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Structure of Barium Tetrakis(1,2-ethanediolato)dialuminate(III), $Ba[Al_2(C_2H_4O_2)_4]$

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Abstract. $M_r = 431{\cdot}51$, orthorhombic, $Ccc2$, $a = 13{\cdot}774\ (15)$, $b = 10{\cdot}828\ (10)$, $c = 9{\cdot}105\ (12)$ Å, $V = 1358\ (9)$ Å^3, $Z = 4$, $D_x = 2{\cdot}111$, $D_m = 2{\cdot}17$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}166$ mm^{-1}, $F(000) = 840{\cdot}0$, $T = 298$ K, $R = 0{\cdot}0436$ for 620 independent reflections. The Al coordination is unusual, being a distorted trigonal bipyramid (*i.e.* five coordinate) rather than tetrahedral or octahedral; two polyhedra share edges to form a dimer. Al—O bond lengths [apical 1·924 (7), 1·884 (7) Å; equatorial 1·863 (7), 1·80 (1), 1·72 (1) Å] and angles are compared with those in other structures containing five-coordinated Al atoms.

Introduction. In an attempt to prepare new examples of framework aluminates, a systematic investigation of syntheses using mixed organic/aqeuous solvents was undertaken. During these investigations, good crystals of a new phase were observed, later found to be $Ba[Al_2(C_2H_4O_2)_4]$. Although not a framework aluminate, the structure of this phase is interesting since it contains pentacoordinated Al.

Experimental. Needle-shaped crystals suitable for intensity collection were obtained by the hydrothermal reaction of a mixture of barium hydroxide hydrate $[Ba(OH)_2.8H_2O]$, aluminium isopropoxide [Al(OPr-iso)$_3$], water and ethylene glycol (mole ratio 1:2:9:40) at 473 K for two weeks. Chemical analysis gave $BaAl_2O_{8.7}C_7H_{15}$. Density measured by displacement of toluene, giving a value slightly higher than the X-ray density. This was probably due to non-essential water, as the product had been dried only by washing with acetone. X-ray powder diffraction pattern obtained using α-Al_2O_3 as an internal standard.† Under a polarizing microscope, crystals showed parallel extinction and low white interference colours. Crystal with dimensions $0{\cdot}7 \times 0{\cdot}1 \times 0{\cdot}1$ mm was mounted on a glass fibre. Precession photographs showed: system orthorhombic, $a = 13{\cdot}8$, $b = 10{\cdot}8$, $c = 9{\cdot}1$ Å, possible space groups $Cccm$ or $Ccc2$. Crystal transferred to an automatic four-circle diffractometer (Nicolet $P3$) for data collection. Mo $K\alpha$ radiation, graphite monochromator. Unique reflections with $h,k,l \geq 0$; max. $(\sin\theta)/\lambda = 0{\cdot}5946$ Å^{-1}; θ–2θ scans; scan speed and width automatically selected by diffractometer; background count measured on either side of each reflection. Lattice parameters from a least-squares fit to the centred angles of 14 reflections with $17{\cdot}5 < 2\theta < 22{\cdot}7°$. Two standard reflections (004 and 040) remeasured after every 50 measurements, no systematic change observed (average variation 2·6%). 634 unique reflections; 14 with $I < 2\sigma(I)$ classified as unobserved. No absorption correction (crystal mounted along needle axis, X-ray beam approximately perpendicular to the axis, max. deviation 25°, hence max. and min. path lengths 0·11 and 0·1 mm respectively). Programs supplied by Ahmed, Hall, Pippy & Huber (1967) (adapted for use on the Honeywell 66/80 by J. S. Knowles and R. A. Howie of this University). Positions for the Ba and Al atoms obtained from a Patterson map, space group $Ccc2$ assumed. Remainder of structure obtained from subsequent electron density and difference maps, to give overall cell contents $Ba_4Al_8C_{32}O_{32}$. At this point, structure appeared to have centre of symmetry, so was refined in space group $Cccm$: block-diagonal least-squares refinement on F; scattering factors from *International Tables for X-ray Crystallography* (1962) were for neutral atoms (except Ba^{2+}). Isotropic temperature factors used for all atoms other than Ba, which was assumed to be vibrating anisotropically. Refinement proceeded well ($R = 0{\cdot}07$) except that the C—C bond lengths were too short and the mirror plane imposed a torsion angle of 0° on an ethylene glycol group. Refinement was thus continued in $Ccc2$, although problems were encountered because of the strong pseudosymmetry. R dropped significantly; the C—C bond lengths and the suspect torsion angle increased. Using the weighting scheme $w^{1/2} = \{1 + [(|F_o| - P_2)/P_1]^2\}^{-1/2}$ ($P_1 = 100{\cdot}0$ and $P_2 = 50{\cdot}0$ obtained by trial and error) the refinement converged giving $R = 0{\cdot}0436$, $wR = 0{\cdot}0437$ and $(\Delta/\sigma)_{\max} = 0{\cdot}123$. A final difference map showed no significant features. H atoms were not located.†

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† JCPDS file No. 36-2000; see also deposition footnote.

† Lists of structure factors, full tables of bond lengths and angles and powder diffraction data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39987 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and isotropic temperature factors*

Figures in parentheses represent e.s.d.'s corresponding to the least significant digit(s).

	x	y	z	B_{iso}(Å^2)
Ba	0	0	$\frac{1}{4}$	1·353*
Al	0·1502 (2)	0·1954 (3)	−0·0004 (9)	1·22 (4)
O(1)	0·2807 (5)	0·1501 (6)	−0·001 (2)	1·3 (1)
O(2)	0·1255 (5)	0·0245 (6)	0·009 (2)	1·5 (1)
O(3)	0·0715 (7)	0·2206 (9)	−0·145 (1)	2·2 (2)
O(4)	0·0924 (6)	0·2092 (8)	0·176 (1)	1·5 (1)
C(1)	0·2980 (8)	0·024 (1)	−0·026 (1)	1·9 (2)
C(2)	0·2091 (9)	−0·048 (1)	0·025 (2)	2·2 (2)
C(3)	−0·029 (1)	0·330 (2)	0·295 (2)	3·1 (3)
C(4)	0·074 (1)	0·309 (2)	0·269 (2)	3·4 (3)

* Calculated from the anisotropic temperature factors of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk) \times 10^{-5}]$;

	B_{11}	B_{22}	B_{33}	$B_{23} = B_{13} = B_{12}$
Ba	167 (3)	313 (6)	399 (8)	0

Table 2. *Important interatomic distances* (Å) *and bond angles* (°)

E.s.d.'s in the least significant digit(s) are given in parentheses.

Ba–O(2)	2·81 (2)	(×2)	C(1)–C(2)	1·52 (2)
O(2^{i})	2·94 (2)	(×2)	O(1)	1·41 (1)
O(3^{i})	2·76 (1)	(×2)	C(2)–O(2)	1·40 (1)
O(4)	2·68 (1)	(×2)	C(3)–C(4)	1·46 (2)
			O(3^{i})	1·43 (2)
Al–O(1)	1·863 (7)		C(4)–O(4)	1·40 (2)
O(1^{ii})	1·924 (7)			
O(2)	1·884 (7)			
O(3)	1·72 (1)			
O(4)	1·80 (1)			

O(1)–Al–O(1^{i})	75·6 (6)	O(1)–C(1)–C(2)	108 (1)
O(2)	85·2 (6)	O(2)–C(2)–C(1)	110 (1)
O(3)	130·2 (6)	O(3^{i})–C(3)–C(4)	109 (1)
O(4)	116·8 (5)	O(4)–C(4)–C(3)	113 (2)
O(2)–Al–O(1^{i})	160·7 (6)		
O(3)	94·4 (5)		
O(4)	87·8 (5)		
O(3)–Al–O(1^{i})	99·8 (6)		
O(4)	112·9 (5)		
O(4)–Al–O(1^{i})	98·6 (5)		

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

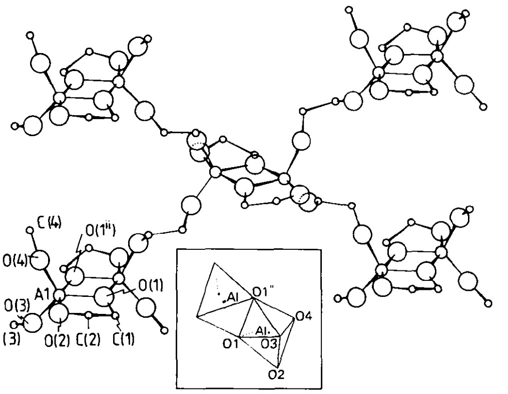

Fig. 1. Projection of the structure onto the (010) plane. The insert shows a single dimer rotated to show the trigonal bipyramids more clearly.

Discussion. Table 1 lists the final positional parameters and the isotropic temperature factors (or equivalent in the case of Ba). Table 2 lists the important bond distances and angles.

Fig. 1 shows a projection of the structure onto the (010) plane (Ba atoms excluded for clarity). Each Al atom is coordinated by five O atoms from ethylene glycol groups to give a highly distorted trigonal bipyramid; pairs of these then share edges giving dimers of formula $[Al_2(C_2H_4O_2)_4]^{2-}$. A pseudo mirror plane passes through the two Al atoms, the shared edge and the apical O atoms. The dimers are linked *via* the ethylene glycol groups to form a two-dimensional polymer. Charge balance is maintained by the Ba atoms. If it is assumed that each C atom carries two protons, the final unit-cell contents are $Ba_4Al_8C_{32}H_{64}O_{32}$, which agrees fairly well with the chemical analysis. C(3)–C(4) and C(1)–C(2) have slightly different conformations: the dihedral angles are 57·5 and 30° respectively. The C(3)–C(4) bond length is slightly shorter (1·46 Å) than that normally associated with a C–C single bond (1·54 Å). However, in view of the high e.s.d. (0·02 Å) and the fact that C(1)–C(2) is normal (1·52 Å), this reduction in bond length is probably not a real effect, but is caused by the computational problems associated with the pseudo mirror plane (which gives near-correlations between non-symmetry-related atoms).

Fig. 2 shows that the Ba atoms are surrounded by four dimers in an approximate tetrahedron. Two O atoms from each dimer are bonded to Ba, giving a coordination number of eight. A high coordination number (8–9) is typical of Ba, as are the fairly long Ba–O bond lengths of 2·7–2·8 Å.

Five coordination

Examples of other compounds containing AlO_5 trigonal bipyramids are: Al_2SiO_5(andalusite) (Burnham & Buerger, 1961); $Al_2PO_4(OH_3)$(augelite) (Araki, Finney & Zoltai, 1968); $(Mg,Fe)Al_3SiBO_9$-

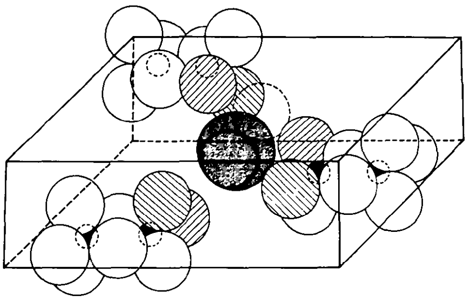

Fig. 2. Coordination of the Ba atoms. Largest circles represent Ba, medium O and smallest Al. The O atoms shown as broken circles are those from the fourth dimer, omitted for clarity. Ba is eight-coordinate with respect to O (hatched and broken circles).

Table 3. *Comparison of* Al—O *bond lengths and angles in phases containing pentacoordinated* Al

	$Ba[Al_2(C_2H_4O_2)_4]$	Andalusite	Augelite	Grandidierite†	$CaO.6Al_2O_3$	$AlYO_3$
(1) Bond lengths (Å)						
(*a*) apical	1·924*	1·866*	2·054	1·933	2·187 (×2)	2·12 (×2)
	1·884	1·816	1·798	1·797		
(*b*) equatorial	1·863	1·845*	1·750	1·827	1·839 (×3)	1·82 (×3)
	1·80	1·818 (×2)	1·779 (×2)	1·868 (×2)		
	1·72					
(2) Bond angles (°)						
(*a*) apical	98·6	92·5 (×2)	77·5 (×2)	80·8 (×2)	90·0 (×3)	90·0 (×3)
	99·8	74·1	90·7	90·9		
	75·6					
	94·4	98·9 (×2)	96·8 (×2)	94·7 (×2)	90·0 (×3)	90·0 (×3)
	87·8	86·8	99·4	100·5		
	85·2					
	160·7	160·9	170·0	168·6	180·0	180·0
(*b*) equatorial	130·2	126·2 (×2)	122·8 (×2)	112·1	120·0 (×3)	120·0 (×3)
	116·8	105·9	109·0	132·0 (×2)		
	112·9					
(3) *R* factors						
(*a*) $R_{\text{t.b.}}$	0·078	0·081	0·070	0·072	0	0
(*b*) $R_{\text{t.p.}}$	0·078	0·087	0·108	0·084	0·124	0·124

* The O atom is shared with another five-coordinate Al atom (see text).

† The values for grandidierite are recalculated from the coordinates in Stephenson & Moore (1968); there are some errors in thc bond lengths and angles given in the original paper (Moore, 1984, personal communication).

(grandidierite) (Stephenson & Moore, 1968); $CaO.6Al_2O_3$ (Kato & Saalfeld, 1968); $AlYO_3$ (Bertaut & Mareschal, 1963). Of these, only andalusite contains dimers similar to those found in this structure, but whereas in the present case the dimers are relatively isolated, in andalusite they are part of a framework (the coordinating O atoms are also shared by tetrahedral SiO_4 groups and/or octahedral AlO_6 groups). Furthermore, this new aluminate is the only one that does not contain anionic species such as AlO_6 or SiO_4 groups.

Table 3 compares the Al—O bond lengths and angles of phases containing pentacoordinated Al. In general, the apical Al—O bond lengths are longer than the equatorial bond lengths. This is in line with observations for isolated molecules such as PCl_5 [2·124 and 2·020 Å (Adams & Bartell, 1971)] and appears to represent an energetic compromise. Electrostatic binding energy should be maximized where all bonds between the central atom and its ligands are equal. On the other hand, repulsion between ligands is minimized where they are equidistant from one another (*i.e.* ideally close-packed), which would imply a ratio of $1:\sqrt{2}$ between equatorial and apical bonds. In the extended structures, these considerations are modified by the further coordination of the O atoms. For example, grandidierite is not in line with the argument, possibly because the coordinating O atoms are also part of a variety of other polyhedra, *e.g.* MgO_5, SiO_4 and AlO_6 groups; in particular, the O atom involved in the long equatorial bond is attached to a B atom. Where the AlO_5 polyhedra share edges, the shared O—Al bond lengths increase (indicated by an asterisk in Table 3), compared to those not shared by other polyhedra. A similar situation occurs where AlO_6 octahedra share edges. Repulsion between the two Al atoms probably accounts for this. The bond angles given for $CaO.6Al_2O_3$ and $AlYO_3$ are those for a true trigonal bipyramid; the other compounds mostly show considerable distortion from the ideal angles.

Zemann (1963) points out that the trigonal bipyramid and tetragonal pyramid are remarkably similar. He suggests the use of the expression

$$R = \sum_{1}^{10} \mid L\hat{M}L\,(\text{theor.}) - L\hat{M}L\,(\text{exp.}) \mid / \sum_{1}^{10} L\hat{M}L\,(\text{theor.})$$

in which $L\hat{M}L$ is the bond angle between the central metal atom and any two ligands. This can be applied to give an objective assessment of which ideal polyhedron best describes the arrangement. The values for $R_{\text{t.b.}}$ and $R_{\text{t.p.}}$ are also listed for each compound in Table 3, where $R_{\text{t.b.}}$ is the R-factor test for a trigonal bipyramid and $R_{\text{t.p.}}$ that for a tetragonal pyramid using the angles given by Zemann. Of the compounds that do not contain ideal trigonal bipyramids, augelite and grandidierite contain those closest to ideality. In contrast, those in andalusite and this new phase are furthest from ideal. Indeed, they show very little difference between $R_{\text{t.b.}}$ and $R_{\text{t.p.}}$ and the coordination could equally well be described as a distorted tetragonal pyramid. Thus, where there is some doubt in deciding the coordination polyhedron of a metal atom, the test is obviously useful.

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trans-Bis(dinitrogen)tetrakis(methyldiphenylphosphine)molybdenum(0) Benzene Solvate, $[Mo(N_2)_2\{P(CH_3)(C_6H_5)_2\}_4].1\cdot5(C_6H_6)$

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Abstract. $M_r = 1069\cdot9$, triclinic, $P\bar{1}$, $a = 11\cdot776$ (2), $b = 14\cdot353$ (2), $c = 17\cdot425$ (2) Å, $\alpha = 76\cdot51$ (1), $\beta = 71\cdot45$ (1), $\gamma = 82\cdot52$ (1)°, $U = 2710$ Å^3, $Z = 2$, $D_x = 1\cdot31$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0\cdot71069$ Å, $\mu = 4\cdot0$ cm^{-1}, $F(000) = 1114$, $T = 295$ K, $R = 0\cdot052$ for 5693 observed $[I > 3\sigma(I)]$ reflections. The molybdenum atom is approximately octahedrally coordinated by four phosphorus atoms $[\langle Mo{-}P\rangle = 2\cdot496$ (2) Å] and two nitrogen atoms [Mo—N = $1\cdot989$ (5), $2\cdot000$ (5) Å]. The N—N bond lengths are $1\cdot133$ (7) and $1\cdot154$ (7) Å. Bulky ligands pack around the metal with four pairs of adjacent phenyl rings on different P atoms nearly parallel thus resulting in an approximate D_{2d} symmetry for the complex.

Introduction. The title complex undergoes a variety of unusual substitution reactions where the phosphine ligands are replaced by P-, N-, or S-donor ligands while the labile dinitrogen ligands are retained (Morris & Ressner, 1983; Morris, Ressner, Sawyer & Shiralian, 1984, and references therein). The lability of the bulky phosphine ligands can be attributed to a weakening of the molybdenum–phosphorus bonds by inter-ligand steric interactions. This structure determination supports this conclusion.

Experimental. Preparation of the complex $Mo(N_2)_2$-$(PMePh_2)_4$ as reported (George & Noble, 1979; Lazarowych, Morris & Ressner, 1985). Crystals obtained by slow evaporation of a benzene solution in a nitrogen-filled glovebox. Dark red block-shaped crystal, overall dimensions $0\cdot19 \times 0\cdot21 \times 0\cdot24$ mm, sealed in Lindemann capillary. Precession photographs gave preliminary cell and space-group information. Further work on Enraf–Nonius CAD-4 diffractometer, graphite monochromatized Mo $K\bar{\alpha}$ radiation. Accurate unit-cell dimensions by least-squares fit of diffracting positions of 25 reflections ($8\cdot7 < \theta < 15\cdot4$°). Data collected using ω–2θ scans, ω scan ranges $(0\cdot70 + 0\cdot35 \tan\theta)$°. Scan rates conditional on information collected in prescans selected to give $I/\sigma(I)$ of 25 within max. scan time of 80 s. Gradual decrease in intensities of 3 standard reflections monitored every 12 000 s of exposure time corrected for after data reduction [max. rescale factor (on F) $1\cdot23$]. Backgrounds by extending scan by 25% on either side of peak measured for half the time taken to collect peak. 8792 reflections in quadrants (h, $\pm k$, $\pm l$) with $2\theta \le 50$° measured. Correction for Lorentz, polarization and crystal decay. 644 zero $F_{\rm obs}$ excluded, 447 symmetry-equivalent data averaged ($R_{\rm merge} = 0\cdot02$) to give 7515 reflections. Structure solved using Patterson, least-squares and Fourier methods. Least-squares refinement of occupancy factors for solvent molecules indicated $1\cdot5$ molecules of benzene in asymmetric unit. All hydrogen atoms in $Mo(N_2)_2(PMePh_2)_4$ molecule located in difference Fourier map but, owing to program limitations, only methyl hydrogen atoms refined. Blocked least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$, with all non-hydrogen atoms except those in solvent with anisotropic thermal parameters, converged (max. $\Delta/\sigma = 0\cdot07$) to $R = 0\cdot052$ ($wR = 0\cdot054$) for 5693 observed data with $I > 3\sigma(I)$. $w = [\sigma^2(F) + 0\cdot0006F^2]^{-1}$. Most significant features in final difference Fourier map attributable to phenyl hydrogen atoms ($\le 0\cdot57$ e Å^{-3}). Programs: Enraf–Nonius (1979) *SDP* and *SHELX* (Sheldrick, 1976) on PDP 11/23 and SEL75 computers. Atomic scattering factors from *SHELX*. The final atomic positional and thermal parameters are included in Table 1, selected bond

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