

between five- and six-coordinate values and this may be attributed to weak dimer association. The Ti—N distances in the title compound [2.42 (1)–2.51 (1) Å] are similar to those in $\text{TiCl}_3 \cdot 3\text{pyridine}$ [2.38 (1)–2.48 (1) Å] suggesting similar bond strengths in the two environments.

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Structure of Ammonium Tris(oxalato)gallate(III) Trihydrate, (I) (NH_4)₃[Ga(C₂O₄)₃].3H₂O, and Ammonium Tris(oxalato)aluminum(III) Trihydrate, (II) (NH_4)₃[Al(C₂O₄)₃].3H₂O

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Abstract. (I), $M_r = 441.94$, triclinic, $P\bar{1}$, $a = 7.901$ (1), $b = 10.674$ (2), $c = 10.710$ (2) Å, $\alpha = 83.14$ (1), $\beta = 70.18$ (1), $\gamma = 69.88$ (1)°, $V = 798.0$ Å³, $Z = 2$, $D_x = 1.839$, $D_m = 1.823$ Mg m⁻³ (by flotation), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.798$ mm⁻¹, $F(000) = 452$, $T = 293$ (1) K, final $R = 0.047$ for 3326 observed reflections; isomorphous to (II), $M_r = 399.20$, triclinic, $P\bar{1}$, $a = 7.888$ (4), $b = 10.667$ (4), $c = 10.643$ (2) Å, $\alpha = 83.33$ (2), $\beta = 70.44$ (2), $\gamma = 69.10$ (4)°, $V = 788.3$ Å³, $Z = 2$, $D_x = 1.682$, $D_m = 1.664$ Mg m⁻³ (by flotation), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.206$ mm⁻¹, $F(000) = 416$, $T = 293$ (1) K, final $R = 0.047$ for 3210 observed reflections. The Ga and the Al atoms are six-coordinated by O atoms from the bidentate oxalate groups in the form of a distorted octahedron. The average Ga—O bond distance is 1.97 (1) Å and Al—O 1.90 (1) Å. The coordination octahedra are linked together by hydrogen bonds.

Introduction. The structure determinations of the title compounds were undertaken as part of studies of M^{III} oxalate complexes (van Niekerk & Schoening, 1952a,b; Bulc, Golič & Šiftar, 1982, 1983).

Experimental. (I) prepared from freshly precipitated gallium hydroxide, aqueous solution of oxalic acid and ammonium oxalate (1:1.5:1.5); crystallization effected by addition of absolute ethanol. (II) prepared from aqueous solution of aluminium oxalate and ammonium oxalate (1:3). Crystal size 0.20 × 0.25 × 0.28 (I),

0.30 × 0.30 × 0.20 mm (II), Enraf–Nonius CAD-4 diffractometer, cell dimensions determined by least-squares refinement from θ values of 54 (I), 64 (II) reflections, range $9 < \theta < 16$ (I), $10 < \theta < 15^\circ$ (II), graphite-monochromatized Mo $K\alpha_1$ radiation, $\lambda = 0.70926$ Å, no absorption correction applied; three-dimensional diffractometer data collected with Mo $K\alpha$ radiation, ω – 2θ scan, 2θ scan width (°) = $0.8 + 0.3 \times \tan\theta$, aperture (mm) = $2.4 + 0.9 \tan\theta$, max. scan time 40 s, $2\theta_{\text{max}} 60^\circ$, full sphere measured, $(\sin\theta/\lambda)_{\text{max}} 0.7$ Å⁻¹, standard reflections 053, 04 $\bar{3}$, 15 $\bar{1}$ (I), 063, 06 $\bar{1}$, 035 (II); 9434 (I), 9325 (II) measured, 4639 (I), 4567 (II) unique reflections, $R_{\text{int}}[\sum(I-|I|)/\sum I] = 4.5\%$ (I), 2.7% (II), 1313 (I), 1357 (II) unobserved reflections [$I < 3.5|4|\sigma(I)$], Patterson and Fourier methods, difference Fourier synthesis to reveal H atoms; full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms, H atoms not refined, yielded final $R = 0.047$ (I), 0.047 (II), $R_w = 0.067$ (I), 0.054 (II); empirical weighting function $w = W_F \times W_S$, where $W_F(|F_o| < 7.0) = |F_o|/7.0$, $W_F(|F_o| > 13.0) = 13.0/|F_o|$, $W_F(7.0 < |F_o| < 13.0) = 1.0$ and $W_S(\sin\theta < 0.45) = (\sin\theta/0.45)^{1.5}$, $W_S(\sin\theta > 0.50) = 0.50/\sin\theta$, $W_S(0.45 < \sin\theta < 0.50) = 1.0$ (I) and $W_F(|F_o| < 2.0) = (|F_o|/2.0)^{1.5}$, $W_F(|F_o| > 6.0) = 6.0/|F_o|$, $W_F(2.0 < |F_o| < 6.0) = 1.0$ and $W_S(\sin\theta < 0.44) = (\sin\theta/0.44)^{2.5}$, $W_S(\sin\theta > 0.95) = 0.95/\sin\theta$, $W_S(0.44 < \sin\theta < 0.95) = 1.0$ (II) applied in order to keep $\sum w(\Delta F)^2$ uniform over the ranges of $(\sin\theta/\lambda)$ and $|F_o|$, $(\Delta/\sigma)_{\text{max}}$ in final refinement cycle 1.74 (I), 1.13

(II), $(\Delta/\sigma)_{av}$ 0.13 (I), 0.11 (II), $m/n = 15.4$ (I), 14.6 (II), $S\{ = [\sum w(\Delta F)^2/(m-n)]^{1/2} \} = 0.76$ (I), 0.27 (II), max. and min. height in final difference Fourier synthesis 0.3 and -0.5 (I), 0.2 and $-0.2 e \text{ \AA}^{-3}$ (II); atomic scattering and dispersion factors for neutral atoms Ga, Al, C, N and O from Cromer & Mann (1968), Cromer & Liberman (1970) and for H from Stewart, Davidson & Simpson (1965); DEC-10 computer at RCU Ljubljana, XRAY76 system of programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. The final fractional coordinates with U_{eq} (Hamilton, 1959) for non-H atoms are listed in Table 1.* A view of the unit cell of (NH₄)₃[Al(C₂O₄)₃].3H₂O is given in Fig. 1.

The Ga and the Al atoms are coordinated by six O atoms from oxalate groups in the form of a distorted octahedron. The average Ga—O distance is 1.97 (I) and Al—O 1.90 (I) Å. The distortion of the octahedron is seen from the values of the bond angles O—Ga—O and O—Al—O. They are in the range 82.6 (I) to 98.1 (I) (I) and 83.9 (I) to 96.8 (I)° (II) respectively (Table 2a).

The three oxalate groups act as bidentate ligands and lie in general positions. The bond distances and bond angles are almost the same for both compounds and are similar to the values in the other oxalate complexes (Table 2b). The oxalate groups each deviate from planarity; the maximum deviation of the O atoms from the least-squares planes is 0.07 (I) and 0.08 Å (II). Maximum values of the torsion angles along the C—C bond are 7.3 (I) and 7.6° (II).

The three crystallographically independent ammonium ions and water molecules are in general positions, and the coordination octahedra of metallic atoms are linked together by hydrogen bonds. The ammonium ions are each surrounded by five O atoms with average N...O distances 2.91 (4), 2.95 (4), 2.94 (6) (I) and 2.91 (4), 2.96 (6), 2.96 (10) Å (II). The hydrogen-bond lengths N—H...O are within the normal range 2.896 (5) to 2.975 (7) (I) and 2.881 (2) to 3.059 (5) Å (II).

In the structure there are three distinct water molecules, also indicated by chemical analysis and density measurements. In the Ga compound two water molecules O(21) and O(22) were clearly observed, whereas the molecule O(31) seems to be disordered among four positions. This was clearly visible in the difference Fourier map during the refinement. For these positions a final sum of the refined population

Table 1. Final fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^4$)

	x	y	z	$U_{eq}(\text{Å}^2)$
(I)				
Ga	1403 (1)	2392 (1)	2773 (1)	313 (2)
O(1)	2911 (3)	3485 (3)	1653 (3)	317 (12)
O(2)	2560 (4)	5448 (3)	606 (3)	418 (12)
O(3)	-728 (3)	3844 (3)	2375 (3)	388 (12)
O(4)	-1325 (4)	5856 (3)	1429 (4)	535 (16)
O(5)	1156 (4)	3204 (3)	4402 (3)	462 (13)
O(6)	-523 (8)	3373 (5)	6553 (4)	818 (25)
O(7)	-470 (4)	1608 (3)	4010 (3)	452 (13)
O(8)	-2442 (6)	1832 (5)	6081 (4)	684 (21)
O(9)	3714 (4)	961 (3)	2870 (3)	421 (12)
O(10)	5647 (4)	-1008 (3)	1932 (3)	430 (13)
O(11)	1587 (4)	1280 (3)	1371 (3)	405 (12)
O(12)	3132 (5)	-770 (3)	556 (3)	488 (14)
C(1)	1915 (4)	4599 (3)	1280 (3)	315 (13)
C(2)	-249 (4)	4820 (3)	1721 (4)	357 (14)
C(3)	-117 (6)	2975 (4)	5440 (4)	456 (18)
C(4)	-1127 (5)	2064 (4)	5189 (4)	420 (17)
C(5)	4245 (4)	-10 (3)	2072 (3)	347 (14)
C(6)	2904 (5)	142 (3)	1242 (3)	346 (14)
N(1)	5254 (4)	3383 (3)	8471 (4)	414 (15)
N(2)	71 (5)	1786 (4)	9178 (4)	513 (17)
N(3)	4408 (11)	1742 (10)	5360 (8)	1194 (49)
O(21)	2063 (8)	3 (5)	6825 (6)	950 (29)
O(22)	6716 (13)	2488 (9)	1980 (13)	1361 (53)
O(31)	3215 (40)	4529 (21)	5187 (31)	989 (146)
O(32)	4107 (62)	4542 (52)	5902 (73)	1490 (454)
O(33)	4160 (85)	4393 (45)	4261 (83)	1875 (477)
O(34)	4388 (61)	6619 (62)	7042 (55)	1150 (463)
(II)				
Al	1381 (1)	2407 (1)	2781 (1)	319 (2)
O(1)	2868 (1)	3433 (1)	1705 (1)	366 (5)
O(2)	2586 (2)	5395 (1)	643 (1)	432 (5)
O(3)	-702 (2)	3822 (1)	2419 (1)	400 (5)
O(4)	-1357 (2)	5840 (1)	1460 (2)	543 (7)
O(5)	1142 (2)	3212 (1)	4347 (1)	450 (6)
O(6)	-481 (4)	3377 (2)	6534 (2)	827 (11)
O(7)	-401 (2)	1633 (1)	3957 (1)	440 (5)
O(8)	-2387 (3)	1805 (2)	6042 (2)	671 (9)
O(9)	3614 (2)	1009 (1)	2899 (1)	393 (5)
O(10)	5613 (2)	-988 (1)	1989 (1)	426 (6)
O(11)	1588 (2)	1359 (1)	1391 (1)	388 (5)
O(12)	3096 (2)	-713 (1)	547 (1)	492 (6)
C(1)	1919 (2)	4566 (1)	1310 (1)	329 (6)
C(2)	-257 (2)	4800 (1)	1756 (2)	364 (6)
C(3)	-104 (3)	2981 (2)	5418 (2)	455 (8)
C(4)	-1089 (2)	2062 (2)	5158 (2)	412 (7)
C(5)	4200 (2)	15 (1)	2102 (1)	331 (6)
C(6)	2882 (2)	193 (1)	1251 (1)	343 (6)
N(1)	5286 (2)	3348 (2)	8466 (2)	426 (6)
N(2)	78 (2)	1802 (2)	9185 (2)	532 (7)
N(3)	4412 (5)	1719 (5)	5336 (3)	1155 (21)
O(21)	2004 (4)	-8 (2)	6849 (3)	942 (13)
O(31)	6789 (6)	2463 (4)	1845 (6)	807 (25)
O(32)	6049 (43)	2901 (43)	2645 (35)	3530 (297)
O(41)	3238 (25)	4527 (10)	5119 (17)	918 (78)
O(42)	4055 (46)	4619 (45)	5601 (53)	2708 (430)
O(43)	5871 (53)	5594 (23)	5729 (55)	1385 (270)

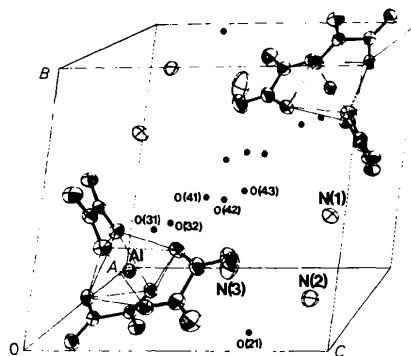


Fig. 1. Unit cell of (NH₄)₃[Al(C₂O₄)₃].3H₂O.

* Lists of structure factors, anisotropic thermal parameters and non-bonded distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39600 (38 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 (°)*

(a) Coordination octahedron			
(I)		(II)	
Ga—O(1)	1.968 (3)	Al—O(1)	1.900 (1)
Ga—O(3)	1.988 (3)	Al—O(3)	1.909 (1)
Ga—O(5)	1.962 (4)	Al—O(5)	1.886 (2)
Ga—O(7)	1.976 (3)	Al—O(7)	1.906 (1)
Ga—O(9)	1.962 (3)	Al—O(9)	1.890 (1)
Ga—O(11)	1.960 (3)	Al—O(11)	1.886 (2)
O(1)—Ga—O(3)	82.6 (1)	O(1)—Al—O(3)	83.9 (1)
O(1)—Ga—O(5)	92.0 (1)	O(1)—Al—O(5)	91.2 (1)
O(1)—Ga—O(9)	91.4 (1)	O(1)—Al—O(9)	90.9 (1)
O(1)—Ga—O(11)	98.1 (1)	O(1)—Al—O(11)	96.8 (1)
O(3)—Ga—O(5)	95.4 (1)	O(3)—Al—O(5)	94.4 (1)
O(3)—Ga—O(7)	89.0 (1)	O(3)—Al—O(7)	89.1 (1)
O(3)—Ga—O(11)	90.9 (1)	O(3)—Al—O(11)	90.9 (1)
O(5)—Ga—O(7)	82.7 (1)	O(5)—Al—O(7)	84.1 (1)
O(5)—Ga—O(9)	91.3 (1)	O(5)—Al—O(9)	91.0 (1)
O(7)—Ga—O(9)	97.7 (1)	O(7)—Al—O(9)	96.5 (1)
O(7)—Ga—O(11)	88.1 (1)	O(7)—Al—O(11)	88.5 (1)
O(9)—Ga—O(11)	83.5 (1)	O(9)—Al—O(11)	84.3 (1)
(b) Oxalate ligands			
Ligand 1		Ligand 1	
C(1)—C(2)	1.550 (5)	C(1)—C(2)	1.552 (2)
C(1)—O(1)	1.284 (4)	C(1)—O(1)	1.283 (2)
C(1)—O(2)	1.230 (5)	C(1)—O(2)	1.225 (2)
C(2)—O(3)	1.279 (5)	C(2)—O(3)	1.279 (2)
C(2)—O(4)	1.222 (4)	C(2)—O(4)	1.224 (2)
O(1)—C(1)—C(2)	114.8 (3)	O(1)—C(1)—C(2)	112.4 (1)
O(2)—C(1)—C(2)	120.2 (3)	O(2)—C(1)—C(2)	121.5 (1)
O(1)—C(1)—O(2)	125.0 (3)	O(1)—C(1)—O(2)	126.1 (1)
C(1)—C(2)—O(3)	114.0 (3)	C(1)—C(2)—O(3)	113.3 (1)
C(1)—C(2)—O(4)	120.0 (3)	C(1)—C(2)—O(4)	120.2 (1)
O(3)—C(2)—O(4)	126.0 (3)	O(3)—C(2)—O(4)	126.5 (2)
Ligand 2		Ligand 2	
C(3)—C(4)	1.548 (8)	C(3)—C(4)	1.547 (3)
C(3)—O(5)	1.286 (5)	C(3)—O(5)	1.298 (2)
C(3)—O(6)	1.213 (7)	C(3)—O(6)	1.211 (3)
C(4)—O(7)	1.276 (5)	C(4)—O(7)	1.278 (2)
C(4)—O(8)	1.226 (6)	C(4)—O(8)	1.226 (3)
O(5)—C(3)—C(4)	114.2 (4)	O(5)—C(3)—C(4)	112.7 (2)
O(6)—C(3)—C(4)	119.8 (5)	O(6)—C(3)—C(4)	120.6 (2)
O(5)—C(3)—O(6)	126.0 (6)	O(5)—C(3)—O(6)	126.7 (3)
C(3)—C(4)—O(7)	114.4 (3)	C(3)—C(4)—O(7)	112.6 (2)
C(3)—C(4)—O(8)	120.5 (4)	C(3)—C(4)—O(8)	121.5 (2)
O(7)—C(4)—O(8)	125.1 (5)	O(7)—C(4)—O(8)	125.9 (2)
Ligand 3		Ligand 3	
C(5)—C(6)	1.557 (6)	C(5)—C(6)	1.545 (3)
C(5)—O(9)	1.284 (5)	C(5)—O(9)	1.286 (2)
C(5)—O(10)	1.224 (4)	C(5)—O(10)	1.221 (2)
C(6)—O(11)	1.285 (4)	C(6)—O(11)	1.284 (2)
C(6)—O(12)	1.217 (5)	C(6)—O(12)	1.220 (2)
O(9)—C(5)—C(6)	114.3 (3)	O(9)—C(5)—C(6)	112.5 (1)
O(10)—C(5)—C(6)	119.4 (4)	O(10)—C(5)—C(6)	120.8 (2)
O(9)—C(5)—O(10)	126.4 (4)	O(9)—C(5)—O(10)	126.7 (2)
C(5)—C(6)—O(11)	114.0 (3)	C(5)—C(6)—O(11)	112.6 (1)
C(5)—C(6)—O(12)	120.7 (3)	C(5)—C(6)—O(12)	121.5 (1)
O(11)—C(6)—O(12)	125.3 (4)	O(11)—C(6)—O(12)	125.9 (2)

parameters is 1.05 [0.36 (5), 0.23 (5), 0.25 (6), 0.21 (5)]. In the similar Al compound only one water molecule has a fixed position. Two are disordered among five positions with the sum of the refined population parameters 0.95 [0.63 (2), 0.32 (2)] and 0.82 [0.30 (3), 0.36 (5), 0.16 (3)] respectively.

The problem of crystal water is constantly present in the known structure determinations of tris(oxalato)-metallate(III) complexes. In ammonium tris(oxalato)-chromate(III) the authors established that the water content is uncertain and the complex is discussed as the dihydrate (van Niekerk & Schoening, 1952b). In potassium tris(oxalato)chromate(III) the position of the third water molecule is doubtful (van Niekerk &

Schoening, 1952a) and in potassium tris(oxalato)-rhodate(III) the water molecule which corresponds to the 0.5 H₂O was found to be disordered (Dalzell & Eriks, 1971). Our tests on similar complexes also lead to the conclusion that all the sites are not fully occupied by water molecules. With the determination of these two structures we can conclude that the water is disordered on several sites. In addition, sites partially occupied by water molecules have extremely high temperature factors. The additional maxima in the difference electron-density map confirm this fact. Consequently, due to disordered crystal-water molecules the network of hydrogen bonds is unclear.

Ammonium tris(oxalato)gallate(III) trihydrate and ammonium tris(oxalato)aluminate(III) trihydrate seem to be isostructural with ammonium tris(oxalato)-chromate(III) dihydrate (van Niekerk & Schoening, 1952b). In the Cr complex location of one of the three ammonium ions with a rather short N...N contact (3.06 Å) is uncertain. In our case according to chemical coordination the positions of the ammonium ion and the water molecule are reversed. While the third water molecule was indicated, the new positions of ammonium ions as water molecules seem to be correct.

From the solved crystal structures it can be seen that the Ga and Al compounds are structurally completely different from the same compounds of other elements of Group III, where the symmetry is changed as well as coordination number. The coordination number alters from six for (NH₄)₃[Ga(C₂O₄)₃].3H₂O and (NH₄)₃-[Al(C₂O₄)₃].3H₂O, to eight for NH₄[In(C₂O₄)₂].2H₂O (Bulc *et al.*, 1983) and to nine for NH₄[Y(C₂O₄)₂].H₂O (McDonald & Spink, 1967).

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