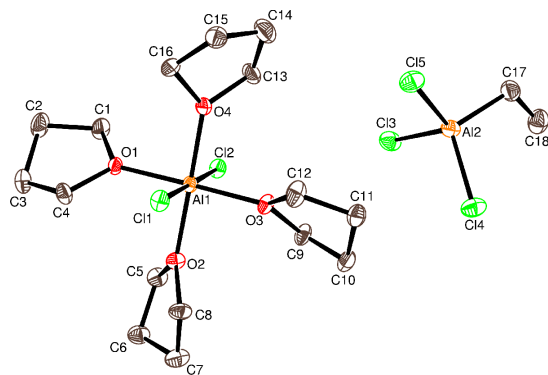
The title compound,  $[\text{AlCl}_2(\text{C}_4\text{H}_8\text{O})_4][\text{AlCl}_3(\text{C}_2\text{H}_5)]$ , was prepared by the unsymmetrical cleavage reaction of the  $\text{EtAlCl}_2$  dimer with tetrahydrofuran (THF). The  $[\text{AlCl}_2(\text{THF})_4]^+$  cation forms an approximately regular octahedron, and the  $[\text{AlCl}_3\text{Et}]^-$  anion is tetrahedral.

## Comment

Because of the anticipated catalytic properties in polymerization processes, cationic complexes of aluminium with Lewis bases have attracted well deserved attention in the past few years, and there is a useful review available, summarizing different synthetic routes of their formation (Atwood, 1998). The action of Lewis bases towards  $\text{AlCl}_3$  and its alkyl derivatives generally results in either symmetrical or unsymmetrical dissociation of the dimers, the former leading to neutral donor-acceptor complexes or complex cations with displaced halides as anionic counterparts, while the latter affords complex ions, based on central aluminium atoms. Whether the dimer will dissociate in a symmetrical or unsymmetrical manner depends on a number of factors, including the halide type and steric requirements of the organic ligands.

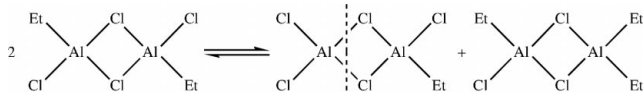


In the present work,  $[\text{AlCl}_2(\text{THF})_4][\text{AlCl}_3\text{Et}]$  (THF is tetrahydrofuran), (I), was isolated from a mixture of  $\text{EtAlCl}_2$  and THF. It is thus legitimate to consider the redistribution reactions in  $\text{EtAlCl}_2$  solution, leading to intermediates capable of  $[\text{AlCl}_2(\text{THF})_4][\text{AlCl}_3\text{Et}]$  formation upon unsymmetrical dissociation (see scheme below). In a similar way, the  $\text{EtAlCl}_2$  dimer has been previously treated with a pentadentate macrocyclic ether, yielding the analogous complex  $[\text{AlCl}_2(\text{benzo-15-crown-5})][\text{AlCl}_3\text{Et}]$  (Bott *et al.*, 1985). The interactions of monodentate THF with dimeric aluminium species were tested several times, with ambiguous conclusions. Spectroscopic investigations of a saturated THF solution of  $\text{AlCl}_3$  by Derouault *et al.* (1977) mainly revealed the presence of neutral adducts  $\text{AlCl}_3\cdot\text{THF}$  and  $\text{AlCl}_3\cdot 2\text{THF}$ , the latter being slightly ionized into  $[\text{AlCl}_2(\text{THF})_4][\text{AlCl}_4]$ . The ionic salt was later isolated as the only product in the reaction of stoichiometric quantities of  $\text{AlCl}_3$  with THF by Means *et al.*


**Figure 1**

A perspective view of  $[\text{AlCl}_2(\text{THF})_4][\text{AlCl}_3\text{Et}]$ , with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

(1987), and its structure was confirmed by an X-ray single-crystal diffraction study. The neutral adducts  $\text{AlCl}_3 \cdot \text{THF}$  and  $\text{AlCl}_3 \cdot 2\text{THF}$  were prepared in indirect ways, and their structures were also determined (Engelhardt *et al.*, 1996; Cowley *et al.*, 1981). This result demonstrates that even a very simple system may show a range of complicated equilibria and that the isolated products strongly depend upon the reaction conditions involved. It is therefore interesting to study the reactions of THF with other dimeric  $R_n\text{AlX}_{3-n}$  compounds with respect to the principal products and mechanisms of their formation.



Both ions of the title compound have been involved separately as counter-ions in different substances; however, dichlorotetrakis(tetrahydrofuran)aluminium trichloroethylaluminate is the first crystallographically characterized example of these ions forming a single compound. According to the Cambridge Structural Database (Version 5.25, January 2004 update), four crystallographically characterized  $[\text{AlCl}_2(\text{THF})_4]^+$  units are known, three times in  $[\text{AlCl}_2(\text{THF})_4][\text{AlCl}_4]$ ; the  $[\text{AlCl}_3\text{Et}]^-$  anion occurs in six cases (Allen, 2002).

In the cation, the  $\text{AlCl}_2\text{O}_4$  core is almost perfectly octahedral, and the Al–Cl and Al–O distances average 2.244 (1) and 1.939 (4) Å, respectively. All the THF ligands adopt an envelope conformation. The mean Al–Cl bond length in the anion is about 0.083 Å shorter than that in the cation. Apparently, there is a slight distortion from ideal tetrahedral geometry because of the presence of the ethyl group, with a mean C–Al–Cl value of 111.6 (1)°. The Cl5–Al2–C17–C18 dihedral angle is 176.9 (2)°. Such an *anti* conformation is typical for the other crystallographically characterized examples of the  $[\text{AlCl}_3\text{Et}]^-$  anion, with the exception of the above-mentioned complex with benzo-15-crown-5, in which case the corresponding dihedral angle is 5.4°.

## Experimental

The synthesis was carried out under anhydrous conditions of dry nitrogen using conventional Schlenk techniques. A solution of  $\text{EtAlCl}_2$  (369.5 mg, 2.91 mmol) in heptane (3.0 ml) was added to THF (10 ml) with stirring. The colorless mixture was stirred for 1 h and then concentrated to 2 ml. Colorless crystals were obtained after three weeks at 253 K.

### Crystal data

$[\text{AlCl}_2(\text{C}_4\text{H}_8\text{O})_4][\text{AlCl}_3(\text{C}_2\text{H}_5)]$   
 $M_r = 548.69$   
 Monoclinic,  $P2_1/c$   
 $a = 8.8285$  (17) Å  
 $b = 20.225$  (3) Å  
 $c = 14.638$  (3) Å  
 $\beta = 91.353$  (15)°  
 $V = 2613.0$  (8) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.395$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 60 reflections  
 $\theta = 8.2\text{--}25.4^\circ$   
 $\mu = 0.64$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Prism, colorless  
 0.40 × 0.40 × 0.15 mm

### Data collection

Kuma KM-4 CCD diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 15493 measured reflections  
 4485 independent reflections  
 3905 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -19 \rightarrow 24$   
 $l = -17 \rightarrow 16$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.096$   
 $S = 1.09$   
 4485 reflections  
 262 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.2019P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.35$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>

H atoms were treated as riding, with C–H distance of 0.98 and 0.99 Å. The  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}(\text{C})$  for  $\text{CH}_2$  groups, and at  $1.5U_{\text{eq}}(\text{C})$  for terminal  $\text{CH}_3$  groups.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the Ministry of Education of the Czech Republic (MSM 143100011) and by the Grant Agency of the Czech Republic (203/02/0436 and 203/04/0296).

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.  
 Atwood, D. A. (1998). *Coord. Chem. Rev.* **176**, 407–430.  
 Bott, S. G., Elgamil, H. & Atwood, J. L. (1985). *J. Am. Chem. Soc.* **107**, 1796–1797.  
 Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Cowley, A. H., Cushner, M. C., Davis, R. E. & Riley, P. E. (1981). *Inorg. Chem.* **20**, 1179–1181.  
 Derouault, J., Granger, P. & Forel, M. T. (1977). *Inorg. Chem.* **16**, 3214–3218.  
 Engelhardt, L. M., Junk, P. C., Raston, C. L., Skelton, B. W. & White, A. H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3297–3301.  
 Means, N. C., Means, C. M., Bott, S. G. & Atwood, J. L. (1987). *Inorg. Chem.* **26**, 1466–1468.  
 Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.