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

Giovanni C. Valle

Centro di Studio sui Biopolimeri del C.N.R., c/o Dipartimento di Chimica Organica, Via F. Marzolo 1, I-35131 Padova, Italy G. Giorgio Bombi and Benedetto Corain * Università di Padova, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Via F. Marzolo 1, I-35131 Padova, Italy Mosé Favarato and Paolo Zatta Centro C.N.R. per lo Studio delle Emocianine ed Altre Metalloproteine, Via L. Loredan 6, I-35131 Padova, Italy

The crystal structures of $[Al(nta)(H_2O)_2] \cdot (CH_3)_2 CO \cdot H_2O(1)$ and $[Al(H_2O)_2][Al_2(nta)_2(\mu - OH)_2] - OH \cdot 3H_2O(2)$ (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 nta³⁻ is uncomplicated, *i.e.* quadridentate and non-bridging, and the geometry around Al¹¹¹ is distorted octahedral, owing to the geometric requirements of the nta³⁻ 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 (H₃nta) 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 rain³ or, conceivably, by the action of complexones⁴ 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 nta³⁻ 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-4H-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} -nta³⁻ 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 cm³), 0.1 mol dm⁻³ NH₃ 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 cm³), stirred for 30 min, and filtered again; this procedure was repeated four times. The resulting Al(OH)₃ was treated with H₃nta (10 mmol) in water (100 cm³) 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 cm³, acetone (30

cm³) was added with vigorous stirring. An oily white precipitate was obtained, which transformed into a white powder upon addition of ethanol (10 cm³) 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 C₆AlN_{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)(H₂O)₂]·(CH₃)₂CO·H₂O (1) and the second [Al(H₂O)₂][Al₂(nta)₂(µ-OH)₂]OH·3H₂O (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 —2 θ scan mode, up to 2 θ = 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)].

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

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

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, nta³⁻ displays

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

(a) Crystal data	(1)	(2)
Formula	C ₉ H ₁₈ AlNO ₁₀	C ₁₂ H ₂₅ Al ₃ N ₂ O ₂₀
М	327	598
Habitat	Orthorhombic	Monoclinic
Space group	$P2_{1}2_{1}2_{1}$	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
$D_{\rm c}/{\rm g~cm^{-3}}$	1.409	1.733
µ/cm ⁻¹	1.20	2.09
<i>F</i> (000)	688	1 240
Crystal dimensions/mm	$0.6 \times 0.6 \times 0.6$	$0.3 \times 0.3 \times 0.3$
(b) Intensity measurem	ents	
Scan rate/° min-1	1.8	1.2
Number of reflections		
measured	2 1 3 7	2 918
unique		2769 (R = 0.03)
(c) Structure refinemen	t	
Refinement	Block	Full-matrix least squares
Reflections included	1 800	1 839
$[I \ge 3\sigma(I)]$		
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	+0.32	+0.41
map/e Å ⁻³	-0.30	-0.43
P/		

* Common to both; Mo- K_{α} radiation ($\lambda = 0.710.69$ Å); Z = 4; 22(1) °C; Philips PW1100 diffractometer, graphite monochromator: Scon type 20— θ ; maximum 2 $\theta = 56^{\circ}$; Lorentz polarization corrections, unit weights.

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

a rather complicated ligating behaviour. Thus, with iron(III) it exhibits both four- and three-co-ordination¹⁶ and with dysprosium(III),¹⁷ praseodymium(III), and neodymium(III)¹⁸ it gives rise to co-ordination polymers, thus behaving as a bridging ligand.

We find that A^{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 nta³⁻.

The Al–O distances ($d_{av} = 1.871$ Å) compare well with those observed in the hydrolytically stable complexes tris(acetyl-acetonate) ($d_{av} = 1.879$ 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 [Al₂{OCH(CF₃)₂}₄(μ -OH)₂](en)₂] (3) (en =



Figure 1. Molecular structure of $[Al(nta)(H_2O)_2] \cdot (CH_3)_2 CO \cdot H_2O(1)$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Al	0.903 9(1)	0.043 9(1)	0.857 9(1)	C(9)	0.317 4(7)	-0.036 0(15)	0.832 8(18)
OW(2)	0.907 1(1)	-0.0331(3)	1.054 0(3)	H(1)W(2)	1.028 2(38)	0.110 2(74)	0.911 9(90)
OW(1)	1.004 7(1)	0.072 8(3)	0.858 1(3)	H(2)W(2)	1.036 0(35)	0.027 2(73)	0.816 0(86)
O(2)	0.894 0(1)	0.229 4(3)	0.916 3(3)	H(1)W(1)	0.939 3(37)	-0.0903(76)	1.114 2(88)
O(1)	0.920 5(1)	-0.1165(3)	0.740 4(3)	H(2)W(1)	0.872 5(37)	-0.0487(73)	1.105 6(89)
O(3)	0.804 0(1)	0.020 8(3)	0.861 8(3)	H(1)C(4)	0.895 8(37)	0.343 7(70)	0.557 2(80)
O(5)	0.908 9(2)	0.442 7(3)	0.833 5(4)	H(2)C(4)	0.970 5(35)	0.259 2(71)	0.633 6(87)
O(4)	0.943 3(2)	-0.2068(3)	0.505 3(4)	H(1)C(2)	0.795 7(35)	0.059 8(72)	0.532 7(79)
O(6)	0.700 3(1)	0.069 7(4)	0.747 5(4)	H(2)C(2)	0.787 3(34)	0.206 1(70)	0.577 9(78)
N(1)	0.887 3(2)	0.124 7(3)	0.633 6(4)	H(1)C(6)	0.892 7(36)	0.037 3(68)	0.404 2(77)
C(3)	0.904 9(2)	0.319 0(4)	0.808 3(5)	H(2)C(6)	0.971 2(35)	0.071 0(71)	0.478 0(83)
C(4)	0.915 2(2)	0.265 8(4)	0.641 7(5)	H(1)W(3)	0.997 0(36)	-0.1607(69)	0.119 2(83)
C(5)	0.929 5(2)	-0.1085(4)	0.591 0(5)	H(2)W(3)	1.047 2(34)	-0.1246(71)	0.229 0(85)
C(6)	0.925 1(2)	0.034 8(5)	0.520 7(5)	H(1)C(7)	0.206 8(32)	0.092 8(67)	0.798 4(77)
C(1)	0.766 8(2)	0.067 9(5)	0.747 9(5)	H(2)C(7)	0.230 8(30)	0.259 1(62)	0.814 9(75)
C(2)	0.807 2(2)	0.121 1(5)	0.606 5(5)	H(3)C(7)	0.235 8(33)	0.166 7(61)	0.984 4(75)
OW(3)	1.0038	-0.1699	0.2081	H(1)C(9)	0.375 4(30)	-0.0848(64)	0.790 1(73)
O(7)	0.343 8(3)	0.158 5(8)	0.697 6(7)	H(2)C(9)	0.282 8(32)	-0.0887(64)	0.789 2(77)
C(7)	0.240 3(6)	0.169 2(11)	0.853 7(14)	H(3)C(9)	0.317 5(32)	-0.045 7(66)	0.968 2(74)
C(8)	0.302 9(5)	0.100 7(9)	0.784 6(9)				

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Atom	<i>X</i> /	a	Y/b	Z/c		Atom	X	<i> a</i>	Y/b	Z	:/c	
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Al(1)	0.720	5(1) ().170 0(1)	0.056 1(1)	C(3)	0.659	5(2)	0.227 1(3)	0.2	73 1(4	4)
$ \begin{array}{c} O(1) & 0.798 \ S(2) & 0.082 \ S(2) & 0.032 \ I(3) & C(5) & 0.635 \ S(2) & 0.010 \ S(3) & 0.063 \ 4(5) \\ O(2) & 0.650 \ 6(2) & 0.027 \ 2(2) & 0.138 \ I(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(2) & 0.007 \ 7(31) & 0.342 \ 2(43) \\ OW(2) & 1.027 \ 4(2) & -0.135 \ (3) & 0.016 \ 3(4) & H(2)C(2) & 0.865 \ 9(25) & 0.114 \ 8(31) & 0.335 \ 1(44) \\ OW(2) & 1.027 \ 4(2) & -0.106 \ 6(2) & 0.200 \ 0(5) & H(1)C(2) & 0.685 \ 9(25) & 0.114 \ 8(31) & 0.206 \ 5(25) \\ OH(1) & 0.510 \ 9(2) & -0.006 \ 6(2) & 0.200 \ 0(5) & H(1)C(2) & 0.663 \ 3(35) & 0.016 \ 4(41) & 0.274 \ 1(60) \\ O(4) & 0.910 \ S(2) & 0.003 \ 6(2) & 0.146 \ 2(3) & HW(1) & 0.833 \ 8(28) & 0.266 \ 5(33) & 0.172 \ 5(49) \\ O(6) & 0.519 \ 9(2) & -0.027 \ 9(3) & 0.032 \ 8(4) & H(2)W(2) & 1.057 \ 1(31) & -0.069 \ 5(3) & -0.027 \ 7(55) \\ O(6) & 0.519 \ 9(2) & -0.059 \ 1(3) & 0.028 \ 4(4) & H(2)W(2) & 1.055 \ 1(37) & -0.166 \ 4(43) & 0.040 \ 7(63) \\ O(1) & 0.746 \ 1(2) & 0.047 \ 1(3) & 0.144 \ 8(4) & H(2)W(3) & 0.965 \ 9(43) & -0.212 \ 2(6) & -0.115 \ 7(92) \\ C(1) & 0.849 \ 1(2) & 0.047 \ 1(3) & 0.144 \ 8(4) & H(2)W(3) & 0.965 \ 9(43) & -0.021 \ 2(6) & -0.115 \ 7(92) \\ C(1) & 0.849 \ 1(2) & 0.047 \ 1(3) & 0.144 \ 8(4) & H(2)W(3) & 0.965 \ 9(43) & -0.088 \ 1(78) & -0.168 \ 5(111) \\ \hline Table \ 4. Selected \ bond \ distances \ (Å) \ and \ angles \ (°) \ within \ [A(H_1O_2)_2](A_1(nta)_2(n-OH_2)OH \ 3H,QO(2) & -0.115 \ 5(71) \\ C(1) -O(4) \ 1.285(5) \ C(3) -O(2) \ 1.284(3) \ O(3) -A1 \ 1.889(3) \ O(1) -A1(1) \ 2.794(4) \ O(3) -A1(4) \ 1.89(2) \\ C(1) -C(2) \ 1.524(6) \ O(2) -A-1 \ 1.888(3) \ O(3) -A1 \ 1.889(3) \ O(1) -A1(1) \ 2.794(4) \ O(3) -A1(4) \ 1.89(2) \\ C(1) -C(2) \ 1.524(6) \ O(2) -A-1 \ 1.888(3) \ O(3) -A1 \ 1.889(3) \ O(1) -A1(1) \ 2.794(4) \ C(3) -C(4) \ 1.525(5) \\ C(1) -O(4) \ 1.234(5) \ C(5) -O(6) \ 1.233(5) \ C(1) -O(4) \ 1.232(4) \ O(3) -A1(1) \ 1.89(2) \\ C(1) -C(2) \ 1.524(5) \ C(3) -O(5) \ 1.234(5) \ C(5) -O(6) \ 1.234(5) \ C(5) -O(6) \ 1.234(5) \ C(5) -O(6) \ 1.232$	Al(2)	1.000	0(0) - 0).120 6(1)	0.250 00	3)	C(4)	0.729	7(3)	0.162 9(4)	0.3	53 3(́4	4)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O(1)	0.798	5(2) (0.0825(2)	0.032 1	3)	C(5)	0.635	5(2)	0.010 6(3)	0.0	65 4(:	5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(2)	0.650	6(2) ((237 2(2))	0.138 1	3)	C(6)	0.690	6(3)	0.014 5(4)	0.2	17 5(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	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)) 0.3	42 2(4	43)
$ \begin{array}{c} 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) & 0.437 0(50) \\ OH(1) & 0.509 0(0) & -0.052 9(5) & 0.750 0(0) & H(2)C(6) & 0.660 3(55) & 0.016 4(41) & 0.274 1(66) \\ O(4) & 0.910 5(2) & 0.003 6(2) & 0.146 2(3) & HW(1) & 0.818 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) & -0.099 5(39) & -0.027 7(56) \\ O(6) & 0.591 9(2) & -0.059 1(3) & 0.028 4(4) & H(2)W(2) & 1.035 1(37) & -0.046 3(42) & 0.047 7(56) \\ O(6) & 0.591 9(2) & -0.059 1(3) & 0.028 4(4) & H(2)W(2) & 1.035 1(37) & -0.166 4(43) & 0.040 7(53) \\ N(1) & 0.746 1(2) & 0.097 1(2) & 0.248 5(3) & H(1)W(3) & 0.952 9(33) & -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) & 0.925 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) \\ \hline Table 4. Selected bond distances (Å) and angles (*) within [Al(na1)(H2O)2](Al2(na1)2(µ-OH)2)OH-32(G) (-0.165 5(12)) \\ O(1)-A1 & 1.893(3) & O(2)-A1 & 1.888(3) & O(3)-A1 & 1.863(3) & O(1)-A(1) & 1.9904(2) & C(3)-C(5) & 1.223(4) \\ O(1)-A(1) & 1.2805(5) & C(3)-O(2) & 1.232(5) & C(5)-O(3) & 1.237(5) \\ C(1)-O(1) & 1.234(5) & C(3)-O(5) & 1.234(5) & C(1)-O(1) & 1.229(4) & C(3)-C(4) & 1.528(6) \\ O(1)-A(1) & 1.234(5) & C(3)-O(2) & 1.234(5) & C(5)-O(3) & 1.233(4) \\ O(1)-A(1) & 1.477(5) & C(4)-N(1) & 1.479(5) & C(6)-N(1) & 1.586(6) & O(1)-A(1) & 1.890(2) & C(5)-O(3) & 1.233(4) \\ O(1)-A(1) & 1.234(5) & C(3)-O(2) & 1.234(5) & C(5)-O(3) & 1.234(6) & C(3)-C(4) & 1.528(6) & C(3)-C(4) & 1.528(6) & C(3)-C(6) & 1.501(5) & C(1)-O(1) & 1.279(4) & C(3)-C(4) & 1.528(6) & C(3)-C(4) & 1.528(6) & C(3)-C(4) & 1.528(6) & C(3)-C(6) & 1.501(5) & C(1)-O(1) & 1.279(4) & C(3)-C(4) & 1.528(6) & C(3)-C(6) & 1.501(5) & C(1)-O(1) & 1.279(4) & C(3)-C(4) & 1.528(6) & C(3)-C(6) & 1.501(5) & C(1)-O(1) & 1.283(4) & C(3)-C(6) & 1.23$	OW (1)	0.799	2(2) ().265 6(2)	0.111 5(3)	H(2)C(2)	0.865	9(25)	0.114 8(31)) 0.3	35 1(4	44)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	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)) 0.3	97 0(:	50)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	OW(3)	0.437	6(3) ().218 6(4)	0.847 1(6)	H(2)C(4)	0.719	5(29)	0.127 4(35)	0.4	30 5(:	52)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	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)	0.2	74 1(50)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	OH(2)	0.500	0(0) -0	0.052 9(5)	0.750 0(0)	H(2)C(6)	0.725	8(35)	-0.046 3(42)	0.2	45 7(51)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(4)	0.910	5(2) 0	0.003 6(2)	0.146 2(3)	HW(1)	0.838	3(28)	0.266 5(33)	0.1	72 5(4	49)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	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)) -0.0	27 7(:	56)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	O(6)	0.591	9(2) -0	0.059 1(3)	0.028 4(4)	H(2)W(2)	1.065	1(37)	-0.166 4(43)) 0.0	40 7(0	53)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1)	0.746	1(2) 0	0.097 1(2)	0.248 5(3)	H(1)W(3)	0.965	9(43)	-0.241 2(49)) -0.1	10 5('	71)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	C(1)	0.849	1(2) 0	0.047 1(3)	0.144 8(4)	H(2)W(3)	0.929	2(53)	-0.312 3(64)) -0.1	15 7(9	92)
Table 4. Selected bond distances (Å) and angles (°) within [Al(nta)(H ₂ O) ₂]-(CH ₃) ₂ CO-H ₂ O (1) Table 6. Bond distances (Å) and angles (°) within [Al(H ₂ O) ₂][(Al ₂ (nta) ₂ (μ -OH ₃) ₂ O(H ₃ O(Z)) O(1)-AI 1.893(3) O(2)-AI 1.888(3) O(3)-AI 1.863(3) O(1)-AI(1) 1.904(2) C(3)-O(5) 1.223(4) O(1)-AI 1.285(5) C(3)-O(2) 1.282(5) C(5)-O(6) 1.234(5) C(3)-O(2) 1.224(5) C(5)-O(6) 1.233(5) C(1)-O(1) 1.279(4) C(3)-C(4) 1.529(6) C(1)-C(1) 1.234(5) C(3)-O(2) 1.234(5) C(5)-O(6) 1.233(5) C(1)-O(1) 1.279(4) C(3)-AI(1) 1.891(2) C(1)-C(2) 1.520(6) C(3)-C(4) 1.529(6) C(5)-C(6) 1.508(6) C(1)-C(2) 1.524(4) O(3)-AI(1) 1.891(2) O(1)-AI-O(2) 162.6(1) O(1)-AI-O(3) 91.0(1) O(1)-AI(1) 1.878(2) C(6)-N(1) 1.848(4) O(2)-AI-N(1) 82.0(1) O(2)-AI-O(3) 94.0(1) O(1)-AI(1)-O(1) 1.184(2) O(2)-AI(1)-O(1) 93.3(1) O(2)-AI-N(1) 83.8(1)	C(2)	0.831	1(2) ().064 9(3)	0.284 8(4)	H[OH(2)]	0.524	8(67)	-0.083 1(78)) -0.1	68 5(111)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Table 4. Selected bond distances (Å) and angles (°) withinTable 6. Bond distances (Å) and angles (°) within $[Al(nta)(H_2O)_2]$ -(CH ₃) ₂ CO-H ₂ O (1)Table 6. Bond distances (Å) and angles (°) within $[Al(H_2O)_2]$ [Al ₂ (nta) ₂ (µ-OH) ₂]OH-3H ₂ O (2)						within						
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	O(1)-A1	1.893(3)	O(2)-A1	1.888(3)	O(3)-A1	1.863(3)	O(1) - A!(1)		1.904(2)	C(3)-C	D(5)		1.223(4)
$ \begin{array}{c} C(1)-C(1) & 1.285(5) & C(3)-C(2) & 1.282(5) & C(5)-C(3) & 1.274(5) & C(1)-C(1) & 1.279(4) & C(3)-C(4) & 1.525(5) \\ C(1)-O(4) & 1.234(5) & C(3)-C(2) & 1.234(5) & C(5)-O(6) & 1.233(5) & C(1)-O(4) & 1.228(4) & O(3)-A1(1) & 1.891(2) \\ C(2)-N(1) & 1.477(5) & C(4)-N(1) & 1.479(5) & C(6)-N(1) & 1.501(5) & C(2)-N(1) & 1.481(4) & OH(1)-A1(1) & 1.816(2) \\ C(1)-C(2) & 1.520(6) & C(3)-C(4) & 1.529(6) & C(5)-C(6) & 1.508(6) & C(1)-C(2) & 1.524(5) & C(5)-O(3) & 1.228(4) \\ O(1)-A1-O(2) & 162.6(1) & O(1)-A1-OW(1) & 87.2(1) & C(3)-O(2) & 1.293(4) & C(5)-C(6) & 1.501(5) \\ O(1)-A1-OW(2) & 99.3(1) & O(1)-A1-OW(1) & 87.2(1) & C(3)-O(2) & 161.5(1) & O(1)-A1(1)-O(3) & 90.3(1) \\ O(2)-A1-N(1) & 82.0(1) & O(2)-A1-OW(1) & 87.9(1) & O(1)-A1(1)-O(2) & 161.5(1) & O(1)-A1(1)-O(3) & 90.3(1) \\ O(2)-A1-N(1) & 81.8(1) & O(3)-A1-OW(1) & 178.1(1) & O(1)-A1(1)-O(1) & 91.0(1) & O(1)-A1(1)-O(3) & 90.3(1) \\ O(2)-A1-N(1) & 81.8(1) & O(3)-A1-OW(1) & 178.1(1) & O(1)-A1(1)-OH(1) & 91.0(1) & O(2)-A1(1)-OH(1) & 98.5(1) \\ O(3)-A1-OW(2) & 91.6(1) & OW(1)-A1-N(1) & 85.2(1) & O(1)-A1(1)-OH(1) & 91.4(1) & O(2)-A1(1)-OH(1) & 98.5(1) \\ OW(1)-A1-OW(2) & 91.6(1) & OW(1)-A1-N(1) & 95.1(1) & O(2)-A1(1)-OH(1) & 91.4(1) & O(2)-A1(1)-OH(1) & 178.2(1) \\ A1-O(2)-C(3) & 119.6(3) & A1-O(3)-C(5) & 118.6(3) & O(3)-A1(1)-OH(1) & 91.4(1) & O(3)-A1(1)-OH(1) & 174.2(1) \\ A1-N(1)-C(6) & 106.0(2 & C(2)-N(1)-C(4) & 115.0(3) & OH(1)-A1(1)-OH(1) & 93.6(1) & OH(1)-A1(1)-N(1) & 86.3(1) \\ A1-N(1)-C(6) & 106.0(2 & C(2)-N(1)-C(6) & 110.7(3) & A1(1)-OH(1) & 178.6(1) & A1(1)-O(1)-C(5) & 116.0(2) \\ O(1)-C(1)-C(2) & 116.7(3) & O(1)-C(1)-O(4) & 112.9(4) & A(1)-O(2)-C(3) & 119.3(2) & A1(1)-O(1)-C(4) & 114.9(3) \\ O(2)-C(3)-C(6) & 117.5(3) & O(1)-C(1)-O(4) & 123.9(4) & A(1)-N(1)-C(6) & 110.2(3) & C(4)-N(1)-C(6) & 116.0(2) \\ O(1)-C(1)-C(2) & 116.7(3) & O(1)-C(1)-O(4) & 123.9(4) & A(1)-N(1)-C(6) & 110.2(3) & C(4)-N(1)-C(6) & 116.0(2) \\ O(1)-C(1)-C(4) & 119.4(4) & C(1)-C(2)-N(1) & 108.6(3) & O(1)-C(1)-C(6) & 116.0(2) & C(3)-C(6)-N(1) & 118.1(3) \\ O(2)-C(3)-C(6) & 119.9(4) & C(3)-C(6)-N(1) & 11$	N(1)-AI	2.086(4)	OW(2)-Al	1.829(3)	OW(1)-A	1.889(3)	N(1) - A(1)		2.073(3)	C(4)	$\mathbf{N}(1)$		1.480(4)
$\begin{array}{c} C(1)-C(2) & 1.234(5) & C(3)-C(3) & 1.234(5) & C(5)-O(6) & 1.233(5) & C(1)-O(4) & 1.228(4) & O(3)-Al(1) & 1.891(2) \\ C(2)-N(1) & 1.477(5) & C(4)-N(1) & 1.479(5) & C(6)-N(1) & 1.501(5) & C(2)-N(1) & 1.481(4) & OH(1)-Al(1) & 1.816(2) \\ C(1)-C(2) & 1.520(6) & C(3)-C(4) & 1.529(6) & C(5)-C(6) & 1.508(6) & C(1)-C(2) & 1.524(5) & C(5)-O(6) & 1.223(4) \\ O(2)-Al(1) & 1.909(2) & C(5)-O(6) & 1.222(64) \\ O(1)-Al-O(2) & 162.6(1) & O(1)-Al-O(3) & 91.0(1) & OH(1)-Al(1) & 1.878(2) & C(6)-N(1) & 1.484(5) \\ O(1)-Al-OW(2) & 99.3(1) & O(1)-Al-OW(1) & 87.2(1) & C(3)-O(2) & 1.293(4) & C(5)-C(6) & 1.501(5) \\ O(2)-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(1)-Al(1)-OH(1) & 91.0(1) & O(1)-Al(1)-OH(1) & 98.5(1) \\ O(3)-Al-OW(2) & 97.6(1) & O(3)-Al-OW(1) & 178.1(1) & O(1)-Al(1)-OH(1) & 91.0(1) & O(1)-Al(1)-OH(1) & 98.5(1) \\ O(4)-Al-OW(2) & 91.6(1) & OW(1)-Al-N(1) & 95.1(1) & O(2)-Al(1)-OH(1) & 91.0(1) & O(2)-Al(1)-OH(1) & 98.5(1) \\ OW(1)-Al-OW(2) & 91.6(1) & OW(1)-Al-N(1) & 95.1(1) & O(2)-Al(1)-OH(1) & 91.4(1) & O(3)-Al(1)-OH(1) & 100.0(1) \\ OW(2)-Al-N(1) & 173.2(1) & Al-O(1)-C(1) & 117.0(3) & O(2)-Al(1)-OH(1) & 91.4(1) & O(3)-Al(1)-OH(1) & 100.0(1) \\ OW(2)-Al-N(1) & 173.2(1) & Al-O(1)-C(1) & 117.0(3) & O(2)-Al(1)-OH(1) & 91.4(1) & O(3)-Al(1)-OH(1) & 174.2(1) \\ Al-N(1)-C(2) & 105.2(2) & Al-N(1)-C(4) & 107.2(2) & OH(1)-Al(1)-OH(1) & 91.4(1) & O(3)-Al(1)-OH(1) & 174.2(1) \\ Al-N(1)-C(6) & 1106.0(2) & C(2)-N(1)-C(4) & 115.0(3) & OH(1)-Al(1)-OH(1) & 79.6(1) & OH(1)-Al(1)-OH(1) & 174.2(1) \\ Al-N(1)-C(6) & 1105.0(2) & C(2)-N(1)-C(4) & 115.0(3) & OH(1)-Al(1)-OH(1) & 79.6(1) & OH(1)-Al(1)-OH(1) & 95.5(1) \\ Al-N(1)-C(6) & 1105.0(2) & Al-(1)-C(4) & 115.0(3) & OH(1)-Al(1)-OH(1) & 79.6(1) & OH(1)-Al(1)-OH(1) & 95.5(1) \\ Al-N(1)-C(6) & 1105.0(3) & C(4)-N(1)-C(6) & 1105.3(2) & C(2)-N(1)-C(4) & 114.9(3) \\ O(2)-C(3)-C(4) & 1115.9(4) & O(2)-C(3)-O(5) & 124.2(4) & C(2)-N(1)-C(6) & 1102.3() & C(4)-N(1)-C(6) & 1124.3(3) \\ O(3)-C(5)-C(6) & 118.9(4) & O(3)-C(5)-O(6) & 123.2(4) & C(2)-N(1)-C(4) & 114$	C(1) - O(1)	1.285(5)	C(3) - O(2)	1.282(5)	C(5) - O(3)	1.274(5)	C(1) - O(1)		1.279(4)	C(3)-C(3)	C(4)		1.525(5)
$\begin{array}{c} C(2) - N(1) & 1.471(5) & C(4) - N(1) & 1.479(5) & C(6) - N(1) & 1.501(5) & C(2) - N(1) & 1.481(4) & OH(1) - AI(1) & 1.816(2) \\ C(1) - C(2) & 1.520(6) & C(3) - C(4) & 1.529(6) & C(5) - C(6) & 1.508(6) & C(1) - C(2) & 1.524(5) & C(5) - O(3) & 1.2283(4) \\ O(1) - AI - O(2) & 162.6(1) & O(1) - AI - O(3) & 91.0(1) & OH(1) - AI(1) & 1.878(2) & C(6) - N(1) & 1.484(4) \\ O(1) - AI - OW(2) & 99.3(1) & O(1) - AI - OW(1) & 87.2(1) & C(3) - O(2) & 1.293(4) & C(5) - C(6) & 1.501(5) \\ O(1) - AI - N(1) & 82.0(1) & O(2) - AI - OW(1) & 87.9(1) & O(1) - AI(1) - OI(1) & 91.0(1) & O(1) - AI(1) - OI(3) & 90.3(1) \\ O(2) - AI - OW(2) & 97.6(1) & O(2) - AI - OW(1) & 87.9(1) & O(1) - AI(1) - OH(1) & 91.0(1) & O(1) - AI(1) - OH(1) & 98.5(1) \\ O(3) - AI - OW(2) & 88.1(1) & O(3) - AI - N(1) & 85.2(1) & O(1) - AI(1) - OH(1) & 91.0(1) & O(2) - AI(1) - OH(1) & 98.5(1) \\ OW(1) - AI - OW(2) & 91.6(1) & OW(1) - AI - N(1) & 95.1(1) & O(2) - AI(1) - OH(1) & 91.4(1) & O(2) - AI(1) - OH(1) & 100.0(1) \\ OW(2) - AI - N(1) & 173.2(1) & AI - O(1) - C(1) & 117.0(3) & O(2) - AI(1) - OH(1) & 91.4(1) & O(3) - AI(1) - OH(1) & 174.2(1) \\ AI - O(2) - C(3) & 119.6(3) & AI - O(3) - C(5) & 118.6(3) & O(3) - AI(1) - OH(1) & 91.4(1) & O(3) - AI(1) - OH(1) & 174.2(1) \\ AI - O(2) - C(3) & 119.6(3) & AI - O(3) - C(5) & 118.6(3) & O(3) - AI(1) - OH(1) & 91.4(1) & O(3) - AI(1) - OH(1) & 174.2(1) \\ AI - N(1) - C(2) & 105.2(2) & AI - N(1) - C(4) & 107.2(2) & OH(1) - AI(1) - OH(1) & 93.4(1) - OH(1) - N(1) & 178.6(1) & AI(1) - OH(1) & 174.2(1) \\ AI - N(1) - C(6) & 1106.0(2) & C(2) - N(1) - C(6) & 1103.0(3) & OH(1) - AI(1) - OH(1) & 79.6(1) & OH(1) - AI(1) - N(1) & 95.5(1) \\ AI - N(1) - C(6) & 1105.0(3) & C(4) - N(1) & 108.7(3) & AI(1) - OH(1) & 79.6(1) & OH(1) - AI(1) - N(1) & 188.1(2) \\ C(2) - C(1) - O(4) & 119.4(4) & C(1) - C(2) - N(1) & 108.7(3) & AI(1) - O(1) - C(2) & 115.8(3) & O(1) - C(1) - C(4) & 114.9(3) \\ O(2) - C(3) - C(6) & 119.9(4) & C(2) - C(3) - O(5) & 124.2(4) & C(2) - C(1) - O(4) & 119.7(3) & C(1) - C(2) - N(1) & 108.8(3) \\ O(3) - C(5) - C(6) & 1118.0($	C(1) = O(4)	1.234(5)	C(3) - O(5)	1.234(5)	C(5) - O(6)	1 233(5)	C(1) = O(4)		1 228(4)	O(3) - 4			1.891(2)
$ \begin{array}{c} C(1)-C(2) & 1.520(6) & C(3)-C(4) & 1.529(6) & C(5)-C(6) & 1.508(6) & C(1)-C(2) & 1.524(5) & C(5)-O(6) & 1.2283(4) \\ C(1)-Al-O(2) & 162.6(1) & O(1)-Al-O(3) & 91.0(1) & OH(1)-Al(1) & 1.878(2) & C(5)-O(6) & 1.226(4) \\ O(1)-Al-OW(2) & 99.3(1) & O(1)-Al-OW(1) & 87.2(1) & C(3)-O(2) & 1.293(4) & C(5)-C(6) & 1.501(5) \\ O(1)-Al-N(1) & 82.0(1) & O(2)-Al-OW(1) & 87.9(1) & O(1)-Al(1)-O(2) & 161.5(1) & O(1)-Al(1)-O(3) & 90.3(1) \\ O(2)-Al-OW(2) & 97.6(1) & O(2)-Al-OW(1) & 87.9(1) & O(1)-Al(1)-O(1) & 91.0(1) & O(1)-Al(1)-O(3) & 90.3(1) \\ O(2)-Al-OW(2) & 97.6(1) & O(2)-Al-OW(1) & 87.9(1) & O(1)-Al(1)-O(1) & 91.0(1) & O(1)-Al(1)-O(3) & 90.3(1) \\ O(2)-Al-OW(2) & 97.6(1) & O(2)-Al-OW(1) & 178.1(1) & O(1)-Al(1)-O(1) & 91.0(1) & O(1)-Al(1)-O(1) & 98.5(1) \\ O(2)-Al-OW(2) & 91.6(1) & OW(1)-Al-N(1) & 95.1(1) & O(2)-Al(1)-OH(1) & 91.4(1) & O(2)-Al(1)-OH(1) & 98.5(1) \\ OW(1)-Al-OW(2) & 91.6(1) & OW(1)-Al-N(1) & 95.1(1) & O(2)-Al(1)-OH(1) & 91.4(1) & O(3)-Al(1)-OH(1) & 100.0(1) \\ OW(2)-Al-N(1) & 173.2(1) & Al-O(1)-C(5) & 118.6(3) & O(3)-Al(1)-OH(1) & 91.4(1) & O(3)-Al(1)-OH(1) & 174.2(1) \\ Al-O(2)-C(3) & 119.6(3) & Al-O(3)-C(5) & 118.6(3) & O(3)-Al(1)-OH(1) & 94.6(1) & O(3)-Al(1)-OH(1) & 174.2(1) \\ Al-N(1)-C(2) & 105.2(2) & Al-N(1)-C(4) & 107.2(2) & OH(1)-Al(1)-OH(1) & 79.6(1) & OH(1)-Al(1)-N(1) & 95.5(1) \\ Al-N(1)-C(2) & 105.2(2) & Al-N(1)-C(4) & 115.0(3) & OH(1)-Al(1)-OH(1) & 79.6(1) & OH(1)-Al(1)-N(1) & 95.5(1) \\ Al-N(1)-C(6) & 112.0(3) & C(4)-N(1)-C(4) & 115.0(3) & OH(1)-Al(1)-OH(1) & 79.6(1) & OH(1)-Al(1)-N(1) & 95.5(1) \\ Al-N(1)-C(6) & 112.0(3) & C(4)-N(1)-C(4) & 113.0(3) & OH(1)-Al(1)-OH(1) & 79.6(1) & OH(1)-Al(1)-N(1) & 95.5(1) \\ Al-N(1)-C(6) & 112.0(3) & C(4)-N(1)-C(6) & 110.7(3) & Al(1)-O(2)-C(3) & 119.3(2) & Al(1)-O(3)-C(5) & 116.0(2) \\ O(1)-C(1)-C(2) & 116.7(3) & O(1)-C(1)-O(4) & 123.9(4) & Al(1)-N(1)-C(6) & 105.3(2) & C(2)-N(1)-C(4) & 114.9(3) \\ O(2)-C(3)-C(6) & 119.9(4) & O(2)-C(3)-O(5) & 124.2(4) & C(2)-C(1)-O(4) & 119.7(3) & C(1)-C(2)-N(1) & 108.8(3) \\ O(3)-C(5)-C(6) & 118.0(3) & O(3)-C(5)-O(6) & 124.2(3) \\ O(3)-C$	C(2) - N(1)	1.251(5) 1.477(5)	C(4) - N(1)	1 479(5)	C(6) - N(1)	1 501(5)	C(2) - N(1)		1 481(4)	OH(1/	(1)		1.816(2)
$\begin{array}{c} (0) - (1) - (2) -$	C(1)-C(2)	1.520(6)	C(3)-C(4)	1.529(6)	C(5)-C(6)	1.508(6)	C(1)-C(2)		1.524(5)	C(5)-C	$\mathbf{\hat{D}}(3)$		1.283(4)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	-(-)		-(-) -(-)		-(-) -(-)		O(2) - Al(1)		1.909(2)	C(5)-C	D(6)		1.226(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(1)-Al-O(2)	162.6(1)	O(1)–Al-	-O(3)	91.0(1)	OH(1)-Al(1)		1.878(2)	C(6)-1	N		1.484(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O(1)-Al-OV	V(2)	99.3(1)	O(1)-Al	$-\mathbf{O}\mathbf{W}(1)$	87.2(1)	C(3)-O(2)		1.293(4)	C(5)-C	ത്		1.501(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(1) - AI - N(1)	82.0(1)	O(2)-Al	-O(3)	94.0(1)	-() -(-)		()	- (-)			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(2) - Al - OW	Ń(2)	97.6(1)	O(2)-Al	$-\mathbf{O}\mathbf{W}(1)$	87.9(1)	O(1) - Al(1) - O(1) -	D(2)	161.5(1)	O(1)-A	AI(1) - O(3)		90.3(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(2)-AI-N(1)	81.8(1)	O(3) - Al	$-\mathbf{OW}(1)$	178.1(1)	O(1) - Al(1) - O(1) -	$\dot{OH}(1)$	91.0(1)	Q(1)-4	$\dot{\mathbf{A}}(1) - \dot{\mathbf{O}}\dot{\mathbf{H}}(1)$	3	98.5(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(3)-Al-OV	Ń(2)	88.1(1)	O(3)-Al	-N(1)	85.2(1)	O(1) - Al(1) - N	N(1)	80.4(1)	O(2) - A	Al(1) - O(3)	,	89.1(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	OW(1)-Al-0	OW(2)	91.6(1)	OW(1)-	Al - N(1)	95.1(1)	O(2) - Al(1) - O(2) - Al(1) - O(2) - Al(1) - O(2) - Al(1) - O(2) - O(2	$\dot{OH(1)}$	91.4(1)	O(2)-A	Al(1)–OH(1)	100.0(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	OW(2)-Al-1	N(1)	173.2(1)	Al-O(1)	-C(1)	117.0(3)	O(2)-Al(1)-N	N(1)	81.1(1)	O(3)-A	AI(1) - OH(1))	174.2(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Al-O(2)-C(3)	3)	119.6(3)	Al-O(3)	-C(5)	118.6(3)	O(3) - Al(1) - Al(1) - Al(1) - Al(1) - O(3) - Al(1) -	$\dot{OH}(1')$	94.6(1)	O(3)-A	AI(1) - N(1)		86.3(1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Al-N(1)-C(2	2)	105.2(2)	Al-N(1)	-C(4)	107.2(2)	OH(1)-Al(1)	-OH(1')	79.6(1)	OH(1)	-AI(1)-N(1))	99.5(1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Al-N(1)-C(6)	5)	106.0(2)	C(2)-N(1)-C(4)	115.0(3)	OH(1')-Al(1))-N(1)	178.6(1)	Al(1)-	O(1) - C(1)		118.1(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(2)-N(1)-C	C(6)	112.0(3)	C(4)-N(1)-C(6)	110.7(3)	Al(1)-O(2)-O	C(3)	119.3(2)	Al(1)-0	O(3) - C(5)		116.0(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(1)-C(1)-C	C(2)	116.7(3)	O(1)-C(1)–O(4)	123.9(4)	Al(1) - N(1) - O(1) -	C(2)	106.5(2)	Al(1)-1	N(1) - C(4)		106.7(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(2)-C(1)-C	D(4)	119.4(4)	C(1) - C(2)	2) - N(1)	108.7(3)	Al(1) - N(1) - O(1) -	C(6)	105.3(2)	C(2)-N	V(1) - C(4)		114.9(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(2)-C(3)-C	C(4)	115.9(4)	O(2)-C(3)-O(5)	124.2(4)	C(2)-N(1)-C	(6)	110.2(3)	C(4)-N	V(1) - C(6)		112.4(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(4)C(3)C) (5)	119.9(4)	C(3)-C(4	4)–N(1)	108.6(3)	O(1)-C(1)-C	(2)	115.8(3)	O(1)-0	C(1)-O(4)		124.5(3)
$\frac{C(6)-C(5)-O(6)}{Table 5. Shorter intermolecular and related hydrogen-atom distances} = \frac{C(6)-C(5)-O(6)}{C(4)-C(3)-O(5)} = \frac{112.1(4)}{112.1(4)} = \frac{O(2)-C(3)-O(4)}{O(2)-C(3)-O(5)} = \frac{1124.6(3)}{120.9(3)} = \frac{O(2)-C(3)-O(5)}{O(3)-C(5)-O(6)} = \frac{O(2)-O(5)}{120.9(3)} = \frac{O(2)-O(5)}{O(3)-C(5)-O(6)} = \frac{O(2)-O(5)}{O(3)-O(5)} = \frac{O(2)-O(5)}{O(5)} = O$	O(3)-C(5)-C	C(6)	117.5(3)	O(3)-C(5)-O(6)	123.2(4)	C(2)-C(1)-O	(4)	119.7(3)	C(1)-C	C(2) - N(1)		107.8(3)
$\frac{C(4)-C(3)-O(5)}{O(3)-C(5)-C(6)} \frac{120.9(3)}{118.0(3)} \frac{C(3)-C(4)-N(1)}{O(3)-C(5)-O(6)} \frac{108.2(3)}{124.2(3)} \frac{C(4)-C(3)-O(5)}{C(6)-C(5)-O(6)} \frac{117.7(3)}{117.7(3)} \frac{C(5)-C(6)-N(1)}{C(5)-C(6)-N(1)} \frac{113.8(3)}{113.8(3)}$	C(6)-C(5)-C	D(6)	119.3(4)	C(5)-C(5)-N(1)	112.1(4)	O(2)-C(3)-C	(4)	114.4(3)	O(2)-0	C(3)-O(5)		124.6(3)
O(3)-C(5)-C(6) 118.0(3) O(3)-C(5)-O(6) 124.2(3) Table 5. Shorter intermolecular and related hydrogen-atom distances $C(6)-C(5)-O(6)$ $117.7(3)$ $C(5)-C(6)-N(1)$ $113.8(3)$							C(4)-C(3)-O	(5)	120.9(3)	C(3)-C	C(4) - N(1)		108.2(3)
Table 5. Shorter intermolecular and related hydrogen-atom distances $C(6)-C(5)-O(6)$ 117.7(3) $C(5)-C(6)-N(1)$ 113.8(3)					· · · · · · · · · · · · · · · · · · ·		O(3)-C(5)-C	(6)	118.0(3)	O(3)-0	C(5)-O(6)		124.2(3)
	Table 5. Sho	orter interi	nolecular and	related hy	drogen-atom	distances	C(6)-C(5)-O	(6) - A I(1')	117.7(3)	C(5)-C	C(6)–N(1)		113.8(3)

Table 3. Fractional	co-ordinates fo	or compound (2)
---------------------	-----------------	-----------------

T (Å) in compound (1)

$OW(3) \cdots O'$	$W(2)^a = 2.592(5)$	$[H(1)W(2)\cdots OW(3)]$	1.634(10)]
$OW(3) \cdots O($	(7) ^{<i>a</i>} 2.827(5)	$[H(2)W(3)\cdots O(7)]$	2.064(10)]
$OW(2) \cdots O($	$(6^{\rm I})^{b}$ 2.604(5)	$[H(2)W(2)\cdots O(6)]$	1.820(10)]
$OW(1) \cdots O($	$(4^{II})^{b}$ 2.614(5)	$[H(2)W(1)\cdots O(4)]$	1.827(10)]
$OW(1) \cdots O($	(5 ^{III}) ^b 2.635(5)	$[H(1)W(1) \cdots O(5)]$	1.998(10)]
Symmetry equivalent $\frac{3}{2} - z; \stackrel{\text{III}}{=} 2 - z^{b}$ Intermolecula	ivalent positions: $x, \frac{1}{2} + y, \frac{3}{2} - z.$ Ir hydrogen bridge	$\frac{1}{2} = x, -y, \frac{1}{2} = z; \frac{1}{2} = z; \frac{1}{2} = \frac{1}{2}$ a Intramolecular hydropes.	$-x, -\frac{1}{2} + y,$ gen bridges.

ethylenediamine) $(d_{av} = 2.094 \text{ Å}).^{22}$ 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 nta³⁻.

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

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

$Al(2) \cdots OW(1^{I})$	2.496(3)	$Al(2) \cdots O(4)$	2.355(3)
$O(5) \cdots Al(2^{II})$	2.527(3)	$OW(3) \cdots OH(1^{III})$	2.775(5)
$O(4) \cdots OW(1^{IV})$	2.884(5)*	$OW(3) \cdots OH(2^{v_1})$	2.672(6)*
$O(6) \cdots OW(3^{V})$	2.690(5)*	$O(2) \cdots OW(1^{VIII})$	2.758(6)*
$O(6) \cdots OW(2^{VII})$	2.702(5)*		
Symmetry equivalent $-z; {}^{III} - \frac{1}{2} + x, \frac{1}{2} - y,$ $-y, 1 - z; {}^{VII} x, y, 1$ + Hydrogen bridges	positions: $\frac{1}{2} - 1 + z$; $\frac{1}{2} - x$, + z; $\frac{1}{2} - x$, + z; $\frac{1}{2} + x$,	$\begin{array}{c} x, \frac{1}{2} - y, -z; \ ^{II} - \frac{1}{2} - \\ -y, -z; \ ^{V} 1 - x, -y, \\ \frac{1}{2} + y, z \end{array}$	$-x, \frac{1}{2} - y, $ $1 - z; ^{VI}x, $

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) $(d_{av} = 1.901 \text{ Å})$ compare well with those observed in (1) $(d_{av} = 1.881 \text{ Å})$. 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) $(d_{av} = 1.847 \text{ Å})$ 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-\cdots Al distance of the nta³⁻ complex [$d_{av} = 2.842(2) \text{ Å}$] 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 H₃nta.²⁴

Acknowledgements

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

References

- 1 R. Perry, P. W. W. Kirk, T. Stephenson, and J. N. Lester, *Water Res.*, 1984, 18, 255.
- 2 C. T. Driscoll, jun., J. P. Baker, J. J. Bisogni, jun., and C. L. Schofield, *Nature (London)*, 1980, 284, 161.
- 3 S. C. Tam and R. J. P. Williams, J. Inorg. Biochem., 1986, 26, 35.
- 4 U. Förster, in 'Metal Pollution in the Aquatic Environment,' eds. U. Förster and G. W. T. Wittman, Springer, Berlin, 1981, p. 197.
- 5 See, for example, 'Amendment of NYCRR Part 659,' State of New York, 1985.
- 6 A. E. Martell and R. M. Smith, 'Critical Stability Constants,' Plenum, New York, 1974, vol. 1, pp. 139–144; 1982, vol. 5, pp. 62, 63.
- 7 G. G. Bombi, B. Corain, R. Giordano, D. Pagani, A. G. Sesti, and P. Zatta, in 'Neuroendocrine System and Aging,' eds. P. Vezzadini, A. Facchini, and G. Labò, Eurage, Rijswijk, 1986, p. 253.
- 8 P. Zatta, R. Giordano, B. Corain, M. Favarato, and G. G. Bombi, Toxicol. Lett., 1987, 39, 185.
- 9 D. R. Crapper McLachlan, Neurobiol. Aging, 1986, 7, 525.
- 10 P. Main, MULTAN 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of New York, 1980.
- 11 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
- 12 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
- 13 J. D. Oliver, B. L. Barnett, and L. C. Štrickland, Acta Crystallogr., Sect. B, 1984, 40, 377; L. S. White, P. V. Nilsson, L. M. Pignolet, and L. Que, jun., J. Am. Chem. Soc., 1984, 106, 8312; K. Wieghart, U. Quilitzsch, J. Weiss, and B. Nuber, Inorg. Chem., 1980, 19, 2514.
- 14 V. V. Fomenko, T. N. Palynova, and M. Porai-Koshits, Zh. Strukt. Khim., 1975, 16, 651; R. J. Butcher and B. R. Penfold, J. Cryst. Mol. Struct., 1976, 6, 13.
- 15 S. H. Whitlow, Acta Crystallogr., Sect. B, 1972, 28, 1914.
- 16 L. L. Martin and R. A. Jacobson, Inorg. Chem., 1972, 11, 2789.
- 17 L. L. Martin and R. A. Jacobson, Inorg. Chem., 1972, 11, 2785.

- 19 B. W. McClelland, Acta Crystallogr., Sect. B, 1975, 31, 2496.
- 20 E. L. Mutterties and L. J. Guggenberger, J. Am. Chem. Soc., 1972, 94, 8046.
- 21 M. M. Finnegan, S. J. Rettig, and C. Orvig, J. Am. Chem. Soc., 1986, 108, 5033.
- 22 J-P. Laussac, R. Enjalbert, J. Galy, and J-P. Laurent, J. Coord. Chem., 1983, 12, 133.
- 23 W. B. Pearson, 'Lattice Spacing and Structures of Metals and Alloys,' Pergamon, London, 1957.
- 24 R. H. Stanford, jun., Acta Crystallogr., 1967, 23, 825.

Received 20th June 1988; Paper 8/02435I