Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 34.
A Crystal Structure Determination of the Al(methylmalonate)$_2$(CH$_3$OH)$_2^-$ Complex with Na$^+$ as Counter-Ion

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The crystal structure of sodium bis(trans)-2-methylpropanedionatedimethanolaluminate(III), [Na$^+$][Al(C$_4$H$_4$O$_4$)$_2$(CH$_3$OH)$_2^-$], has been determined by single crystal X-ray diffraction. The compound crystallises in the trigonal space group R$\bar{3}$, with $a = 12.046(2)$, $c = 28.705(6)$ Å and $Z = 9$. The refinement of 103 parameters on 946 reflections [$I > 2.0\sigma(I)$] gave a final R-value of 0.064 ($R_w = 0.066$, $S = 1.000$). The structure consists of octahedral Al(C$_4$H$_4$O$_4$)$_2$(CH$_3$OH)$_2^-$ complexes and sodium ions. In these complexes, methylmalonate coordinates to Al^{3+} bidentately in the equatorial plane of the octahedron, while methanol coordinates at the apices. As such, it represents a rare single-crystal example of direct aluminium(III)-methanol coordination. The complexes, arranged in layers, are connected to each other by octahedrally coordinated sodium ions, in special position 6c, and hydrogen bonds. The layers, with the methyl group of methylmalonate pointing out from the layers, are stacked perpendicular to the [001] direction and are held together by other octahedrally coordinated sodium ions, in special position 3b.
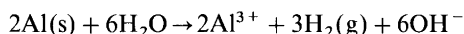
As part of a continuing project to study the aqueous equilibrium chemistry of aluminium(III), it has become of interest to determine also the three-dimensional structures of complexes that appear. Therefore, a new project has been started with the aim of determining crystal and molecular structures of bio- and geochemically relevant aluminium compounds. The importance of such structure determinations is obvious to applied toxicologists and geologists, trying to interpret the effect of aluminium on living organisms and in geological processes. In a recent review of the literature,[1] it was reported that crystal determinations of aluminium compounds with small water-soluble organic ligands are rare. Thus, the mononuclear complexes reported in the literature are a number of AlL$_3$ complexes which have been crystallised with (malonate^{2-}),[2] (lactate$^-$),[3] (oxalate^{2-}),[4] (glycolate^{2-})[5] and (maltolate$^-$)[6] as ligands and two AlL$_2$(H$_2$O)$_2^-$ complexes, which have been crystallised with (malonate^{2-})[7] and (methylmalonate^{2-}).[8] Reported structures also include one trinuclear and one tetranuclear

complex with (citrate^{4-})[9] and (malate^{3-}),[10] respectively. The aluminium complexes primarily considered in the present project are those indicated in the series of potentiometric investigations within the title series. The aim of the present study was to crystallise the Al(methylmalonate)$_2^-$ complex from a strict aqueous solution, as compared to Tapparo et al.,[7] who crystallised the corresponding malonate complex by addition of dimethylformamide to the aqueous phase. Also, to avoid the possibility of sodium chloride formation during crystallisation, the synthesis solution was prepared in the absence of chloride ions. During evaporation, however, no crystalline material was obtained, and instead the solution slowly congealed into a transparent glass. Therefore, in order to obtain a crystalline material it became necessary either to lower the solubility of the complex according to the method of Tapparo et al.[7] or to change the solvent totally. In this study the second alternative was chosen, and methanol was selected as solvent for the AlL$_2$ glass formed. Methanol is a highly polar solvent, a weak complexation agent, and has previously been shown to be a good solvent for crystallisation of aluminium compounds.[11,12]

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Experimental

Materials and methods. The choice of synthesis conditions for the AlL_2^- complex was based on thermodynamic calculations, performed with the program SOLGASWATER[13] and using the equilibrium model of Marklund and Öhman.[14] The total concentrations used in this calculation were well outside the experimental limits used for the determination of this model, and the calculated result may therefore differ somewhat from the actual composition. In Fig. 1 the calculated distribution diagram for the H^+–Al^{3+}-methylmalonic acid system is shown at $[Al]_{tot} = 0.3$ M; $[C_4H_6O_4]_{tot} = 0.6$ M and the vertical line indicates the composition chosen for the synthesis solution. As is seen, this composition does not correspond to the composition at which AlL_2^- concentration is at its maximum, since at this point the pH buffer capacity of the solution is rather low. The preparation of such a solution would therefore imply a risk that, with just a small error in the synthesis composition, the pH would become too high with subsequent $Al(OH)_3(s)$ precipitation. The synthesis solution was generated by adding 35.43 g of methylmalonic acid (0.30 mol) (Sigma), 4.05 g of aluminium metal (0.15 mol) (Merck *p.a.*) and 5.20 g of sodium hydroxide (0.13 mol) (EKA *p.a.*) to 500 ml of water. The use of metallic aluminium together with sodium hydroxide to generate the total amount of OH^- needed was motivated by the desire to avoid the presence of chloride ions, and thereby the possibility of sodium chloride formation, during evaporation. Aluminium metal contributes to the total amount of OH^- by following the reaction:

$$2Al(s) + 6H_2O \rightarrow 2Al^{3+} + 3H_2(g) + 6OH^-$$

The synthesis mixture was slowly refluxed overnight in the presence of a few grains of $HgCl_2(s)$ to speed up the aluminium oxidation rate. The solution was then filtered to remove some small amounts of liquid Hg, and the
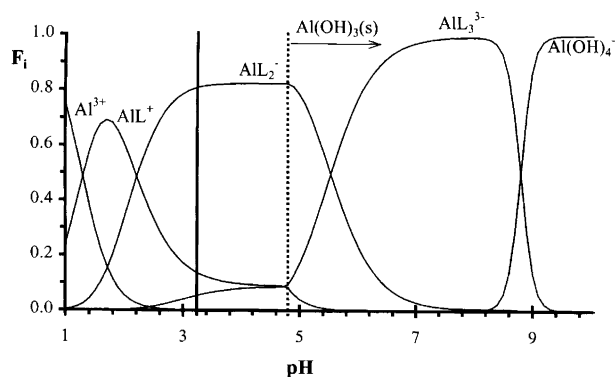
resulting pH was checked to be approximately 3.2, i.e. in agreement with the expected value. The solution obtained was then divided into two parts which were slowly evaporated at room temperature and in a refrigerator, respectively. Both of the procedures, however, resulted in syrup like substances that eventually congealed to a glass. About 0.5 g of this glass was then dissolved in 20 ml methanol (Baker *p.a.*), and after 4–6 weeks of extremely slow evaporation in a refrigerator colourless six-sided flat crystals of suitable size were formed. During initial cell determinations it was found that the crystals decomposed when exposed to the normal atmosphere. Therefore, the crystal used for data collection was enclosed in a sealed glass capillary along with some of the mother liquor. The composition, according to structure refinement from X-ray diffraction data, suggests the total formula $AlNaC_{10}H_{16}O_{10}$.

Data collection. The intensities of the reflections were measured with a SYNTEX R3 four-circle X-ray diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The background of the reflections was measured on each side of the peak for a total time equal to the scan time. In all, 7130 reflections were collected, giving 1406 unique reflections after merging symmetry-equivalent reflections ($R_{int} = \Sigma|I_0 - \bar{I}_0|/\Sigma I_0 = 0.030$). Refinements were based on the merged data set. Three standard reflections, showing variations of up to 1.7%, were used to scale intensities and their standard deviations. In addition to Lorentz and polarisation corrections, an empirical absorption correction was applied. A psi-scan was carried out in steps of 10°, using eleven reflections, distributed evenly in the measured 2θ-range, and resulted in a transmission factor variation of 0.829–0.965. The cell parameters were determined from a least-squares fit to observed 2θ angles for 25 reflections in the 2θ range 16.02–21.40°. The experimental details are summarised in Table 1.

Refinements. The Xtal3.2 program package[15] was used to perform the calculations on 946 reflections with $I > 2.0\sigma(I)$. The structure was solved by direct methods and subsequent difference-Fourier synthesis, and refined by full-matrix least-square calculations. Extinction correction was made according to the Zachariasen formalism. Scattering factors used for the refinements were those of Al^{3+}, Na^+, Cl^-, O^- and C, and anomalous dispersion was considered.[16] All non-hydrogen atoms found were refined anisotropically, resulting in 103 parameters, and ended at $R = 0.064$. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters. The fractional atomic coordinates and equivalent displacement parameters are listed in Table 2 and selected bond lengths and angles are given in Table 3.

Fig. 1. Species distribution diagram for the H^+–Al^{3+}-methylmalonic acid system at $[Al^{3+}]_{tot} = 0.3$ M and $[C_4H_6O_4]_{tot} = 0.6$ M. F_i is defined as the ratio between aluminium(III) in a species and the total aluminium(III) in solution. The vertical full line indicates the composition of the crystallisation solution, and the dotted line indicates the calculated precipitation limit for $Al(OH)_3(s)$.

Table 1. Crystal and experimental data for [Na⁺]-[Al(C₄H₄O₄)₂(CH₃OH)₂⁻].

Formula	[Na⁺][Al(C₄H₄O₄)₂(CH₃OH)₂⁻]
M_r/g mol⁻¹	346.20
Crystal system	Trigonal
Space group	$R\bar{3}$
a/Å	12.046(2)
c/Å	28.705(6)
V/Å³	3607(1)
Z	9
D_c/g cm⁻³	1.43
μ(Mo Kα)/mm⁻¹	0.20
F(000)	1674
Crystal colour	Transparent
Crystal size/mm	0.30 × 0.19 × 0.15
Temperature/K	293
No. of reflns. for cell determination	25
2θ range/°	16.02 < 2θ < 21.40
Scan mode	0–2θ
2θ range/°	4.16 < 2θ < 50.10
hkl range	0 ⩽ h ⩽ 12
	0 ⩽ k ⩽ 12
	−33 ⩽ l ⩽ 34
2θ scan speed/° min⁻¹	2.02–11.72
Total no. of reflns. measured	7130
Total no. of independent reflns.	1406
Test reflns. (deviation %)	−3 0 3 (1.7)
	0 1 2 (1.6)
	−3 5 4 (1.7)
Refinement on	F
No. of obs. independent reflns., $I > 2.0\sigma(I)$	946
No. parameters refined	103
Weights calcd. according to	$1/w = \sigma^2(F_{obs}) + 50.97$ + 11.96F_{obs} − 148.32 sin θ
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.064
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.066
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	1.000
Extinction coefficient	1759
$(\Delta/\sigma)_{max}$	0.0002
Min/max residual electron density/e Å⁻³	−0.60/0.81

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters with e.s.d. values in parentheses.

Atom	x/a	y/b	z/c	U_{eq}/Å² [a]
Al	2/3	5/6	1/3	0.0291(7)
O1	0.7830(3)	0.8560(3)	0.3796(1)	0.034(1)
O2	0.5306(3)	0.7034(3)	0.3654(1)	0.033(1)
O3	0.6309(3)	0.9578(3)	0.3620(1)	0.039(1)
O4	0.8540(3)	0.8378(3)	0.4480(1)	0.045(1)
O5	0.4536(5)	0.5529(4)	0.4193(1)	0.054(2)
C1	0.5305(4)	0.6622(5)	0.4067(1)	0.037(2)
C2	0.7658(4)	0.8205(4)	0.4230(2)	0.033(2)
C3	0.6280(5)	0.7579(5)	0.4420(1)	0.042(2)
C4	0.6147(7)	0.6994(7)	0.4898(2)	0.068(3)
C5	0.7193(6)	1.0882(6)	0.3742(2)	0.062(3)
Na1	0	0	0.3593(2)	0.052(1)
Na2	0	0	1/2	0.031(1)
H1	0.7533	1.0905	0.4098	0.035
H2	0.6695	1.1431	0.3727	0.035
H3	0.7995	1.1278	0.3502	0.035
H4	0.5772	0.5952	0.4861	0.035
H5	0.5498	0.7156	0.5108	0.035
H6	0.7095	0.7428	0.5061	0.035
H7	0.5528	0.9333	0.3864	0.035
H8	0.6047	0.8334	0.4459	0.035

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 3. Selected interatomic distances (in Å) and bond angles (in °).

Al–O1	1.848(3)	Al–O2–C1	128.0(3)
Al–O2	1.848(3)	O2–C1–C3	117.7(4)
Al–O3	1.937(4)	O2–C1–O5ⁱ	122.7(4)
O1–C2	1.301(5)	O5ⁱ–C1–C3	119.5(4)
O2–C1	1.285(6)	C1–C3–C2	111.4(4)
C1–O5	1.226(6)	C1–C3–C4	112.6(4)
C2–O4	1.211(6)	C4–C3–C2	112.7(5)
C1–C3	1.543(6)	C3–C2–O1	117.1(4)
C2–C3	1.540(7)	C3–C2–O4	120.8(4)
C3–C4	1.513(8)	O4–C2–O1	122.1(4)
Na1–O1	2.376(4)	C2–O1–A1	130.9(3)
Na1–O2ⁱⁱ	2.751(5)	O4–Na2–O4ⁱ	85.1(1)
Na2–O4	2.388(5)	O4–Na2–O4ⁱⁱⁱ	94.9(1)
O1–Al–O2	93.1(1)	O1–Na1–O1ⁱ	114.2(2)
O1–Al–O2ⁱⁱ	86.9(1)	O2ⁱⁱ–Na1–O2ⁱᵛ	87.1(2)
O1–Al–O3	91.6(2)	O1–Na1–O2ⁱⁱ	58.9(1)
O1–Al–O3ⁱⁱ	88.4(2)	O1–Na1–O2ⁱᵛ	98.0(1)
O2–Al–O3	89.9(2)	O1–Na1–O2ᵛ	145.1(2)
O2–Al–O3ⁱⁱ	90.1(2)		

Symmetry codes: ⁱ$y-x$, $-x$, z; ⁱⁱ$1/3-x$, $2/3-y$, $2/3-z$; ⁱⁱⁱy, $y-x$, $-z$; ⁱᵛ$1/3+y$, $2/3+y-x$, $2/3-z$; ᵛ$1/3+x-y$, $2/3+x$, $2/3-z$.

Structure description and discussion

The structure consists of Na⁺ ions and the Al(C₄H₄O₄)₂(CH₃OH)₂⁻ complex as shown in Fig. 2. Aluminium is octahedrally coordinated, with two methylmalonate ions equatorially coordinated via the carboxylate oxygens (O1 and O2) and two methanol molecules coordinated through their alcohol oxygens (O3) at the apices. The Al–O bond distances for the bidentately coordinated methylmalonate ligands are all 1.848(3) Å. The corresponding bond distances in the previously determined malonate[7] [(1.868(2) and 1.871(2) Å; 1.862(2) and 1.877(2) Å, respectively] and methylmalonate[8] [(1.840(2) and 1.886(2) Å] complexes are more distorted towards one longer and one shorter bond. These differences in bond geometry can probably be related to interactions evolving from packing differences in the three structures. Thus, in the previously published methylmalonate complex,[8] the structure is held together by an 'asymmetrical' hydrogen-bond network

that leads to a significant distortion of the Al–O (methylmalonate) bonds. In the malonate complex[7] the structure is held together by K⁺ ions and a more symmetric hydrogen-bond network, and this induces just a slight distortion of the Al–O (malonate) bonds. Finally, the structure presented in this paper has the highest packing symmetry, in which the complexes are held together by two structurally different Na⁺ ions coordinating to the oxygens of the Al–O octahedron and to the non-coordin-
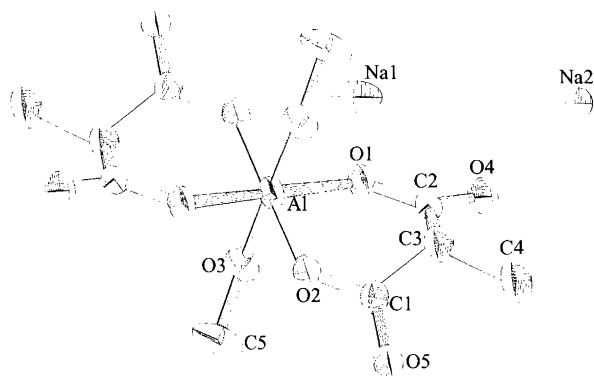
Fig. 2. The Al(C₄H₄O₄)₂(CH₃OH)₂⁻ complex and the sodium ions in special position 6c (Na1) and 3b (Na2), respectively, illustrated with the thermal displacement parameters scaled to include 50% probability.
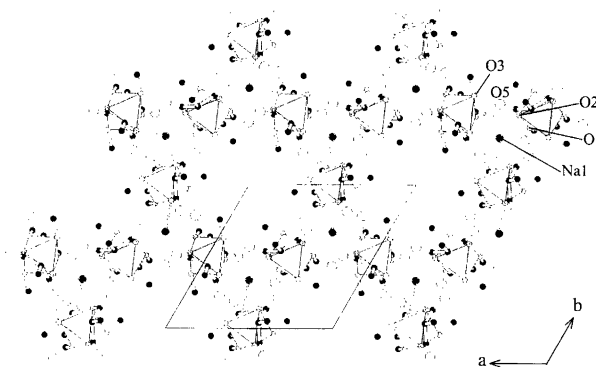

Fig. 3. A packing diagram, illustrating the formation of layers perpendicular to the [001] direction. The sodium ions, in special position 6c (Na1), form a network by coordinating to the carboxylate oxygens (O1 and O2) of three Al(C₄H₄O₄)₂(CH₃OH)₂⁻ complexes. Also indicated in the figure, as dotted lines, are the possible hydrogen bonds formed between O3 and O5.

ated carboxylate oxygens, respectively. As a consequence, the measurable differences in the Al–O (methylmalonate) bond lengths are insignificant. The detailed packing of the present structure is described in further detail below. The Al–O bond distances for the two coordinated methanol molecules are 1.937(4) Å, and this can be compared with the coordination distance for water in the structures of Al-dimalonate[7] [1.909(2) Å] and Al-di(methylmalonate)[8] [1.935(2) Å]. As expected from electrostatic considerations, in all three structures this distance is significantly longer than the average Al–O (ligand) distance. The AlO₆ octahedron is thus not ideal, but somewhat elongated in the Al-solvate direction. Another similarity between the three complexes is that the so-called 'bite angle', i.e. the angle O–Al–O formed between the Al^III ion and the bidentate ligands, is enlarged to about 93°. This enlargement produces yet another deviation from the ideal octahedron, and is discussed in more detail in the previous paper of our series.[8]

The packing of the complexes can be described as layers in which the Al(C₄H₄O₄)₂(CH₃OH)₂⁻ ions are held together by sodium ions in special position 6c (Na1) and probable hydrogen bonds between O5 and the hydrogen at O3 of the coordinating methanol molecule [O–O distance 2.561(5) Å], cf. Fig. 3. The sodium ions in position 6c (Na1) coordinate six oxygens (O1 and O2) in a strongly distorted octahedron with distances of 2.376(4) Å (O1) and 2.751(5) Å (O2), respectively. This large distortion is probably the effect of a local charge minimisation in the structure, and is reflected in the position of the sodium ions, 0.74 Å above and below the plane of the aluminium. The layers so formed are stacked perpendicular to the [001] direction and are related through the inherent 3₁ screw axis (i.e. a rotation of 120° and a translation of 1/3 along the c-axis). The negatively charged layers are held together by sodium ions in special position 3b (Na2) (cf. Fig. 4). These sodium ions coordinate 6 oxygens (O4) in a slightly distorted octahedron (cf. Table 3 and Fig. 4) with the Na2–O4 distance

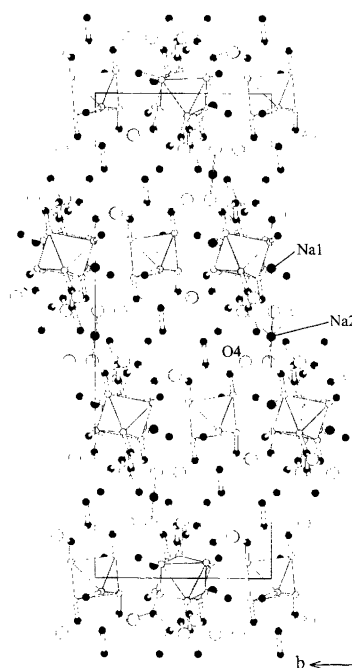

Fig. 4. A packing diagram viewed along the a-axis and showing the stacking of the layers (cf. Fig. 3). The layers are connected via octahedrally coordinated sodium ions in special position 3b (Na2).

2.388(5) Å, which corresponds well with distances reported for six-coordinated Na–O in the literature (2.25–2.78 Å).[17]

Within the layers, the Al(C₄H₄O₄)₂(CH₃OH)₂⁻ ions are orientated with the methyl groups of methylmalonate pointing in a direction out from the layers, possibly giving rise to a small hydrophobic effect, that may decrease the solubility of the phase. The methyl group of methanol does not seem to have any effect on the

packing of the structure. This is somewhat puzzling since, as mentioned above, the evaporation of an aqueous solution of the same composition only yielded a non-crystalline glass phase. However, the effect of the methyl group can possibly be that it decreases the solubility of the complex in the solvent used and, in that way, contributes to the crystal formation.

The present structure determination represents a rare example of an aluminium(III) complex in which methanol molecules are directly coordinated to aluminium(III). This type of direct coordination was only recently characterised by Atwood et al.,[18,19] in crystals resulting from the strict anhydrous treatment of (Shiff base)AlCl complexes with sodium tetraphenylborate and methanol. The Al–O (methanol) distances reported (1.94–2.00 Å) compare well with our findings. Previously reported aluminium(III)–methanol solvates, $[Al(C_9H_7BrNO_2)_3] \cdot CH_3OH$[20] and $[Al(C_9H_8NO_2)_3] \cdot CH_3OH$,[21] both include methanol molecules which are hydrogen bonded to an oxygen atom of the first coordination sphere.

The fact that methanol has managed to coordinate directly to aluminium(III) in the present complex is somewhat surprising, considering the known fact that water molecules very effectively displace alcohols from coordination to aluminium.[22] In a multinuclear NMR study by Akitt et al.,[23] anhydrous $AlCl_3$ was dissolved in methanol and different small amounts of water were added. Resulting spectra indicated that a series of mixed solvate complexes were formed and it was concluded that virtually all water added was directly complexed to aluminium. In the present investigation, where a glass of AlL_2 composition was dissolved in methanol, it seems logical to believe that at least two molecules of water per aluminium have accompanied the glass into the methanol solvent. Therefore, and in view of the above, the crystallisation of a water solvate would have been more expected. A water solvate would also be the expected result considering transfer potentials (water to methanol) for hard metal ions. No transfer potential has actually been reported for aluminium(III), but in a study of alkaline earth metals[24] it was concluded that the preference for water solvation increased with the hardness of the metal ion. Data presented by Beatty et al.[25] and Blandamer et al.[26] however, point in a somewhat different direction. In the study by Beatty et al.,[25] the solvation of AlL_3 (L = pyronato/pyridinato) complexes was measured in a series of solvents, and the solvation in water and methanol was found to be almost the same. This finding imply that solvation phenomena also strongly involve coordinated ligands and that the solvation of $AlL_2(solv)_2^-$, therefore, cannot be compared with the solvation of Al^{3+} ions. Also in the work by Blandamer et al.,[26] where the solvation of different iron(II) complexes in water/methanol mixtures was studied, it was found that the identity of the ligand, as well as the charge of the complex and the counter-ion employed, strongly

affected the solvation process. Once again this shows that the solvation properties of metal–ligand complexes cannot directly be compared with the properties of pure metal–solvate complexes. Unfortunately, it has not been possible to find any literature data on the solvation of mixed metal–ligand–solvate complexes, and we are therefore unable to present any definite explanation as to why the aluminium ion has preferred methanol, instead of water, as solvate in our particular case.

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