Structure of *catena*-Trichloro-μ-(1,4-dioxane-*O,O'*)-aluminium(III) 1,4-Dioxane Solvate, [Al(C4H8O2)Cl3].C4H8O2

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Abstract. $M_r = 309 \cdot 6$, monoclinic, $P2_1/m$, $a = 8 \cdot 080$ (5), $b = 13 \cdot 64$ (5), $c = 6 \cdot 3125$ (5) Å, $\beta = 101 \cdot 85$ (2)°, $Z = 2$, $D_x = 1 \cdot 510$, $D_m = 1 \cdot 50$ Mg m^{-3}, $V = 681 \cdot 0$ Å^3, $\mu = 0 \cdot 66$ mm^{-1}, $F(000) = 320$. The structure has been solved from 1269 diffractometer-measured intensities with Mo $K\alpha$ radiation ($\lambda = 0 \cdot 7107$ Å) and refined by full-matrix least squares to $R = 0 \cdot 035$. The crystal structure consists of distorted trigonal-planar AlCl3 units bridged by dioxane chairs to form chains parallel to the b axis. The chains are separated by layers of dioxane molecules. The geometry around five-coordinate Al is basically trigonal bipyramidal with a considerable distortion (115–129°) of the equatorial Cl atoms.

Introduction. Although many 1,4-dioxane complexes of the Group III halides are known, few definitive structural data are available. We have recently shown that in the metal–metal-bonded Ga^{II} compounds Ga2X4.2(dioxane)(X = Cl, Br), the dioxane acts as a monodentate ligand (Beamish, Small & Worrall, 1979; Small & Worrall, 1982) whereas normally it is a bridging bidentate, *e.g.* in GeCl2.dioxane (Kulishov, Bokii, Struchkov, Nefedov, Kolesnikov & Perl'mutter, 1970). We have attributed this behaviour to the preference of Ga for four coordination since bidentate dioxane would lead to the less stable five-coordinate Ga. On the basis of a crystal structure determination (Brewer, Chadwick & Garton, 1961) it has been proposed that the boat form of dioxane is present in Ga(dioxane)2Cl. This interesting behaviour of the ligand towards Ga has prompted us to carry out a systematic study of Group III halide–dioxane complexes.

Experimental. The complex is very susceptible to moisture and was prepared by condensing excess dry dioxane on to pure AlCl3 *in vacuo*. Needle crystals of AlCl3.2(dioxane) were obtained on standing and satisfactory crystals were transferred to Lindemann-glass tubes in a nitrogen-filled dry-box. Crystal data were obtained from Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda = 1 \cdot 542$ Å); systematic absences allowed $P2_1$ or $P2_1/m$; intensity measurements made on a Stoe STADI-2 two-circle automatic diffractometer

with graphite-monochromatized Mo $K\alpha$ radiation; layers $k = 0 - 13$ measured; $2\theta < 55°$; crystal size $0 \cdot 04 \times 0 \cdot 56 \times 0 \cdot 06$ mm; absorption corrections and scaling of data carried out with the *SHELX* suite of programs (Sheldrick, 1976); 1368 reflections measured, after elimination of those for which $I < 3\sigma(I)$ there remained 1269 unique reflections; we initially assumed space group $P2_1$ and obtained an E map by the *MULTAN* direct-methods program (Main, Lessinger, Woolfson, Germain & Declercq, 1977) which revealed the positions of Al and Cl atoms which had identical y coordinates; the centrosymmetric space group $P2_1/m$ was adopted with these four atoms on the mirror plane at $y = \frac{1}{4}$ and used to phase $(F_o - F_c)$ maps to give the positions of the remaining atoms using *SHELX*; using unit weights, full-matrix least-squares refinements of all atomic positions, anisotropic U_{ij} values for Al,Cl, C, and O, and isotropic U values for H atoms were carried out until convergence was reached at $R = 0 \cdot 035$; atomic scattering factors were those of Cromer & Mann (1968) and Cromer & Liberman (1970). We also carried out the refinement using space group $P2_1$ and a similar R value was obtained. The standard deviations of C–C and C–O are some four times smaller with $P2_1/m$ and the bond lengths and angles are in considerably better agreement with those reported for other dioxane complexes.

Discussion. Final coordinates and equivalent values (U_{eq}) of the anisotropic temperature coefficients are given in Table 1.*

The crystal structure determination shows that AlCl3.2(dioxane) consists of distorted trigonal-planar AlCl3 units bridged by dioxane chairs to form infinite chains parallel to the b axis. The chains are separated by layers of dioxane molecules as shown in Fig. 1.

Trigonal-bipyramidal geometry is observed around Al (Fig. 2) with Cl atoms in the equatorial positions and O atoms located axially. These atomic positions are

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38291 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* (× 10⁴) *and isotropic thermal parameters* (Å² × 10⁴)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

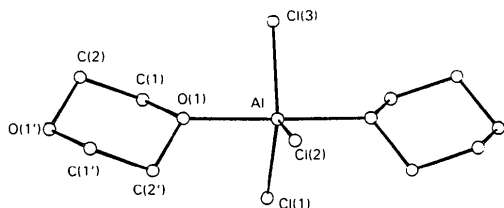|	x	y	z	U_{eq}
Al	9815 (1)	2500†	4572 (2)	409 (5)
Cl(1)	7346 (1)	2500†	5322 (2)	487 (5)
Cl(2)	9841 (2)	2500†	1198 (2)	534 (5)
Cl(3)	12225 (2)	2500†	6745 (2)	568 (5)
O(1)	9818 (2)	3977 (2)	4703 (3)	383 (8)
C(1)	11011 (4)	4538 (2)	3759 (5)	481 (13)
O(2)	6627 (3)	5027 (2)	−449 (4)	716 (14)
C(2)	10366 (4)	5546 (2)	3298 (4)	459 (12)
C(3)	5781 (5)	4136 (4)	−302 (8)	761 (20)
C(4)	4566 (5)	4226 (3)	1164 (8)	727 (20)

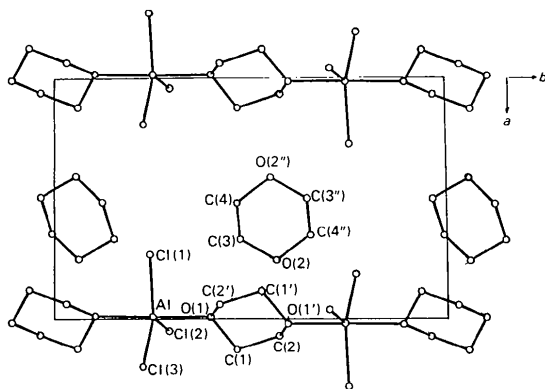†Constrained.

Fig. 1. Coordination around Al.

Fig. 2. Projection on the *xy* plane.

consistent with the generalization that the more electronegative ligands adopt the axial sites of trigonal-bipyramidal main-group systems.

Five-coordinate Al has been shown to occur in AlCl₃.2NH(CH₃)₂ (Lobkovskii, Korobov & Semenko, 1978) and in AlCl₃.2H₄F* (Cowley, Cushner, Davis & Riley, 1981). The mean Al—Cl distance in AlCl₃.2 (dioxane) is 2·139 Å compared with 2·158 Å in AlCl₃.2H₄F and 2·182 Å in AlCl₃.2NH(CH₃)₂. The Al—O distance of 2·017 Å is close to the observed distances in AlCl₃.2H₄F (1·990 Å) and [Al(CH₃)₃]₂.dioxane (2·02 Å) (Atwood & Stucky, 1967).

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* H₄F is tetrahydrofuran (THF).

As shown in Table 2 the angles around Al in the equatorial plane show large deviations (114·9–128·7°) from the ideal values for a trigonal bipyramid (120°). Similar deviations have been observed in the analogous five-coordinate complexes: AlCl₃.2NH(CH₃)₂ (114–126°), AlCl₃.2H₄F (118–121°) and CrCl₃.2N(CH₃)₃. The latter have been attributed to *d*-electronic effects (Greene, Russ & Wood, 1971). Such effects are not possible for the Al complexes and Lobkovskii, Korobov & Semenko (1978) have explained the angular deviations in AlCl₃.2NH(CH₃)₂ in terms of strain resulting from the close intramolecular approach of Cl atoms and methyl groups. Several of the Cl—C distances are less than 3·4 Å. Such deviations are to be expected for five-coordinate trihalide complexes which have axial positions occupied by low-symmetry ligands such as dioxane. The magnitude of the deviations will depend upon the intramolecular interactions of the ligand non-bonding atoms with halogen and also on any strong intermolecular interaction present.

Table 3 gives the relevant torsion angles and non-bonding distances; steric strain is indicated by the fairly short C—Cl and H—Cl distances, and the torsion angles show that the ligand C atoms [C(1) and C(2′)] are staggered and lie between Cl(1),Cl(3) and Cl(2),Cl(3). There is also a fairly strong intermolecular interaction which may be responsible for the large bond angle Cl(1)—Al—Cl(3). It is between O(2) on the 'free' dioxane molecule and C(1′) on the ligand; these atoms are 3·16 Å apart compared with a van der Waals

Table 2. *Bond distances* (Å) *and angles* (°)

The average C—H distance is 0·97 ± 0·07 Å.

Al—Cl(1)	2·142 (1)	Al—Cl(2)	2·134 (1)
Al—Cl(3)	2·140 (2)	Al—O(1)	2·017 (2)
C(1)—O(1)	1·451 (3)	C(1)—C(2)	1·479 (5)
C(2)—O(1′)	1·454 (3)	C(3)—O(2)	1·407 (5)
C(3)—C(4)	1·486 (5)	C(4)—O(2″)	1·412 (4)

Cl(1)—Al—Cl(2)	114·9 (1)	Cl(1)—Al—Cl(3)	128·7 (1)
Cl(2)—Al—Cl(3)	116·4 (1)	O(1)—Al—Cl(1)	89·1 (1)
O(1)—Al—Cl(2)	92·3 (1)	O(1)—Al—Cl(3)	88·9 (1)
Al—O(1)—C(1)	120·3 (2)	Al—O(1)—C(2′)	118·8 (2)
C(2)—C(1)—O(1)	109·5 (2)	C(1)—C(2)—O(1′)	109·8 (2)
C(1)—O(1)—C(2′)	108·4 (2)	C(4)—C(3)—O(2)	111·2 (4)
C(3)—O(2)—C(4)	109·5 (4)	C(3)—C(4)—O(2″)	110·9 (4)

Table 3. *Torsion angles* (°) *and non-bonding distances* (Å)

Symmetry code: the coordinates of atoms marked with primes are related to the corresponding unprimed atoms of Table 1 by: (′)2−x, 1−y, 1−z; (″)1−x, 1−y, 1−z; (‴)1 + x, y, z.

C(1)—O(1)—Al—Cl(1)	−163 (1)	C(1)—O(1)—Al—Cl(2)	−48 (1)
C(1)—O(1)—Al—Cl(3)	68 (1)	C(2′)—O(1)—Al—Cl(1)	59 (1)
C(2′)—O(1)—Al—Cl(2)	174 (1)	C(2′)—O(1)—Al—Cl(3)	−69 (1)

C(1)—Cl(2)	3·257 (3)	C(1)—Cl(3)	3·389 (3)
C(2′)—Cl(1)	3·259 (3)	C(2′)—Cl(3)	3·387 (3)
H(4″)—Cl(1)	2·68 (3)	H(2‴)—Cl(2)	2·65 (3)
C(1′)—O(2)	3·162 (5)		

distance of 3·40 Å. This close contact may be attributed to a dipole interaction between O(2) and C on the ligand which has acquired a positive charge due to electron withdrawal from the ligand by Al. The effect of this dipolar interaction is to bring the layers of 'free' dioxane closer to the halogens. Cl(1) and Cl(3) which point towards layers of dioxane molecules are affected more than Cl(2), resulting in a large angle.

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Crystal Structures of Ethylenediaminetetraacetato Metal Complexes. I. A Comparison of Crystal Structures Containing Hexacoordinated Metal Ions, $[(H_2O)_4X(C_{10}H_{12}N_2O_8)Y]_n.2nH_2O$

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Abstract. (1) $X = $ Mn, $Y = $ Cu, $n = 1$, $M_r = 514\cdot8$, orthorhombic, space group $Pn2_1a$, $a = 14\cdot626$ (3), $b = 13\cdot068$ (4), $c = 9\cdot969$ (3) Å, $V = 1905$ (2) Å^3, $Z = 4$, $D_x = 1\cdot79$ Mg m^{-3}, $F(000) = 1056$, final $R = 0\cdot044$ for 1658 observed reflections; (2) $X = $ Mn, $Y = $ Co, $n = 1$, $M_r = 510\cdot3$, orthorhombic, space group $Pn2_1a$, $a = 14\cdot584$ (3), $b = 13\cdot366$ (4), $c = 9\cdot799$ (3) Å, $V = 1910$ (2) Å^3, $Z = 4$, $D_x = 1\cdot77$ Mg m^{-3}, $F(000) = 1048$, final $R = 0\cdot059$ for 1633 observed reflections; (3) $X = $ Mg, $Y = $ Zn, $n = 1$, $M_r = 486\cdot1$, orthorhombic, space group $Pn2_1a$, $a = 14\cdot476$ (4), $b = 13\cdot237$ (4), $c = 9\cdot746$ (3) Å, $V = 1886$ (2) Å^3, $Z = 4$, $D_x = 1\cdot71$ Mg m^{-3}, $F(000) = 1008$, final $R = 0\cdot049$ for 1617 observed reflections. A half-normal-probability-plot comparison of these structures and others from the literature show that the main differences are essentially due to the different ionic radii of X and Y. [For the isostructural Mn–Zn and Mn–Ni compounds the following cell parameters were determined by automatic diffractometer: $a = 14\cdot594$ (4), $b = 13\cdot294$ (4), $c = 9\cdot841$ (3) Å and $a = 14\cdot499$ (4), $b = 13\cdot250$ (4), $c = 9\cdot768$ (3) Å respectively.]

Introduction. A systematic structural study of metal coordination compounds with the ethylenediaminetetraacetato (EDTA) ligand is being carried out by the Departments of Crystallography and Mineralogy (Faculty of Geology) and Inorganic Chemistry (Faculty of Pharmacy) of the University of Barcelona, in order to determine the influence of the different metals on coordination of EDTA. Thereby the crystal structures of the isostructural compounds $[(H_2O)_4Mn(EDTA)Co]_n.2nH_2O$ (Mn–Cu), $[(H_2O)_4Mn(EDTA)Co]_n.2nH_2O$ (Mn–Co) and $[(H_2O)_4Mg(EDTA)Zn]_n.2nH_2O$ (Mg–Zn) were determined.