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Crystal structure of hexakis(μ_2-acetato)-tris(acetonitrile-κN)-μ_3-oxo-trialuminum(III) tetrachloroaluminate, $[Al_3(C_2H_3O_2)_6(C_2H_3N)_3O][AlCl_4]$

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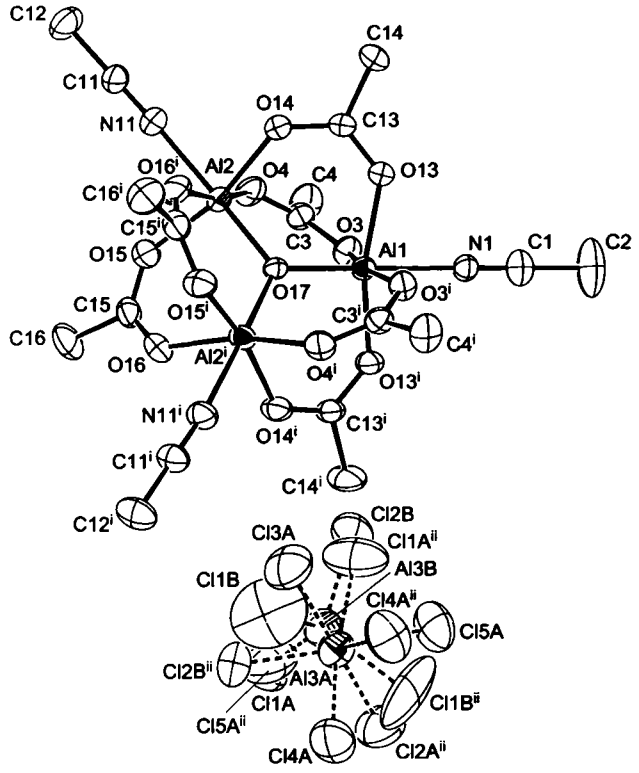

Abstract

$C_{18}H_{27}Al_4Cl_4N_3O_{13}$, orthorhombic, $C222_1$ (no. 20), a = 11.867(5) Å, b = 15.421(5) Å, c = 19.181(5) Å, V = 3510.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.140, T = 293 K.

Source of material

The title compound was prepared as followed: aluminum trichloride (1.33 g, 0.01 mol) was carefully dissolved in 50 mL of anhydrous acetonitrile. The exothermic dissolution was followed by evaporating acetonitrile under reduced pressure. The obtained gummy material was redissolved in 10 mL of boiling acetic acid. After a week, translucent crystals appeared in the solution. A suitable crystal was taken for crystallographic studies.

Discussion

Oxo-centered trinuclear metal complexes are of great interest in the field of organometallic chemistry. By example, the structure of a dititanium(III)samarium(III) mixed complex [1] was recently described as electron-transfer reagents in organic transformations. Compounds with oxo-bridged polynuclear Fe(III) centers have been found to perform important biological functions, such as oxygen storage and transport in a variety of proteins [2]. The Fe(III) complexes in which carboxylate ligands serve as a bridge between metals are particularly interesting and useful models for systematical studies of weak metal-metal interactions in multinuclear metal complexes [3]. To our knowledge oxo-centered trinuclear Al(III) complexes have been up to date not studied. In the course of our studies concerning Al(III) metabolism and biodisponibility we have been interested in the interactions of Al(III) with organic coordinating molecules. A crystalline complex of hexakis(*N*,*N*-dimethylformamide-*O*)aluminum(III) tris(tribromide) was described [4]. In a further work, we have succeeded in the synthesis of a novel oxo-centered trinuclear Al(III) complex with carboxylate and acetonitrile ligands.

The title compound contains one trinuclear oxo-centered aluminum(III) cation complex and one $[AlCl_4]^-$ counter ion. Each of the Al(III) ions is coordinated by one acetonitrile ligand, four acetate anions and the bridging oxide ion in a distorted octahedral environment. The angles around Al atoms deviate by the maximum of 7.1(1)° from the ideal value of 90°. In addition, each pair of Al^{3+} ions is bridged by two acetate ligands. In the first octahedron Al1/N1/O3/O3^i/O13/O13^i/O17 (symmetry code i: $-x,y,\frac{1}{2}-z$), the Al1 atom is 0.189(2) Å out of the basal plane P1 formed by O3, O3^i, O13 and O13^i with N1 and O17 in apical position. In the two other octahedra Al2/N11/O4/O14/O15/O16^i/O17, the Al2 atom is 0.179(2) Å out the basal plane P2 formed by O4, O14, O15 and O16^i with N11 and O17 in apical positions. The Al—O bond distances (1.885(5) Å to 1.909(6) Å) in the basal planes P1 and P2 fall within the range expected for octahedral aluminum complexes with bidentate acetate O atom donors (∠P1/P2 = 59.75(8)°). The Al—N bond distances (2.077(8) Å and 2.063(8) Å) are significantly larger than those reported for other Al(III)$(CH_3CN)_n$ complexes, n = 5,6, (in the range of 1.91 Å – 2.02 Å [5-7]). The corresponding carboxylate C—O distances and O–C–O angles (1.23(1) Å to 1.268(9) Å, 124.5(7)° to 126.0(7)°) are in the limit of three e.s.ds. with values typical for a delocalized double bond (average: 1.25(1) Å, 125.1(7)°, respectively). The central $[Al_3O]^{7+}$ and the N atoms of the coordinating CH_3CN molecule, situated *trans* to the central oxide ion, are strictly planar. The Al—O17 distances (1.797(6) Å and 1.809(4) Å) are shorter than the other Al—O distances. The Al···Al contact distances (average: 3.125(2) Å) are sufficiently large to preclude direct metal-metal bonding. This cation complex is a useful model for studying weak Al···Al interactions in multinuclear metal complexes. The crystal structure is completed by one $[AlCl^{4-}]$ counter ion disordered over two sites denoted by the suffix A (occupancy of 0.66) or B (occupancy of 0.33). A value of 0.0(2) was obtained for the Flack parameter.

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Table 1. Data collection and handling.

Crystal:	colorless, parallelepipedic, size 0.20 × 0.25 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.59 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3090, 3090
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1832
$N(param)_{refined}$:	235
Programs:	SIR97 [8], SHELXL-97 [9], CAMERON [10], WinGX [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2A)	8c	0.5	–0.0129	0.4463	0.7965	0.190
H(2B)	8c	0.5	–0.0587	0.4463	0.7199	0.190
H(2C)	8c	0.5	0.0715	0.4463	0.7336	0.190
H(4A)	8c		–0.3751	0.1657	0.7554	0.112
H(4B)	8c		–0.3997	0.0811	0.7127	0.112
H(4C)	8c		–0.3424	0.1606	0.6763	0.112
H(12A)	8c		–0.3638	–0.1980	0.9683	0.124
H(12B)	8c		–0.3204	–0.2781	0.9258	0.124
H(12C)	8c		–0.4269	–0.2269	0.9004	0.124
H(14A)	8c		–0.0142	0.1476	0.9790	0.143
H(14B)	8c		–0.1009	0.0735	0.9952	0.143
H(14C)	8c		–0.1434	0.1634	0.9675	0.143
H(16A)	8c		–0.0900	–0.2312	0.5883	0.133
H(16B)	8c		–0.2061	–0.1859	0.6020	0.133
H(16C)	8c		–0.1688	–0.2648	0.6481	0.133

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al(1)	4b		0	0.1255(1)	¾	0.033(1)	0.0369(8)	0.041(1)	0	0.0039(9)	0
Al(2)	8c		–0.1088(1)	–0.05000(8)	0.79592(7)	0.0496(9)	0.0422(6)	0.0426(7)	–0.0104(6)	0.0057(7)	0.0009(6)
N(1)	4b		0	0.2599(3)	¾	0.044(3)	0.039(3)	0.055(3)	0	0.008(3)	0
C(1)	4b		0	0.3313(4)	¾	0.045(4)	0.050(4)	0.073(5)	0	–0.026(4)	0
C(2)	4b		0	0.4255(5)	¾	0.14(1)	0.045(4)	0.20(1)	0	–0.06(1)	0
O(3)	8c		–0.1515(3)	0.1406(2)	0.7240(2)	0.039(2)	0.049(2)	0.064(2)	–0.001(2)	0.001(2)	0.004(2)
C(3)	8c		–0.2361(4)	0.0941(3)	0.7381(3)	0.041(3)	0.052(2)	0.054(3)	–0.003(2)	0.005(2)	–0.002(2)
O(4)	8c		–0.2309(3)	0.0220(2)	0.7681(2)	0.040(2)	0.063(2)	0.073(2)	–0.005(2)	0.012(2)	0.007(2)
C(4)	8c		–0.3481(4)	0.1284(4)	0.7189(4)	0.038(3)	0.072(3)	0.115(5)	–0.001(3)	–0.003(3)	0.005(3)
N(11)	8c		–0.2295(4)	–0.1204(3)	0.8489(2)	0.068(3)	0.054(2)	0.059(3)	–0.016(2)	0.012(2)	0.000(2)
C(11)	8c		–0.2827(5)	–0.1649(3)	0.8813(3)	0.069(4)	0.058(3)	0.052(3)	–0.021(3)	0.003(3)	–0.003(2)
C(12)	8c		–0.3546(6)	–0.2219(4)	0.9224(3)	0.080(5)	0.093(4)	0.076(4)	–0.039(4)	0.008(4)	0.009(3)
O(13)	8c		–0.0393(3)	0.1409(2)	0.8458(2)	0.067(2)	0.046(2)	0.041(2)	–0.007(2)	0.011(2)	–0.004(1)
O(14)	8c		–0.0988(3)	0.0112(2)	0.8810(2)	0.070(2)	0.053(2)	0.046(2)	–0.016(2)	0.014(2)	–0.004(2)
C(13)	8c		–0.0734(4)	0.0892(3)	0.8913(2)	0.057(3)	0.052(2)	0.039(3)	–0.005(2)	0.011(2)	–0.005(2)
C(14)	8c		–0.0839(7)	0.1213(4)	0.9649(3)	0.168(8)	0.071(4)	0.047(3)	–0.034(4)	0.030(4)	–0.023(3)
O(15)	8c		–0.1470(3)	–0.1262(2)	0.7227(2)	0.073(3)	0.063(2)	0.051(2)	–0.018(2)	0.003(2)	–0.009(2)
C(15)	8c		–0.0876(6)	–0.1534(3)	0.6736(3)	0.083(5)	0.042(2)	0.044(3)	–0.008(3)	–0.012(3)	–0.004(2)
O(16)	8c		0.0122(4)	–0.1344(2)	0.6636(2)	0.074(3)	0.053(2)	0.057(2)	0.000(2)	0.005(2)	–0.017(2)
C(16)	8c		–0.1431(7)	–0.2143(4)	0.6235(3)	0.123(6)	0.076(3)	0.068(4)	–0.015(4)	–0.013(4)	–0.029(3)
O(17)	4b		0	0.0090(2)	¾	0.034(2)	0.038(2)	0.038(2)	0	0.008(2)	0
Al(3A)	4a	0.67	0.6130(6)	0	½	0.093(4)	0.085(3)	0.091(3)	0	0	0.009(2)
Cl(1A)	8c	0.33	0.465(2)	–0.047(1)	0.4400(8)	0.18(1)	0.25(2)	0.10(1)	–0.07(1)	–0.009(9)	0.029(8)
Cl(3A)	8c	0.33	0.603(1)	–0.0757(7)	0.5907(5)	0.19(1)	0.147(7)	0.115(5)	–0.011(8)	–0.008(6)	0.043(5)
Cl(4A)	8c	0.33	0.7613(7)	–0.0265(5)	0.4406(5)	0.116(6)	0.146(7)	0.168(7)	–0.006(5)	0.036(5)	–0.035(5)
Cl(5A)	8c	0.33	0.5997(9)	0.1285(4)	0.5213(5)	0.164(8)	0.086(4)	0.151(6)	0.038(5)	–0.024(6)	–0.006(4)
Al(3B)	4a	0.33	0.532(2)	0	½	0.17(2)	0.089(7)	0.082(7)	0	0	0.014(5)
Cl(1B)	8c	0.33	0.626(1)	–0.099(1)	0.545(1)	0.22(2)	0.27(2)	0.38(3)	0.19(2)	0.02(2)	0.11(2)
Cl(2B)	8c	0.33	0.432(2)	0.047(1)	0.5779(8)	0.27(2)	0.132(6)	0.079(7)	–0.047(9)	0.004(9)	–0.017(5)

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