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## The Structure of Sodium Bis(tetraethylammonium) Tris(oxalato)aluminate(III) Monohydrate

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**Abstract.** Na[N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].H<sub>2</sub>O, *M<sub>r</sub>* = 591.8, monoclinic, *Cc*, *a* = 16.874 (5), *b* = 11.347 (2), *c* = 17.530 (5) Å, β = 115.76 (2)°, *V* = 3023 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.299 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 0.133 mm<sup>-1</sup>, *F*(000) = 1224, *T* = 293 (1) K, *R* = 0.035 for 2178 observed reflections. The Al atom is coordinated by six O atoms from three oxalate groups in octahedral configuration. The average Al–O bond distance is 1.897 (9) Å. The structure consists of sodium and tetraethylammonium cations, tris(oxalato)aluminate(III) anions and disordered water molecules.

**Introduction.** As part of our study of metal(III) oxalate complexes we have undertaken the analysis of the influence of monovalent cations on the crystal structure and water content of these complexes (Bulc, Golič & Šiftar, 1982, 1983, 1985). We tried to prepare tetraethylammonium tris(oxalato)aluminate(III). However, due to impurities in tetraethylammonium hydroxide we obtained sodium bis(tetraethylammonium) tris(oxalato)aluminate(III) monohydrate. This compound falls into the scope of our work and therefore we determined its crystal structure.

**Experimental.** Crystals of the compound under investigation were grown from an aqueous solution of aluminium oxalate and sodium tetraethylammonium oxalate (1:3). Crystal size 0.37 × 0.43 × 0.43 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo *K*α radiation. Space group *Cc* deduced from the systematic absences and distributions of |*E*| and confirmed by the successful structure analysis. A trial refinement in the centrosymmetric space group *C2/c* failed. Cell parameters by least-squares refinement of 25 reflections within 10 < θ < 15°, intensity measurement by ω–2θ scan, ω scan width (°) = 0.7 + 0.3 tan θ, aperture (mm) = 2.4 +

Table 1. Final fractional coordinates (×10<sup>4</sup>) and equivalent isotropic temperature factors *U*<sub>eq</sub> (Å<sup>2</sup> × 10<sup>3</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Al	5000	1302 (1)	5000	40.5 (4)
Na	8218 (1)	3694 (1)	6471 (1)	48.8 (6)
O(1)	4554 (2)	180 (2)	4101 (1)	45 (1)
O(2)	3730 (2)	99 (2)	2707 (2)	53 (1)
O(3)	4568 (1)	2433 (2)	4107 (1)	47 (1)
O(4)	3917 (2)	2538 (2)	2696 (2)	51 (1)
C(1)	4141 (2)	629 (3)	3360 (2)	42 (1)
C(2)	4204 (2)	1992 (2)	3363 (2)	41 (1)
O(5)	5517 (1)	2496 (2)	5822 (1)	47 (1)
O(6)	6771 (2)	3504 (2)	6455 (2)	61 (1)
O(7)	6115 (1)	1238 (2)	4985 (1)	48 (1)
O(8)	7398 (2)	2184 (2)	5499 (2)	59 (1)
C(3)	6308 (2)	2762 (3)	5968 (2)	43 (1)
C(4)	6666 (2)	2010 (3)	5447 (2)	42 (1)
O(9)	3925 (1)	1389 (2)	5089 (1)	49 (1)
O(10)	3145 (2)	385 (3)	5615 (2)	62 (1)
O(11)	5262 (1)	51 (2)	5784 (1)	47 (1)
O(12)	4601 (2)	–1106 (2)	6364 (2)	64 (1)
C(5)	3810 (2)	563 (3)	5521 (2)	42 (1)
C(6)	4623 (2)	–276 (3)	5934 (2)	43 (1)
N(1)	1050 (2)	601 (3)	7890 (2)	63 (2)
C(11)	2033 (3)	324 (4)	8257 (3)	71 (2)
C(12)	2633 (3)	1310 (5)	8722 (4)	85 (3)
C(21)	790 (3)	940 (4)	8597 (3)	73 (2)
C(22)	934 (4)	7 (6)	9248 (3)	93 (3)
C(31)	574 (4)	–488 (4)	7424 (3)	82 (3)
C(32)	–412 (4)	–412 (7)	7045 (5)	110 (4)
C(41)	815 (3)	1652 (4)	7303 (3)	81 (3)
C(42)	1022 (5)	1528 (7)	6551 (4)	116 (4)
N(2)	7181 (2)	662 (3)	8679 (2)	65 (2)
C(51)	7343 (4)	1695 (5)	9284 (4)	98 (3)
C(52)	7091 (7)	1477 (8)	10004 (4)	137 (5)
C(61)	7687 (4)	–415 (5)	9144 (3)	88 (3)
C(62)	8682 (5)	–254 (9)	9564 (5)	129 (5)
C(71)	7473 (3)	1050 (5)	8019 (3)	90 (3)
C(72)	7379 (3)	170 (8)	7364 (3)	105 (4)
C(81)	6221 (3)	311 (4)	8286 (3)	71 (2)
C(82)	5587 (3)	1287 (5)	7824 (3)	86 (3)
O(20)	3293 (8)	–2193 (8)	2126 (9)	154 (10)
O(21)	4749 (18)	2378 (14)	4149 (26)	330 (33)

0.9 tan θ, maximum scan time 60 s, hemisphere measured, with equality test (*h* + 22/–22, *k* 0/13, *l* –23/+23), [(sin θ)/λ]<sub>max</sub> = 0.66 Å<sup>-1</sup>, standard reflections 10, 0, 6, 915, 821, remeasured every 1500 s of measuring time, showed an average increase in intensity of 6.1% during the data collection, 7258 reflections measured, merging produced 3622 unique reflections

with  $R_{\text{int}} = 0.03$ , 1444 unobserved reflections [ $I < 2.5\sigma(I)$ ], no absorption or extinction correction applied. Crystal structure solved by direct methods (SHELXS86; Sheldrick, 1986) and refined by full-matrix least squares on  $F$ , anisotropic for all non-hydrogen atoms, to final  $R = 0.035$  and  $wR = 0.040$ . Parameters of H atoms of ethyl groups were deduced, assuming that  $C-H = 1.09 \text{ \AA}$  and  $U_{\text{eq}}$  was equal to that of the attached atoms, and were used to calculate fixed contributions to the structure factors. Empirical weighting function  $w = 3(W_F W_S)$ , where  $W_F(|F_o| < 12.00) = (|F_o|/12.00)^{1.5}$ ,  $W_F(|F_o| > 14.00) = (14.00/|F_o|)^{0.8}$ ,  $W_F(12.00 \leq |F_o| \leq 14.00) = 1.0$  and  $W_S \times (\sin\theta < 0.33) = (\sin\theta/0.33)^3$ ,  $W_S(\sin\theta > 0.37) = (0.37/\sin\theta)^4$ ,  $W_S(0.33 \leq \sin\theta \leq 0.37) = 1.0$ , applied to keep  $\sum w(\Delta F)^2$  uniform over ranges of  $(\sin\theta)/\lambda$  and  $|F_o|$ , (shift/e.s.d.) $_{\text{max}}$  in final refinement cycle = 0.25; (shift/e.s.d.) $_{\text{ave}} = 0.04$ ;  $m/n = 7.97$ ,  $S = 0.91$ , max. and min. heights in final difference Fourier synthesis 0.23 and  $-0.44 \text{ e \AA}^{-3}$ ; atomic scattering and dispersion factors for neutral Al, C, N and O from Cromer & Mann (1968), Cromer & Liberman (1970), and for H atoms from Stewart, Davidson & Simpson (1965). DEC-10 computer at RCU Ljubljana, SHELXS86 (Sheldrick, 1986) and XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

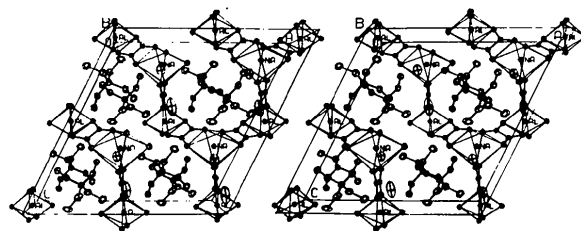
**Discussion.** The final fractional coordinates with  $U_{\text{eq}}$  (Hamilton, 1959) for non-hydrogen atoms are listed in Table 1.\* The relevant bond lengths and bond angles are listed in Table 2. Fig. 1 shows the unit-cell contents. The Al atom is coordinated by six O atoms from three oxalate groups in octahedral configuration. The Al—O distances are in the range from 1.889 (3) to 1.908 (2) Å and *cis*-O—Al—O bond angles range from 84.2 (1) to 95.7 (1)°.

The three oxalate groups act as doubly bidentate bridging ligands among the aluminium and sodium octahedra. Therefore in each oxalate group there are C—O distances corresponding to the aluminium octahedra designated as inner and C—O distances corresponding to the sodium cation octahedra designated as outer O atoms. The average bond lengths [C—O $_{\text{inner}}$  1.277 (5); C—O $_{\text{outer}}$  1.216 (5); C—C 1.555 (8) Å] as well as the average bond angles [O—C—O 126.7 (5); O $_{\text{inner}}$ —C—C 112.9 (4) and O $_{\text{outer}}$ —C—C 120.4 (3)°] correlate well with the corresponding values in other oxalate complexes (Taylor, 1978). The oxalate ligands are almost planar with torsion angles along the C—C bond involving inner O atoms of 7.5 (4), 1.9 (4) and 2.1 (4)° (Stanford & Waser, 1972).

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51357 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances (Å) and angles (°)

Coordination octahedra			
Al—O(1)	1.908 (2)	Al—O(7)	1.894 (3)
Al—O(3)	1.907 (2)	Al—O(9)	1.889 (3)
Al—O(5)	1.893 (2)	Al—O(11)	1.889 (3)
O(1)—Al—O(3)	84.2 (1)	O(5)—Al—O(9)	92.4 (1)
O(1)—Al—O(7)	90.0 (1)	O(5)—Al—O(11)	95.7 (1)
O(1)—Al—O(9)	93.2 (1)	O(7)—Al—O(11)	93.5 (1)
O(1)—Al—O(11)	89.0 (1)	O(9)—Al—O(11)	84.8 (1)
O(3)—Al—O(5)	91.6 (1)	O(1)—Al—O(5)	173.0 (1)
O(3)—Al—O(7)	92.4 (1)	O(3)—Al—O(11)	171.0 (1)
O(3)—Al—O(9)	89.7 (1)	O(7)—Al—O(9)	176.4 (1)
O(5)—Al—O(7)	84.6 (1)		
Oxalate ligands			
Ligand 1			
C(1)—C(2)	1.550 (4)	C(2)—O(3)	1.278 (4)
C(1)—O(1)	1.283 (4)	C(2)—O(4)	1.223 (4)
C(1)—O(2)	1.210 (4)		
O(1)—C(1)—C(2)	112.7 (2)	C(1)—C(2)—O(3)	113.4 (3)
O(2)—C(1)—C(2)	120.7 (3)	C(1)—C(2)—O(4)	120.3 (3)
O(1)—C(1)—O(2)	126.6 (3)	O(3)—C(2)—O(4)	126.4 (3)
Ligand 2			
C(3)—C(4)	1.551 (5)	C(4)—O(7)	1.279 (3)
C(3)—O(5)	1.281 (4)	C(4)—O(8)	1.215 (4)
C(3)—O(6)	1.212 (4)		
O(5)—C(3)—C(4)	113.0 (2)	C(3)—C(4)—O(7)	112.8 (3)
O(6)—C(3)—C(4)	120.0 (3)	C(3)—C(4)—O(8)	120.7 (3)
O(5)—C(3)—O(6)	126.9 (4)	O(7)—C(4)—O(8)	126.5 (3)
Ligand 3			
C(5)—C(6)	1.564 (4)	C(6)—O(11)	1.272 (4)
C(5)—O(9)	1.272 (4)	C(6)—O(12)	1.216 (4)
C(5)—O(10)	1.221 (5)		
O(9)—C(5)—C(6)	113.2 (3)	C(5)—C(6)—O(11)	112.2 (3)
O(10)—C(5)—C(6)	120.6 (3)	C(5)—C(6)—O(12)	120.1 (3)
O(9)—C(5)—O(10)	126.1 (3)	O(11)—C(6)—O(12)	127.6 (3)
Sodium cation			
Na—O(2)	2.386 (3)	Na—O(8)	2.388 (3)
Na—O(4)	2.399 (3)	Na—O(10)	2.406 (3)
Na—O(6)	2.439 (3)	Na—O(12)	2.432 (4)
O(2)—Na—O(4)	71.3 (1)	O(10)—Na—O(2)	90.5 (1)
O(6)—Na—O(2)	91.5 (1)	O(10)—Na—O(12)	70.6 (1)
O(6)—Na—O(4)	93.4 (1)	O(12)—Na—O(2)	92.0 (1)
O(6)—Na—O(8)	70.3 (1)	O(12)—Na—O(4)	90.5 (1)
O(6)—Na—O(10)	106.5 (1)	O(6)—Na—O(12)	175.4 (1)
O(8)—Na—O(4)	97.3 (1)	O(8)—Na—O(2)	158.3 (1)
O(8)—Na—O(10)	105.7 (1)	O(10)—Na—O(4)	153.5 (1)
O(8)—Na—O(12)	106.9 (1)		
Tetraethylammonium cations			
N(1)—C(11)	1.528 (5)	N(1)—C(31)	1.507 (5)
N(1)—C(21)	1.533 (7)	N(1)—C(41)	1.511 (6)
C(11)—N—C(12)	110.6 (3)	C(21)—N—C(31)	111.8 (4)
C(11)—N—C(13)	106.5 (3)	C(21)—N—C(41)	105.6 (3)
C(11)—N—C(41)	111.4 (4)	C(31)—N—C(41)	111.0 (3)
N(2)—C(51)	1.523 (7)	N(2)—C(71)	1.508 (8)
N(2)—C(61)	1.511 (6)	N(2)—C(81)	1.513 (5)
C(51)—N—C(61)	111.0 (3)	C(61)—N—C(71)	110.7 (4)
C(51)—N—C(71)	106.9 (4)	C(61)—N—C(81)	106.0 (3)
C(51)—N—C(81)	110.7 (4)	C(71)—N—C(81)	111.7 (3)

Fig. 1. Stereoview of the unit cell of  $\text{Na}[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$ .

The sodium cation is octahedrally coordinated with outer O atoms from oxalate groups which thus bridge sodium and aluminium coordination octahedra. The Na—O bond distances range from 2.386 (3) to 2.439 (3) Å and *cis*-O—Na—O bond angles range from 70.3 (1) to 106.9 (1)°. Distortion of the octahedron around the Na atom is larger than that of the octahedron around the Al atom. However, the structure of sodium tris(oxalato)aluminatate(III) pentahydrate (Bulc, Golič & Šiftar, 1982) exhibits four different coordination geometries around Na<sup>+</sup> cations compared with only one in this determination.

There are two independent tetraethylammonium cations which display bond lengths and angles similar to those found in previously determined structures (McCool, Marsh, Ingle & Gagne, 1981). The N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub><sup>+</sup> ions have no contacts with any other atoms shorter than 3.1 Å. They lie in the holes of the net of aluminium and sodium octahedra.

The structure is supplemented with disordered water molecules placed on two positions [O(20), O(21)] with population parameters 0.53 (3) and 0.51 (4). The distances O(21)··O(1) 2.92 (2) and O(20)··O(2) 2.77 (1) Å are consistent with O—H··O hydrogen bonding to oxalate groups. Disorder of water molecules was found in previous structure determinations of metal(III) oxalate complexes (Taylor, 1978; Bulc, Golič & Šiftar, 1984; Merrachi, Mentzen & Chassagneux, 1986).

The crystal structure determination of the title compound confirms the expected octahedral configuration around the metal(III) atom. The sodium

cation does not influence the structure configuration nor the water molecule disorder. Its sole influence is on the water content in the compound.

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## Structure of Copper Tris(ethylenediammonium) Bis(cyclo-tetraphosphate) Tetradecehydrate

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**Abstract.** Cu[C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>]<sub>3</sub>[P<sub>4</sub>O<sub>12</sub>]<sub>2</sub>.14H<sub>2</sub>O, *M*<sub>r</sub> = 1133.87, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 13.162 (8), *b* = 13.301 (8), *c* = 12.308 (8) Å, β = 106.69 (1)°, *V* = 2064 (4) Å<sup>3</sup>, *Z* = 2, *D*<sub>x</sub> = 1.824 Mg m<sup>-3</sup>, λ(Ag Kα) = 0.5608 Å, μ = 0.517 mm<sup>-1</sup>, *F*(000) = 1178, *T* = 295 K, final *R* = 0.037 for 3480 independent reflexions. The P<sub>4</sub>O<sub>12</sub> ring anion, one of the ethylenediammonium groups and three water molecules alternate in planes *z* ≈ 0.25 and 0.75. The condensed phos-

phoric group has no internal symmetry. The centrosymmetrical distorted Cu(H<sub>2</sub>O)<sub>6</sub> octahedron, one centrosymmetrical ethylenediammonium group and one water molecule alternate in planes *z* ≈ 0.0 and 0.50. One of the ethylenediammonium groups has its two inner carbon atoms statistically distributed.

**Introduction.** A systematic investigation of the system H<sub>4</sub>P<sub>4</sub>O<sub>12</sub>–M<sup>II</sup>O–ethylenediamine–H<sub>2</sub>O has recently

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