

Pentaacetonitrilebromoaluminium(III) bis[tetrabromoaluminium(III)] acetonitrile solvate

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Received 14 May 2003

Accepted 22 May 2003

Online 30 June 2003

Anhydrous aluminium(III) tribromide crystallizes from acetonitrile as a disolvate, $\text{AlBr}_3 \cdot 2\text{MeCN}$, in the form $[\text{AlBr}(\text{C}_2\text{H}_3\text{N})_5][\text{AlBr}_4]_2 \cdot \text{C}_2\text{H}_3\text{N}$, which is isomorphous with its orthorhombic chloride counterpart.

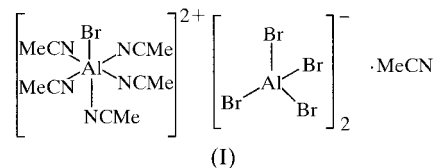
Comment

Aluminium trichloride crystallizes from acetonitrile as the acetonitrile disolvate $\text{AlCl}_3 \cdot 2\text{MeCN}$ (orthorhombic, space group $P2_12_12_1$), which has been shown to be of the form $[\text{AlCl}(\text{NCMe})_5][\text{AlCl}_4]_2 \cdot \text{MeCN}$ ($Z = 4$) by a single-crystal X-ray study (Beattie *et al.*, 1979). By contrast, $\text{FeCl}_3 \cdot 2\text{MeCN}$ (orthorhombic, $Pna2_1$) is of the form *cis*- $[\text{FeCl}_2(\text{NCMe})_4][\text{FeCl}_4]$ ($Z = 4$), while a stoichiometric mixed-metal adduct, $\text{AlCl}_3 \cdot 2\text{FeCl}_3 \cdot 6\text{MeCN}$, can be crystallized in the $P2_12_12_1$ form ($Z = 4$) as $[\text{AlCl}(\text{NCMe})_5][\text{FeCl}_4]_2 \cdot \text{MeCN}$ (Gao *et al.*, 1993). While the form of the cation differs between the pure aluminium and iron complexes, it may be that the difference in form is influenced by increased metal–halide distances throughout the transition, and in this context it is of interest to consider the nature of crystalline material deposited from solutions of aluminium bromide in acetonitrile.

The title compound, (I) (Fig. 1), was found to be isostructural with $\text{AlCl}_3 \cdot 2\text{MeCN}$, the coordinate setting of the former being a connected set based on that of the latter. The volumes of the $\text{AlCl}_3 \cdot 2\text{MeCN}$, $\text{FeCl}_3 \cdot 2\text{MeCN}$ and $\text{AlBr}_3 \cdot 2\text{MeCN}$ units are 258.6, 253.3 (both at 295 K) and 269.0 Å³ (153 K), respectively, while for $\text{AlCl}_3 \cdot 2\text{FeCl}_3 \cdot 6\text{MeCN}$ (295 K), the corresponding value is 257.0 Å³. The present value, even at low temperature, thus exceeds those of all counterpart room-temperature structures by a considerable margin, suggesting that packing volume is not a prime determinant of the struc-

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tural type. The structure of the anion is similar to numerous precedents; in the cation, the Al–N distance *trans* to the halide in (I) [2.003 (7) Å; Table 1] is comparable to the counterpart value in the chloride analogue [2.021 (8) Å] and is



longer than the other Al–N distances in both cases. The present determination appears to be the first that describes bromine coordinated to ‘octahedral’ aluminium(III).

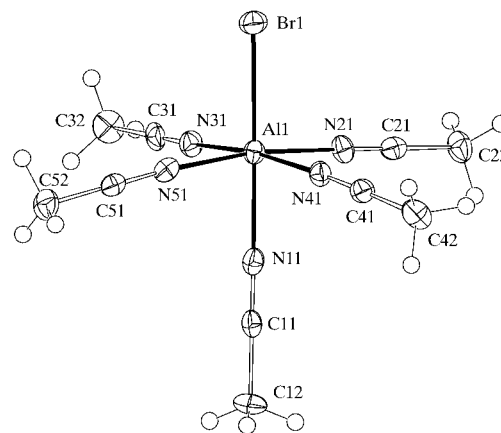


Figure 1

A projection of the cation, showing displacement ellipsoids at the 50% probability level for non-H atoms. H atoms are shown with arbitrary radii of 0.1 Å.

Experimental

Dry acetone (*ca* 5 ml) was added to a small sample (*ca* 0.1 g) of aluminium tribromide in a Schlenk flask and dissolved exothermically, giving a clear solution. The excess solvent was reduced *in vacuo* and the final residue was recrystallized from a few drops, being very soluble. The crystals in isolation from the mother liquor readily decompose on exposure to the atmosphere.

Crystal data

$[\text{AlBr}(\text{C}_2\text{H}_3\text{N})_5][\text{AlBr}_4]_2 \cdot \text{C}_2\text{H}_3\text{N}$
 $M_r = 1046.4$
 Orthorhombic, $P2_12_12_1$
 $a = 10.406$ (1) Å
 $b = 14.479$ (2) Å
 $c = 21.421$ (3) Å
 $V = 3227.5$ (7) Å³
 $Z = 4$
 $D_x = 2.153$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 6185 reflections
 $\theta = 2.6$ – 26.4°
 $\mu = 11.27$ mm⁻¹
 $T = 150$ (2) K
 Block, colourless
 $0.18 \times 0.15 \times 0.12$ mm

Table 1

Selected geometric parameters (Å, °).

Al1—Br1	2.380 (2)	Al2—Br22	2.305 (3)
Al1—N11	2.003 (7)	Al2—Br23	2.293 (3)
Al1—N21	1.972 (7)	Al2—Br24	2.283 (3)
Al1—N31	1.967 (7)	Al3—Br31	2.302 (3)
Al1—N41	1.983 (7)	Al3—Br32	2.287 (3)
Al1—N51	1.972 (7)	Al3—Br33	2.292 (3)
Al2—Br21	2.293 (3)	Al3—Br34	2.288 (3)
Br1—Al1—N11	178.7 (2)	N41—Al1—N51	91.1 (3)
Br1—Al1—N21	94.1 (2)	Br21—Al2—Br22	107.50 (12)
Br1—Al1—N31	92.8 (2)	Br21—Al2—Br23	112.17 (12)
Br1—Al1—N41	94.3 (2)	Br21—Al2—Br24	109.80 (12)
Br1—Al1—N51	93.7 (2)	Br22—Al2—Br23	109.89 (12)
N11—Al1—N21	87.2 (3)	Br22—Al2—Br24	109.20 (12)
N11—Al1—N31	87.6 (3)	Br23—Al2—Br24	108.24 (12)
N11—Al1—N41	85.3 (3)	Br31—Al3—Br32	111.19 (11)
N11—Al1—N51	85.0 (3)	Br31—Al3—Br33	109.81 (11)
N21—Al1—N31	90.5 (3)	Br31—Al3—Br34	107.78 (11)
N21—Al1—N41	87.5 (3)	Br32—Al3—Br33	108.50 (11)
N21—Al1—N51	172.2 (3)	Br32—Al3—Br34	109.08 (12)
N31—Al1—N41	172.7 (3)	Br33—Al3—Br34	110.47 (11)
N31—Al1—N51	89.9 (3)		

Data collection

Bruker SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.126$, $T_{\max} = 0.252$
 32 073 measured reflections
 4571 independent reflections

3187 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\text{max}} = 29.0^\circ$
 $h = -14 \rightarrow 14$
 $k = -19 \rightarrow 19$
 $l = -29 \rightarrow 29$

Refinement

 Refinement on F

$R = 0.029$
 $wR = 0.027$
 $S = 0.99$
 3187 reflections
 272 parameters
 H-atom parameters not refined

 $w = 1/(\sigma^2 F + 0.0004 F^2)$
 $(\Delta/\sigma)_{\text{max}} = 0.016$
 $\Delta\rho_{\text{max}} = 0.67 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.57 \text{ e } \text{Å}^{-3}$

Absolute structure: Flack (1983)

Flack parameter = 0.04 (1)

H atoms were located from difference Fourier maps, placed at idealized positions [$\text{C}-\text{H} = 0.95 \text{ Å}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$] and not refined.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: Xtal3.5 (Hall *et al.*, 1995); program(s) used to solve structure: Xtal3.5; program(s) used to refine structure: CRYLSQ in Xtal3.5; molecular graphics: Xtal3.5; software used to prepare material for publication: BONDLA and CIFIO in Xtal3.5.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1411). Services for accessing these data are described at the back of the journal.

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