Crystal and Molecular Structures of Diaqua(nitrilotriacetato)aluminium(III) and Di-μ-hydroxo-bis(nitrilotriacetato)dialuminate(III) Dianion†

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The crystal structures of $[Al(nta)(H_2O)_2]\cdot(CH_3)_2CO\cdot H_2O$ (**1**) and $[Al(H_2O)_2][Al_2(nta)_2(\mu\text{-}OH)_2]$-$OH\cdot 3H_2O$ (**2**) (nta = nitrilotriacetate) were determined by *X*-ray crystallography and refined to R = 0.043 [(**1**)] and 0.045 [(**2**)]. In both cases the ligating behaviour of nta^{3-} is uncomplicated, *i.e.* quadridentate and non-bridging, and the geometry around Al^{III} is distorted octahedral, owing to the geometric requirements of the nta^{3-} ligand. Compound (**2**) contains dimeric groups in which two Al–nta moieties are joined by two OH bridges; the Al ··· Al distance is equal to 2.842(2) Å. Both crystal lattices are stabilized by significant intermolecular hydrogen bonds.

Nitrilotriacetic acid (H_3nta) and aluminium(III) are regarded as chemical species of primary environmental relevance.[1,2] The toxicity of aluminium(III) and its environmental chemistry have been subjects of intense investigation in recent years. In particular, the mobilization of aluminium(III) by acid rain[3] or, conceivably, by the action of complexones[4] is of concern to environmental scientists. Nitrilotriacetic acid is currently used in several countries, albeit with some limitations, as a detergent builder, while its use for this purpose has been forbidden in the U.S.A.[5] The main concern regarding the dispersion of nta^{3-} in the biosphere arises from its fairly strong co-ordinating ability towards many metal centres,[6] and hence its potential ability to mobilize toxic metal ions from the sediments of lakes, rivers, and estuaries.[4] Neutral complexes between aluminium(III) and nta^{3-} might exert a specific toxic activity towards aquatic biocenoses and superior organisms *e.g.* Mammalia.[7] Two neutral aluminium(III) complexes, *viz.* tris(acetylacetonato)- and tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)-aluminium, have been found to be much more toxic than simple aluminium salts.[8,9]

In the framework of our interest in developing chemical and biological models of aluminium(III) toxicity, we report here on the molecular structure of two Al^{III}–nta^{3-} adducts, as determined by *X*-ray single-crystal analysis.

Experimental

Materials and Methods.—To Al^{III} (10.5 mmol), dissolved as $Al_2(SO_4)_3\cdot 18H_2O$ in water (100 cm^3), 0.1 mol dm^{-3} NH_3 solution was added, at room temperature and with stirring, to pH 9.9. The suspension obtained was stirred for 2 h and filtered. The precipitate was resuspended in ultrapure water (25 cm^3), stirred for 30 min, and filtered again; this procedure was repeated four times. The resulting $Al(OH)_3$ was treated with H_3nta (10 mmol) in water (100 cm^3) at 80 °C, to give a clear colourless solution. After 3 h most of the solvent was removed by a rotating evaporator and to the residual 10 cm^3, acetone (30 cm^3) was added with vigorous stirring. An oily white precipitate was obtained, which transformed into a white powder upon addition of ethanol (10 cm^3) with vigorous stirring. After filtration on a fritted glass filter, 1.76 g of product were obtained. The solid was dried at 50 °C under vacuum for 24 h. Carbon, nitrogen, and aluminium analyses indicate that the crude product contains roughly 1 equivalent of Al per equivalent of nta (Found: C, 26.25; N, 4.45; Al, 10.70%, corresponding to $C_6AlN_{0.8}$). The crude product was dissolved in water and recrystallized either by addition of acetone (vapour diffusion in a closed flask) or by slow solvent evaporation. The first procedure gives $[Al(nta)(H_2O)_2]\cdot(CH_3)_2CO\cdot H_2O$ (**1**) and the second $[Al(H_2O)_2][Al_2(nta)_2(\mu\text{-}OH)_2]OH\cdot 3H_2O$ (**2**); in both cases, the crystals were mixed with a large amount of amorphous material.

Crystal-structure Determinations.—Data were collected on a Philips four-circle diffractometer, θ—2θ scan mode, up to 2θ = 56° by employing monochromatized Mo-K_α radiation (λ = 0.710 69 Å). Crystal data and collection details for both compounds (**1**) and (**2**) are summarized in Table 1.

The structure of (**1**) was solved by direct methods (MULTAN 80[10]) and refined by blocked-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms, with the exception of the methyl group carbon atoms of acetone. Hydrogen atoms were located on a Fourier difference map and refined isotropically. The structure of (**2**) was solved by the Patterson heavy-atom method to determine the position of the Al(1) atom. The other atoms were located in Fourier and succeeding Fourier difference syntheses. The structure refinement was performed anisotropically by full-matrix least squares for all non-hydrogen atoms. Hydrogen atoms were observed in the difference maps and their positions refined with the isotropic parameter *U*.

Scattering factors for Al were taken from ref. 11 and those of the other atoms from the SHELX 76 program.[12] The final refined atomic co-ordinates are reported in Tables 2 [(**1**)] and 3 [(**2**)].

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.

Results and Discussion

Nitrilotriacetate is known to be a versatile ligand, able to behave as quadri- (typical bonding mode),[13] or tri-,[14] or even uni-dentate.[15] Towards trivalent metal centres, nta^{3-} displays a rather complicated ligating behaviour. Thus, with iron(III) it exhibits both four- and three-co-ordination[16] and with dysprosium(III),[17] praseodymium(III), and neodymium(III)[18] it gives rise to co-ordination polymers, thus behaving as a bridging ligand.

Table 1. Experimental details* of the *X*-ray crystallographic study of $[Al(nta)(H_2O)_2]{\cdot}(CH_3)_2CO{\cdot}H_2O$ (**1**) and $[Al(H_2O)_2][Al_2(nta)_2(\mu\text{-}OH)_2][OH]{\cdot}3H_2O$ (**2**)

(*a*) Crystal data	(**1**)	(**2**)
Formula	$C_9H_{18}AlNO_{10}$	$C_{12}H_{25}Al_3N_2O_{20}$
M	327	598
Habitat	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$
a/Å	18.518(3)	17.406(2)
b/Å	9.802(2)	14.121(2)
c/Å	8.493(2)	9.818(2)
β/°		108.3(3)
U/Å^3	1 541.6	2 291.1
D_c/g cm^{-3}	1.409	1.733
μ/cm^{-1}	1.20	2.09
$F(000)$	688	1 240
Crystal dimensions/mm	0.6 × 0.6 × 0.6	0.3 × 0.3 × 0.3
(*b*) Intensity measurements		
Scan rate/° min^{-1}	1.8	1.2
Number of reflections		
measured	2 137	2 918
unique		2 769 (R = 0.03)
(*c*) Structure refinement		
Refinement	Block	Full-matrix least squares
Reflections included [$I \geqslant 3\sigma(I)$]	1 800	1 839
Parameters refined	262	221
R	0.043	0.045
R'	0.043	0.045
Convergence, largest shift	0.09	0.067
Highest peak in final Fourier difference map/e Å^{-3}	+0.32 −0.30	+0.41 −0.43

* Common to both; Mo-K_α radiation (λ = 0.710 69 Å); Z = 4; 22(1) °C; Philips PW1100 diffractometer, graphite monochromator: Scon type 2θ—θ; maximum 2θ = 56°; Lorentz polarization corrections, unit weights.

We find that Al^{III} and nta^{3-} form in the solid state both a simple neutral distorted octahedral species, (**1**), and a dimeric anionic complex, (**2**). In both structures, nta^{3-} behaves as a quadri-dentate non-bridging ligand.

The molecular structure of compound (**1**) consists of discrete monomeric $[Al(nta)(H_2O)_2]$ units, in which Al^{III} is octahedrally surrounded by nta^{3-} and by two water molecules. Each unit comprises also a second, non-co-ordinated, water molecule and one acetone molecule; the latter is connected to OW(2) of the metal-bonded water molecule through OW(3) of the non-co-ordinated water along two hydrogen bridges (Figure 1). Distances and angles for (**1**) are collected in Tables 4 and 5.

The sum of the equatorial angles (360.7°) is in accord with a practically perfect planarity of $AlO(OW)_2N$, while the angle O(1)–Al–O(2) (162.6°) reveals a considerable distortion from an octahedral structure, due to the steric requirements of nta^{3-}.

The Al–O distances (d_{av} = 1.871 Å) compare well with those observed in the hydrolytically stable complexes tris(acetylacetonate) (d_{av} = 1.879 Å),[19] tris(2-hydroxycyclohepta-2,4,6-trien-1-onate) (d_{av} = 1.888 Å),[20] and tris(3-hydroxy-2-methyl-4*H*-pyran-4-onate) complexes (d_{av} = 1.904 Å).[21] Also the Al-N distance [2.086(4) Å] compares well with the metal–nitrogen distances found in $[Al_2\{OCH(CF_3)_2\}_4(\mu\text{-}OH)_2](en)_2]$ (**3**) (en =

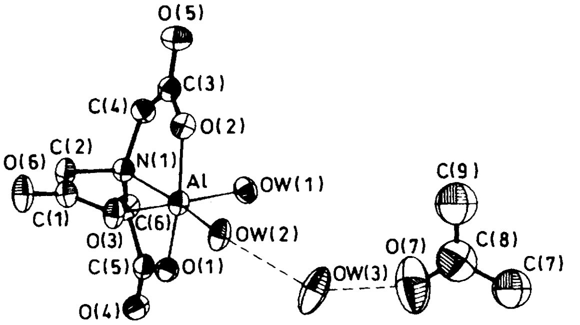

Figure 1. Molecular structure of $[Al(nta)(H_2O)_2]{\cdot}(CH_3)_2CO{\cdot}H_2O$ (**1**)

Table 2. Fractional co-ordinates for compound (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Al	0.903 9(1)	0.043 9(1)	0.857 9(1)
OW(2)	0.907 1(1)	−0.033 1(3)	1.054 0(3)
OW(1)	1.004 7(1)	0.072 8(3)	0.858 1(3)
O(2)	0.894 0(1)	0.229 4(3)	0.916 3(3)
O(1)	0.920 5(1)	−0.116 5(3)	0.740 4(3)
O(3)	0.804 0(1)	0.020 8(3)	0.861 8(3)
O(5)	0.908 9(2)	0.442 7(3)	0.833 5(4)
O(4)	0.943 3(2)	−0.206 8(3)	0.505 3(4)
O(6)	0.700 3(1)	0.069 7(4)	0.747 5(4)
N(1)	0.887 3(2)	0.124 7(3)	0.633 6(4)
C(3)	0.904 9(2)	0.319 0(4)	0.808 3(5)
C(4)	0.915 2(2)	0.265 8(4)	0.641 7(5)
C(5)	0.929 5(2)	−0.108 5(4)	0.591 0(5)
C(6)	0.925 1(2)	0.034 8(5)	0.520 7(5)
C(1)	0.766 8(2)	0.067 9(5)	0.747 9(5)
C(2)	0.807 2(2)	0.121 1(5)	0.606 5(5)
OW(3)	1.0038	−0.1699	0.2081
O(7)	0.343 8(3)	0.158 5(8)	0.697 6(7)
C(7)	0.240 3(6)	0.169 2(11)	0.853 7(14)
C(8)	0.302 9(5)	0.100 7(9)	0.784 6(9)
C(9)	0.317 4(7)	−0.036 0(15)	0.832 8(18)
H(1)W(2)	1.028 2(38)	0.110 2(74)	0.911 9(90)
H(2)W(2)	1.036 0(35)	0.027 2(73)	0.816 0(86)
H(1)W(1)	0.939 3(37)	−0.090 3(76)	1.114 2(88)
H(2)W(1)	0.872 5(37)	−0.048 7(73)	1.105 6(89)
H(1)C(4)	0.895 8(37)	0.343 7(70)	0.557 2(80)
H(2)C(4)	0.970 5(35)	0.259 2(71)	0.633 6(87)
H(1)C(2)	0.795 7(35)	0.059 8(72)	0.532 7(79)
H(2)C(2)	0.787 3(34)	0.206 1(70)	0.577 9(78)
H(1)C(6)	0.892 7(36)	0.037 3(68)	0.404 2(77)
H(2)C(6)	0.971 2(35)	0.071 0(71)	0.478 0(83)
H(1)W(3)	0.997 0(36)	−0.160 7(69)	0.119 2(83)
H(2)W(3)	1.047 2(34)	−0.124 6(71)	0.229 0(85)
H(1)C(7)	0.206 8(32)	0.092 8(67)	0.798 4(77)
H(2)C(7)	0.230 8(30)	0.259 1(62)	0.814 9(75)
H(3)C(7)	0.235 8(33)	0.166 7(61)	0.984 4(75)
H(1)C(9)	0.375 4(30)	−0.084 8(64)	0.790 1(73)
H(2)C(9)	0.282 8(32)	−0.088 7(64)	0.789 2(77)
H(3)C(9)	0.317 5(32)	−0.045 7(66)	0.968 2(74)

Table 3. Fractional co-ordinates for compound (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Al(1)	0.720 5(1)	0.170 0(1)	0.056 1(1)	C(3)	0.659 5(2)	0.227 1(3)	0.273 1(4)
Al(2)	1.000 0(0)	−0.120 6(1)	0.250 0(3)	C(4)	0.729 7(3)	0.162 9(4)	0.353 3(4)
O(1)	0.798 5(2)	0.082 5(2)	0.032 1(3)	C(5)	0.635 5(2)	0.010 6(3)	0.065 4(5)
O(2)	0.650 6(2)	0.237 2(2)	0.138 1(3)	C(6)	0.690 6(3)	0.014 5(4)	0.217 5(5)
O(3)	0.637 4(2)	0.080 0(2)	−0.017 8(3)	H(1)C(2)	0.839 4(24)	0.007 7(31)	0.342 2(43)
OW(1)	0.799 2(2)	0.265 6(2)	0.111 5(3)	H(2)C(2)	0.865 9(25)	0.114 8(31)	0.335 1(44)
OW(2)	1.027 4(2)	−0.136 3(3)	0.016 3(4)	H(1)C(4)	0.780 6(30)	0.206 2(35)	0.397 0(50)
OW(3)	0.437 6(3)	0.218 6(4)	0.847 1(6)	H(2)C(4)	0.719 5(29)	0.127 4(35)	0.430 5(52)
OH(1)	0.501 9(2)	−0.100 6(2)	0.200 0(5)	H(1)C(6)	0.660 3(35)	0.016 4(41)	0.274 1(60)
OH(2)	0.500 0(0)	−0.052 9(5)	0.750 0(0)	H(2)C(6)	0.725 8(35)	−0.046 3(42)	0.245 7(61)
O(4)	0.910 5(2)	0.003 6(2)	0.146 2(3)	HW(1)	0.838 3(28)	0.266 5(33)	0.172 5(49)
O(5)	0.617 6(2)	0.266 0(3)	0.335 9(3)	H(1)W(2)	1.037 1(31)	−0.090 5(39)	−0.027 7(56)
O(6)	0.591 9(2)	−0.059 1(3)	0.028 4(4)	H(2)W(2)	1.065 1(37)	−0.166 4(43)	0.040 7(63)
N(1)	0.746 1(2)	0.097 1(2)	0.248 5(3)	H(1)W(3)	0.965 9(43)	−0.241 2(49)	−0.110 5(71)
C(1)	0.849 1(2)	0.047 1(3)	0.144 8(4)	H(2)W(3)	0.929 2(53)	−0.312 3(64)	−0.115 7(92)
C(2)	0.831 1(2)	0.064 9(3)	0.284 8(4)	H[OH(2)]	0.524 8(67)	−0.083 1(78)	−0.168 5(111)

Table 4. Selected bond distances (Å) and angles (°) within $[Al(nta)(H_2O)_2]\cdot(CH_3)_2CO\cdot H_2O$ (**1**)

O(1)–Al	1.893(3)	O(2)–Al	1.888(3)	O(3)–Al	1.863(3)
N(1)–Al	2.086(4)	OW(2)–Al	1.829(3)	OW(1)–Al	1.889(3)
C(1)–O(1)	1.285(5)	C(3)–O(2)	1.282(5)	C(5)–O(3)	1.274(5)
C(1)–O(4)	1.234(5)	C(3)–O(5)	1.234(5)	C(5)–O(6)	1.233(5)
C(2)–N(1)	1.477(5)	C(4)–N(1)	1.479(5)	C(6)–N(1)	1.501(5)
C(1)–C(2)	1.520(6)	C(3)–C(4)	1.529(6)	C(5)–C(6)	1.508(6)

O(1)–Al–O(2)	162.6(1)	O(1)–Al–O(3)	91.0(1)
O(1)–Al–OW(2)	99.3(1)	O(1)–Al–OW(1)	87.2(1)
O(1)–Al–N(1)	82.0(1)	O(2)–Al–O(3)	94.0(1)
O(2)–Al–OW(2)	97.6(1)	O(2)–Al–OW(1)	87.9(1)
O(2)–Al–N(1)	81.8(1)	O(3)–Al–OW(1)	178.1(1)
O(3)–Al–OW(2)	88.1(1)	O(3)–Al–N(1)	85.2(1)
OW(1)–Al–OW(2)	91.6(1)	OW(1)–Al–N(1)	95.1(1)
OW(2)–Al–N(1)	173.2(1)	Al–O(1)–C(1)	117.0(3)
Al–O(2)–C(3)	119.6(3)	Al–O(3)–C(5)	118.6(3)
Al–N(1)–C(2)	105.2(2)	Al–N(1)–C(4)	107.2(2)
Al–N(1)–C(6)	106.0(2)	C(2)–N(1)–C(4)	115.0(3)
C(2)–N(1)–C(6)	112.0(3)	C(4)–N(1)–C(6)	110.7(3)
O(1)–C(1)–C(2)	116.7(3)	O(1)–C(1)–O(4)	123.9(4)
C(2)–C(1)–O(4)	119.4(4)	C(1)–C(2)–N(1)	108.7(3)
O(2)–C(3)–C(4)	115.9(4)	O(2)–C(3)–O(5)	124.2(4)
C(4)–C(3)–O(5)	119.9(4)	C(3)–C(4)–N(1)	108.6(3)
O(3)–C(5)–C(6)	117.5(3)	O(3)–C(5)–O(6)	123.2(4)
C(6)–C(5)–O(6)	119.3(4)	C(5)–C(6)–N(1)	112.1(4)

Table 5. Shorter intermolecular and related hydrogen-atom distances (Å) in compound (**1**)

OW(3) ··· OW(2)^a	2.592(5)	[H(1)W(2) ··· OW(3)	1.634(10)]
OW(3) ··· O(7)^a	2.827(5)	[H(2)W(3) ··· O(7)	2.064(10)]
OW(2) ··· O(6$^{\mathrm{I}}$)^b	2.604(5)	[H(2)W(2) ··· O(6)	1.820(10)]
OW(1) ··· O(4$^{\mathrm{II}}$)^b	2.614(5)	[H(2)W(1) ··· O(4)	1.827(10)]
OW(1) ··· O(5$^{\mathrm{III}}$)^b	2.635(5)	[H(1)W(1) ··· O(5)	1.998(10)]

Symmetry equivalent positions: $^{\mathrm{I}}\ \frac{3}{2} - x, -y, \frac{1}{2} - z$; $^{\mathrm{II}}\ 2 - x, -\frac{1}{2} + y, \frac{3}{2} - z$; $^{\mathrm{III}}\ 2 - x, \frac{1}{2} + y, \frac{3}{2} - z$. ^{a} Intramolecular hydrogen bridges. ^{b} Intermolecular hydrogen bridges.

ethylenediamine) ($d_{av} = 2.094$ Å).[22] The Al–OW(2) bond [1.829(3) Å] (*trans* to nitrogen) is considerably shorter than Al–OW(1) [1.889(3) Å] (*trans* to oxygen), showing the greater *trans* effect exerted by the carboxylate oxygen of nta^{3-}.

The molecular structure of compound (**2**) consists of two asymmetric units related by an inversion centre (Figure 2).

Table 6. Bond distances (Å) and angles (°) within $[Al(H_2O)_2][Al_2(nta)_2(\mu\text{-}OH)_2]OH\cdot 3H_2O$ (**2**)

O(1)–Al(1)	1.904(2)	C(3)–O(5)	1.223(4)
N(1)–Al(1)	2.073(3)	C(4)–N(1)	1.480(4)
C(1)–O(1)	1.279(4)	C(3)–C(4)	1.525(5)
C(1)–O(4)	1.228(4)	O(3)–Al(1)	1.891(2)
C(2)–N(1)	1.481(4)	OH(1′)–Al(1)	1.816(2)
C(1)–C(2)	1.524(5)	C(5)–O(3)	1.283(4)
O(2)–Al(1)	1.909(2)	C(5)–O(6)	1.226(4)
OH(1)–Al(1)	1.878(2)	C(6)–N(1)	1.484(5)
C(3)–O(2)	1.293(4)	C(5)–C(6)	1.501(5)

O(1)–Al(1)–O(2)	161.5(1)	O(1)–Al(1)–O(3)	90.3(1)
O(1)–Al(1)–OH(1)	91.0(1)	O(1)–Al(1)–OH(1′)	98.5(1)
O(1)–Al(1)–N(1)	80.4(1)	O(2)–Al(1)–O(3)	89.1(1)
O(2)–Al(1)–OH(1)	91.4(1)	O(2)–Al(1)–OH(1′)	100.0(1)
O(2)–Al(1)–N(1)	81.1(1)	O(3)–Al(1)–OH(1)	174.2(1)
O(3)–Al(1)–OH(1′)	94.6(1)	O(3)–Al(1)–N(1)	86.3(1)
OH(1)–Al(1)–OH(1′)	79.6(1)	OH(1)–Al(1)–N(1)	99.5(1)
OH(1′)–Al(1)–N(1)	178.6(1)	Al(1)–O(1)–C(1)	118.1(2)
Al(1)–O(2)–C(3)	119.3(2)	Al(1)–O(3)–C(5)	116.0(2)
Al(1)–N(1)–C(2)	106.5(2)	Al(1)–N(1)–C(4)	106.7(2)
Al(1)–N(1)–C(6)	105.3(2)	C(2)–N(1)–C(4)	114.9(3)
C(2)–N(1)–C(6)	110.2(3)	C(4)–N(1)–C(6)	112.4(3)
O(1)–C(1)–C(2)	115.8(3)	O(1)–C(1)–O(4)	124.5(3)
C(2)–C(1)–O(4)	119.7(3)	C(1)–C(2)–N(1)	107.8(3)
O(2)–C(3)–C(4)	114.4(3)	O(2)–C(3)–O(5)	124.6(3)
C(4)–C(3)–O(5)	120.9(3)	C(3)–C(4)–N(1)	108.2(3)
O(3)–C(5)–C(6)	118.0(3)	O(3)–C(5)–O(6)	124.2(3)
C(6)–C(5)–O(6)	117.7(3)	C(5)–C(6)–N(1)	113.8(3)
Al(1)–OH(1)–Al(1′)	100.6(2)		

Table 7. Shorter intermolecular distances (Å) in compound (**2**)

Al(2) ··· OW(1$^{\mathrm{I}}$)	2.496(3)	Al(2) ··· O(4)	2.355(3)
O(5) ··· Al(2$^{\mathrm{II}}$)	2.527(3)	OW(3) ··· OH(1$^{\mathrm{III}}$)	2.775(5)
O(4) ··· OW(1$^{\mathrm{IV}}$)	2.884(5)*	OW(3) ··· OH(2$^{\mathrm{VI}}$)	2.672(6)*
O(6) ··· OW(3$^{\mathrm{V}}$)	2.690(5)*	O(2) ··· OW(1$^{\mathrm{VIII}}$)	2.758(6)*
O(6) ··· OW(2$^{\mathrm{VII}}$)	2.702(5)*		

Symmetry equivalent positions: $^{\mathrm{I}}\ \frac{3}{2} - x, \frac{1}{2} - y, -z$; $^{\mathrm{II}}\ -\frac{1}{2} - x, \frac{1}{2} - y, -z$; $^{\mathrm{III}}\ -\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$; $^{\mathrm{IV}}\ 2 - x, -y, -z$; $^{\mathrm{V}}\ 1 - x, -y, 1 - z$; $^{\mathrm{VI}}\ x, -y, 1 - z$; $^{\mathrm{VII}}\ x, y, 1 + z$; $^{\mathrm{VIII}}\ -\frac{1}{2} + x, \frac{1}{2} + y, z$
* Hydrogen bridges

The unit cell contains four dimeric anionic complexes, $[Al_2(nta)_2(OH)_2]^{2-}$, four cationic entities $[Al(H_2O)_2]^{3+}$, four ionic hydroxide groups, and twelve water molecules. In the anionic complex both aluminium atoms are octahedrally

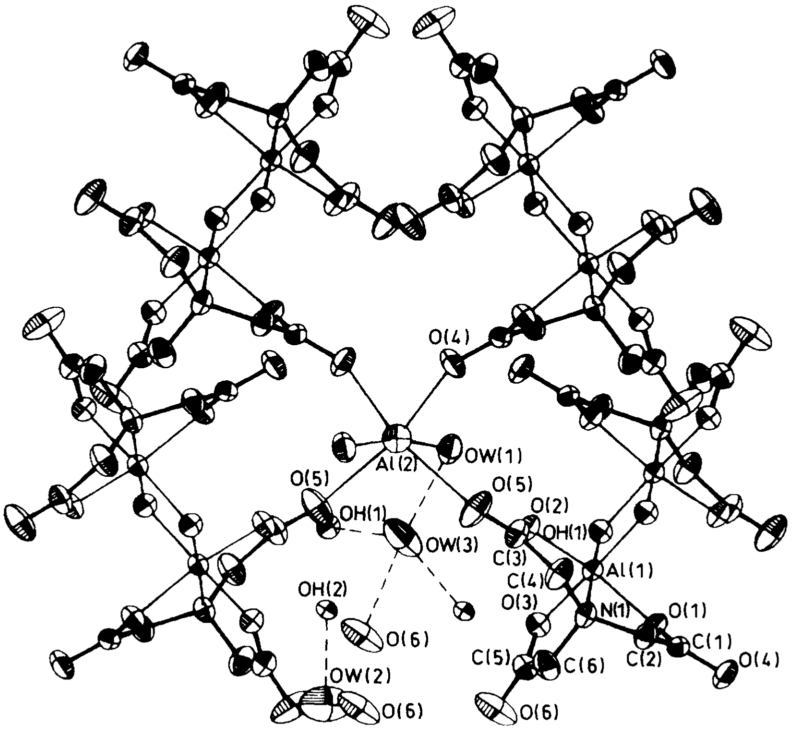

Figure 2. Molecular structure of $[Al(H_2O)_2][Al_2(nta)_2(\mu-OH)_2]OH\cdot 3H_2O$ (**2**)

surrounded by a $O_3N(\mu-OH)_2$ ligand set, and the relevant bond distances compare well with typical figures for ordinary covalent bonds. It is worth remarking that the Al ··· Al distance (d = 2.842 Å) is almost equal to that observed in pure aluminium metal (2.863 Å).[23] Bond distances and angles are collected in Table 6, shorter intermolecular distances in Table 7.

The aluminium atom in the cationic unit is, in turn, surrounded by two *trans* water molecules and by four oxygen atoms belonging to four different anionic units (Figure 2). The distances of the six donor oxygen atoms range from 2.355(3) to 2.527(3) Å, thus indicating the occurrence of weak bonding interactions (sum of the van der Waals radii of Al and O 3.66 Å). Of the remaining sixteen oxygen atoms contained in the cell, eight are located in special position 2, four of them *exactly* and the other four *approximately* (within 0.5 Å) on the binary axis; the remaining eight oxygens [OW(2)] are in a general position. We identify in the first group four water molecules, in the second four ionic hydroxo groups, and in the third eight water molecules of crystallization.

The Al-O distances in the anionic complex (**2**) (d_{av} = 1.901 Å) compare well with those observed in (**1**) (d_{av} = 1.881 Å). The corresponding Al-N distance [2.073(3) Å] compares also well with the metal-nitrogen distances found in (**1**) and in the isopropoxide derivative (**3**).[22] The Al-OH bond lengths in (**2**) (d_{av} = 1.847 Å) appear to be appreciably shorter than the analogous ones in (**3**) (1.893 Å) and, remarkably, also the HO-Al-OH bond angles are slightly greater in (**2**) (79.4°) than in (**3**) (78.2°). Consequently, the Al ··· Al distance of the nta^{3-} complex [d_{av} = 2.842(2) Å] is considerably shorter than in the isopropoxide complex [2.939(5) Å].

Finally, the Al(1)-OH(1) bond [*trans* to nitrogen, 1.816(2) Å] is considerably shorter than Al(1)-OH(1′) [*trans* to oxygen, 1.878(2) Å], as observed in the case of (**1**).

For both compounds (**1**) and (**2**) the crystal lattice appears to be stabilized by strong intermolecular hydrogen bonds (Tables 4 and 5) and the molecular features of the nta^{3-} moiety are similar to those of free H_3nta.[24]

Acknowledgements

We thank Dr. L. Bonoli (Istituto G. Donegani, Novara, Italy) for suggesting the synthetic route to the crude Al-nta adduct.

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Received 20*th June* 1988; *Paper* 8/02435I