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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1415). Services for accessing these data are described at the back of the journal.

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A trimeric aluminium alkoxide: methoxy-aluminium dichloride

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Abstract

The title compound, *cyclo*-tri-μ-methoxo-tris(dichloro-aluminium), $C_3H_9Al_3Cl_6O_3$ or $[Al_3Cl_6(CH_3O)_3]$, has been characterized. Based on a six-membered $[AlO]_3$ ring, the molecular structure is trimeric. The Al—O distances are significantly shorter than those found in structurally related organoaluminium Lewis base–acid

complexes. This is a result of inductive effects due to the electronegative chlorine substituents bonded to the Al atoms.

Comment

Aluminium alkoxides, $[R_2Al(\mu\text{-}OR')]_n$, are of interest as potential catalysts, especially for the ring-opening polymerization of lactone rings (Inoue & Aida, 1993). They may form dimeric or trimeric species (Ouzounis *et al.*, 1983). Furthermore, complexes of the formula $[Me_2Al(\mu\text{-}OR')]_n$ have been found as equilibrium mixtures of trimers and dimers (Rogers *et al.*, 1992). We report here the synthesis and crystal structure of the related aluminium chloride $[Cl_2Al(\mu\text{-}OMe)]_3$, (I).

(I)
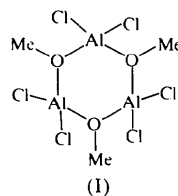
Compound (I) contains a six-membered skeleton composed of three Al and three methoxy O atoms. The average O—Al—O and Cl—Al—Cl angles of 98.5 and 114.9°, respectively, show the distortion of the tetrahedron around the Al atoms. The O atoms are surrounded in a nearly planar fashion. The average of the endocyclic Al—O—Al angle is 122.2°. The $[AlO]_3$ ring puckering analysis ($\varphi = 147.2°$ and $\theta = 90.2°$; Cremer & Pople, 1975) indicates a slightly distorted twisted-boat conformation. The puckering parameters θ and φ are 90° and $(k \times 60 + 30)°$, respectively, for the idealized geometry (Boeyens, 1978). In contrast, $[^tBu_2Al(\mu\text{-}OH)]_3$ has been found to adopt a planar conformation, with significantly larger intra-ring angles at the O atom (142°) and Al···Al distances of 3.49 Å. This observation was explained as intramolecular *tert*-butyl–*tert*-butyl repulsion (Mason *et al.*, 1993). However, the average Al···Al distance is 3.16 Å in (I) and the ring conformation is probably the
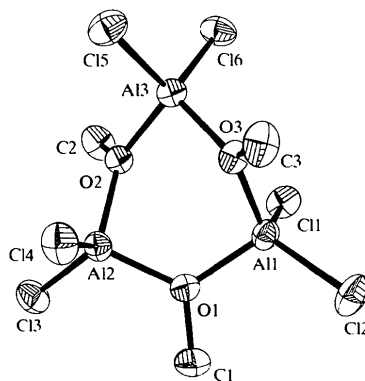

Fig. 1. The molecular structure of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

result of intramolecular repulsion between the exocyclic Cl and methyl substituents.

The six Al—O bond lengths are equivalent, with an average of 1.807 Å. Values of 1.69 and 2.00 Å have been reported for ideal covalent and dative bonds to four-coordinate Al atoms, respectively (Haaland, 1993). Thus, the bonding contributions may be described in terms of two canonical forms, each alternating three covalent and three dative Al—O bonds. However, the observed bond lengths are significantly shorter than those of 1.851 (3) Å reported for the cyclic [Me₂AlOMe]₃ complex from gas-phase data (Drew et al., 1973), as well as those expected for bonds of intermediate type. This difference is a stabilization effect of the donor–acceptor bond due to the formal replacement of both alkyl groups attached to the acceptor atom by electronegative Cl substituents. The Al—Cl bond distances (average 2.096 Å) are typical for four-coordinate Al compounds. The observed intermolecular distances indicate van der Waals-type interactions.

Experimental

All operations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. n-Pentane (100 ml) was added to methylaluminium dichloride (11.26 g, 110 mmol) at room temperature. A mixture of methanol (4 ml, 100 mmol) in n-pentane (50 ml) was added to the stirred solution. The solvent was removed in vacuo [365 K, 3 Torr (1 Torr = 133.322 Pa)], affording the title compound (yield 10.2 g, 79%; m.p. 336.2 K). Crystals of (I) suitable for X-ray analysis were obtained by crystallization from n-pentane at 278 K. ^{1}H NMR (300 MHz, room temperature, C_6D_6): δ 3.27 (s, 3H); ^{13}C NMR (300 MHz, room temperature, C_6D_6): δ 56.68; analysis calculated for CH_3AlCl_2O ($M_r = 129$): C 9.3, H 2.3, Al 20.9, Cl 55.0, O 12.4%; found: C 9.25, H 2.14, Al 21.25, Cl 55.34, O 12.4%.

Crystal data

[Al₃Cl₆(CH₃O)₃]
$M_r = 386.74$
Monoclinic
$P2_1/c$
$a = 10.503 (1)$ Å
$b = 13.889 (2)$ Å
$c = 10.678 (1)$ Å
$\beta = 90.68 (2)°$
$V = 1557.0 (3)$ Å³
$Z = 4$
$D_x = 1.650$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 80 reflections
$\theta = 21.8–23.0°$
$\mu = 1.257$ mm⁻¹
$T = 213 (2)$ K
Block
$0.35 \times 0.35 \times 0.30$ mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
4525 measured reflections
4525 independent reflections
3144 reflections with
$I > 2\sigma(I)$

$\theta_{max} = 29.96°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 3.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.099$
$S = 1.019$
4525 reflections
142 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.5280P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.556$ e Å⁻³
$\Delta\rho_{min} = -0.320$ e Å⁻³
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cl1—Al1	2.0883 (9)	Al2—O1	1.8007 (16)
Cl2—Al1	2.0949 (9)	Al2—O2	1.8088 (16)
Cl3—Al2	2.1019 (9)	Al3—O3	1.8081 (16)
Cl4—Al2	2.0974 (9)	Al3—O2	1.8101 (16)
Cl5—Al3	2.1000 (9)	Al1—Al2	3.1433 (11)
Cl6—Al3	2.0917 (9)	Al1—Al3	3.1703 (10)
Al1—O1	1.8064 (17)	Al2—Al3	3.1778 (10)
Al1—O3	1.8096 (17)		
O1—Al1—O3	99.76 (8)	O1—Al2—Cl3	109.97 (7)
O1—Al1—Cl1	107.16 (6)	O2—Al2—Cl3	110.73 (6)
O3—Al1—Cl1	109.39 (6)	Cl4—Al2—Cl3	115.74 (4)
O1—Al1—Cl2	110.82 (6)	O3—Al3—O2	95.35 (7)
O3—Al1—Cl2	111.83 (6)	O3—Al3—Cl6	114.37 (6)
Cl1—Al1—Cl2	116.49 (4)	O2—Al3—Cl6	110.72 (5)
O1—Al2—O2	100.37 (7)	O3—Al3—Cl5	111.03 (6)
O1—Al2—Cl4	108.18 (6)	O2—Al3—Cl5	111.69 (6)
O2—Al2—Cl4	110.71 (6)	Cl6—Al3—Cl5	112.53 (4)

The crystal was cooled for the diffraction study using an Oxford Cryosystems Cryostream cooler (Cosier & Glazer, 1986). Refinement of disordered methyl H atoms used a riding model and a common isotropic displacement parameter for H atoms on a common parent C atom. The occupancies of the major components on C1, C2 and C3 were refined to 0.52 (5), 0.61 (3) and 0.74 (3), respectively. Puckering parameters were calculated using PLATON (Spek, 1990).

Data collection: DIF4 (Stoe & Cie, 1990a). Cell refinement: DIF4. Data reduction: REDU4 (Stoe & Cie, 1990b). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: SHELXTL/PC (Siemens, 1990).

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(I)
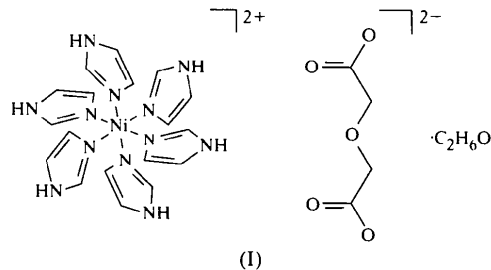
Hexakis(imidazole-N³)nickel(II) oxydiacetate ethanol solvate

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Abstract

The crystal structure of the title complex, [Ni-(C₃H₄N₂)₆](C₄H₄O₅)·C₂H₅OH, is a tightly woven three-dimensional network composed of [Ni(Him)₆]²⁺ cations (Him is imidazole) interlinked by the oxydiacetate anion through six different N—H···O bonds, in which all the N—H imidazole groups, as well as all the carboxylate O atoms, take part. This structure is the first to show an [Ni(Him)₆]²⁺ group which does not display any crystallographic symmetry.

Comment

Nickel(II) has a strong affinity for nitrogen-donor ligands and nickel(II)–imidazole (Him) interactions are important in biological processes. We report herein the synthesis and crystal structure of a new salt, (I), containing the [Ni(Him)₆]²⁺ complex cation and the oxydiacetate (oda) anion.

The molecular diagram and the atomic numbering scheme used are shown in Fig. 1. As is usually found in nickel–imidazole compounds, Ni²⁺ is coordinated by

six monodentate imidazole ligands to form a bulky [Ni(Him)₆]²⁺ cation. The present case is unique, however, in the sense that it is the first structure reported where the group does not display crystallographic symmetry; in all the other references in the literature (*viz.* Konopelski *et al.*, 1976; Ivarsson & Forsling, 1979; van Ingen Schenau, 1975; Dev *et al.*, 1991; Tebbe & Nafepour, 1994; Povse *et al.*, 1998, and references therein), the Ni²⁺ cation occupies a site with 1̄ symmetry or higher. In spite of this formal lack of symmetry, the distortion of the Ni²⁺ coordination polyhedron from a perfect octahedron is quite small, with an Ni—N bond-length range of 2.113 (3)–2.139 (4) Å, and maximum departures from 90 and 180° of ~1.5 (1)°. These values are quite similar to those found in the more symmetric environments in the above references. Perhaps the most significant difference is to be found in the rotation angle
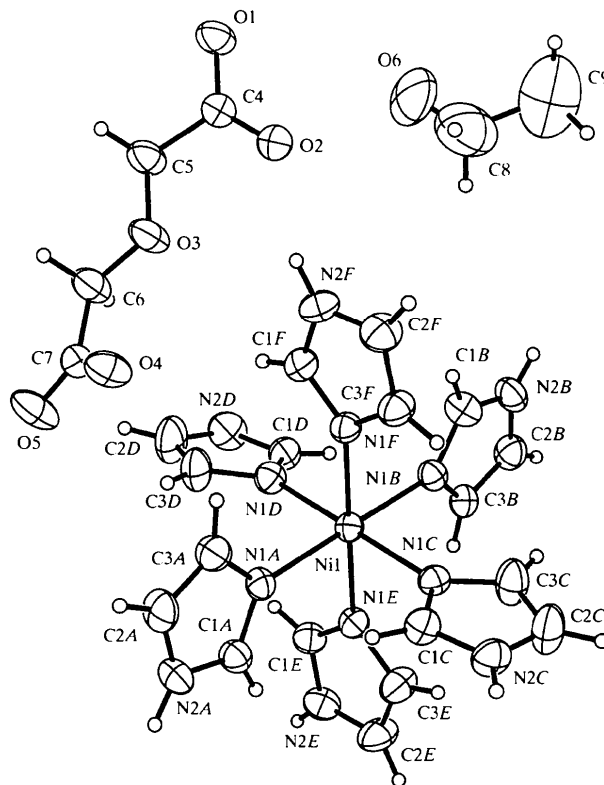

Fig. 1. The molecular diagram, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.