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# Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 33. The Al(methylmalonate)$_2$(H$_2$O)$_2^-$ Complex Crystallised as a Double Salt with Al(H$_2$O)$_6^{3+}$ and Cl$^-$

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The crystal structure of hexaaquaaluminium(III) *trans*-diaquabis(2-methylpropanedionate)aluminate(III) dichloride tetrahydrate, [Al(H$_2$O)$_6^{3+}$][Al(C$_4$H$_4$O$_4$)$_2$(H$_2$O)$_2^-$][Cl$^-$]$_2$·4H$_2$O, was determined by single-crystal X-ray diffraction. The compound crystallises in the triclinic space group $P\bar{1}$, with $a$ = 6.956(1), $b$ = 8.413(2), $c$ = 10.737(2) Å, $\alpha$ = 89.78(2), $\beta$ = 106.90(2), $\gamma$ = 95.25(2)° and $Z$ = 1. The refinement of 148 parameters on 2563 reflections [$I > 2.0\sigma(I)$] gave a final $R$-value of 0.076 ($R_w$ = 0.052, $S$ = 1.082). The double salt was crystallised from aqueous solution and contains two different octahedral aluminium complexes, an Al(H$_2$O)$_6^{3+}$ complex and an AlL$_2$(H$_2$O)$_2^-$ complex with two methylmalonate ions equatorially coordinated and with two molecules of water at the apices. The structure is built up from layers of the Al complexes alternated with layers of chloride ions and water molecules parallel to the (010) plane.

The aqueous chemistry of aluminium(III) has received a great interest due to the toxic and deleterious environmental effects exerted by this element.[1–3] In a number of papers, within the title series, Öhman and co-workers have studied the solution chemistry qualities of aluminium(III) by means of potentiometric titrations and $^{27}$Al-NMR measurements. Since such investigations only give information about the gross composition and the amount of different species forming, while toxicological effects also involve the structure and lability of the different complexes, there is an obvious need for structural information on the suggested species. It is therefore of great interest to determine solid state structures from the investigated systems, since this will allow a full structural characterisation of the proposed complexes to be made.

The crystallisation of aqueous aluminium–ligand complexes into materials suitable for X-ray investigation is associated with severe experimental difficulties, and this is reflected in the fact that only a handful of such structures have been reported in the literature.[4] A general problem that has faced us in many of the systems from which we have attempted to obtain crystals, is the extreme water solubility of the complexes. Instead of crystallising, solutions prepared to contain such complexes gradually attain a syrup-like consistency and finally end up as a glass. Also, if the preparation of these solutions includes the use of both cationic (e.g. Na$^+$) and anionic (e.g. Cl$^-$) counter-ions, a normal phenomenon is that the corresponding salt (i.e. NaCl) is crystallising in extensive amounts. To avoid this obscuring situation, we have developed a technique in which the use of aluminium metal has replaced the use of alkaline sodium salts at solution preparation.

The aluminium/methylmalonic acid ($H_2L$) system was studied by means of potentiometric measurements,[5] and data were explained by a series of three complexes: AlL$^+$, AlL$_2^-$ and AlL$_3^{3-}$. No crystal structure has been reported for AlL$^+$, while for AlL$_2^-$ and AlL$_3^{3-}$, similar complexes with $H_2L$ = malonic acid have been structurally characterised by Tapparo *et al.*[6] and Farago and Amirhaeri,[7] respectively. Therefore, the original aim was to synthesise a crystalline phase containing the AlL$^+$ complex.

## Experimental

*Materials and methods.* From the calculated distribution diagram, which is based on the equilibrium model of

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Marklund and Öhman[5] and executed with the program SOLGASWATER,[8] the composition of the crystallisation solution was chosen as indicated by the vertical full line in Fig. 1. It should be noted that this diagram is extrapolated beyond the experimental ranges used by Marklund and Öhman and that the true species distribution may therefore differ somewhat from the information in the diagram. The crystallisation solution was generated by adding 23.62 g of methylmalonic acid (0.20 mol) (Sigma), 18.45 g of $AlCl_3 \cdot 6H_2O$(s) (0.076 mol) (Fisher p.a.) and 3.56 g of aluminium metal (0.124 mol) (Merck p.a.) to 500 ml of water. The use of metallic aluminium instead of sodium hydroxide to generate the necessary amount of $OH^-$ was, as mentioned above, motivated by the desire to avoid the presence of 'foreign' sodium cations in the crystallisation experiment. These hydroxide ions are generated according to the reaction $2Al(s) + 6H_2O \rightarrow 2Al^{3+} + 3H_2(g) + 6OH^-$, and the amount of aluminium added was based on information from the thermodynamic calculation. The 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 $Al_2O_3$(s), and the resulting pH was checked to be approximately 2.1–2.2, i.e. in agreement with the expected value. Following a slow evaporation for approximately 6 months in a refrigerator, colourless lens-shaped crystals appeared. Elemental analysis of these crystals indicated the total formula $Al_{2.1}Cl_2C_{7.8}H_{32.2}O_{19.8}$. The analyses of C, H (gravimetric) and Al (X-ray fluorescence) were performed by MIKRO KEMI AB (Uppsala, Sweden), the chloride content was analysed via Mohr titration, and the oxygen content was calculated by the difference between the total weight and these analyses. The composition according to structure refinement from X-ray diffraction data suggests the total formula $Al_2Cl_2C_8H_{32}O_{20}$.

*Data collection.* Intensity data were collected on a SYNTEX R3 four-circle diffractometer using graphite-monochromatized Mo $K_\alpha$ 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. Data were collected out to $2\theta = 60°$ for $0 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 11$ and $-15 \leqslant l \leqslant 14$. In all, 3988 reflections were collected, giving 3495 unique reflections after merging symmetry equivalent reflections ($R_{int} = \Sigma|\bar{I}_0 - I_0|/\Sigma I_0 = 0.014$). Refinements were based on the merged data set. Three standard reflections, showing variations of up to 3.4%, 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 11 reflections, distributed evenly in the measured 2θ-range, and resulted in a transmission factor variation of 0.623–0.759. The cell parameters, $a = 6.956(1)$, $b = 8.413(2)$, $c = 10.737(2)$ Å, $\alpha = 89.78(2)$, $\beta = 106.90(2)$, $\gamma = 95.25(2)°$ and $V = 598.6(2)$ Å$^3$, were determined from a least-squares fit to observed 2θ angles for 25 reflections in the 2θ range 20.15–28.98°. The experimental details are summarised in Table 1.

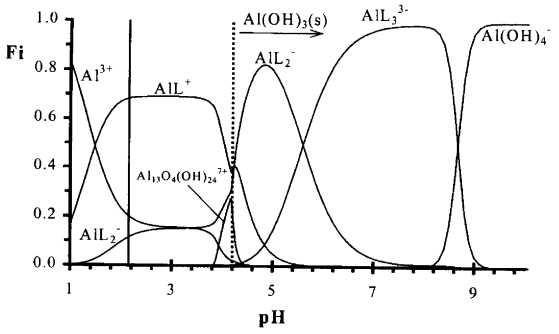


*Fig. 1.* Species distribution diagram for the $H^+$–$Al^{3+}$–methylmalonic acid system at $[Al^{3+}]_{tot} = [C_4H_6O_4]_{tot} = 0.4$ M. **Fi** is defined as the ratio between aluminium(III) in a species and the total aluminium(III) in solution. The vertical full line indicates the composition of the crystallisation solution, and the dotted line indicates the calculated precipitation limit for $Al(OH)_3$(s).

*Refinements.* Calculations were carried out using the Xtal3.2 program package[9] on 2563 reflections with $I > 2.0\sigma(I)$. The structure was solved using direct methods. Scattering factors used for the refinements were those of $Al^{3+}$, $Cl^-$, $O^-$ and C, and anomalous dispersion was considered.[10] All the atoms found were refined anisotropically, and the full matrix refinement, with 148 parameters, gave $R = 0.076$ and $R_w = 0.052$, respectively. The fractional atomic coordinates and equivalent displacement parameters are listed in Table 2, and selected bond lengths and angles are given in Table 3.

## Structure description and discussion

The structure can be described as a salt consisting of a cationic and an anionic complex, chloride ions and water molecules. In Fig. 2 the two different complexes are shown; the cation $Al(H_2O)_6^{3+}$ and the anion $Al(C_4H_4O_4)_2(H_2O)_2^-$. In both complexes the aluminium ion is six coordinated and in an essentially octahedral environment.

In the cationic complex, $Al(H_2O)_6^{3+}$, the bond angles range from 88.7(1) to 91.3(1)° and the bond distances range between 1.870(2) and 1.883(2) Å. This can be compared with the results of Buchanan and Harris[11] who, in an X-ray and neutron diffraction structure determination of $AlCl_3 \cdot 6H_2O$, reported the O–Al–O angle $90 \pm 1°$ and the Al–O bond distance $1.88 \pm 0.02$ Å. The higher degree of distortion in the present hexa-aqua complex can be related to the unsymmetrical surroundings, involving hydrogen bonding and electrostatic effects which are described in more detail below.

In the $Al(C_4H_4O_4)_2(H_2O)_2^-$ complex, where the donors comprise two water molecules in the *trans* position, (O1.3), and two bidentate methylmalonate ligands

*Table 1.* Crystal and experimental data for $[Al(H_2O)_6^{3+}][Al(C_4H_4O_4)_2(H_2O)_2^-][Cl^-]_2 \cdot 4H_2O$

| Formula | $[Al(H_2O)_6^{3+}][Al(C_4H_4O_4)_2(H_2O)_2^-][Cl^-]_2 \cdot 4H_2O$ |
|---|---|
| $M_r$/g mol$^{-1}$ | 573.2 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ (No. 2) |
| $a$/Å | 6.956(1) |
| $b$/Å | 8.413(2) |
| $c$/Å | 10.737(2) |
| $\alpha$/° | 89.78(2) |
| $\beta$/° | 106.90(2) |
| $\gamma$/° | 95.25(2) |
| $V$/Å$^3$ | 598.6(2) |
| $Z$ | 1 |
| $D_c$/g cm$^{-3}$ | 1.59 |
| $\mu$(Mo $K_\alpha$)/mm$^{-1}$ | 0.43 |
| $F$(000) | 316 |
| Crystal colour | Colourless |
| Crystal size/mm | 0.39 × 0.11 × 0.22 |
| Temperature/K | 293 |
| No. of reflns. for cell determination | 25 |
| 2θ range/° | $20.15 < 2\theta < 28.98$ |
| Scan mode | θ–2θ |
| 2θ range/° | $3.96 < 2\theta < 60.14$ |
| *hkl* range | $0 \leqslant h \leqslant 9$<br>$-11 \leqslant k \leqslant 11$<br>$-15 \leqslant l \leqslant 14$ |
| 2θ scan speed/° min$^{-1}$ | 2.02–8.37 |
| Total no. of reflns. measured | 3988 |
| Total no. of independent reflns. | 3495 |
| Test reflns. (deviation %) | 0 1 0 (2.7)<br>0 −2 −2 (3.4)<br>0 −1 −2 (1.7) |
| Refinement on | $F$ |
| No. of obs. indep. reflns. $I > 2.0\sigma(I)$ | 2563 |
| No. of parameters refined | 148 |
| Weights calcd. according to | $1/w = \sigma^2(F_{obs}) + 5.24 + 0.37F_{obs} - 32.30 \sin\theta + 9.91 \times 10^{-4}F_{obs}^2 - 1.16 \sin\theta F_{obs} + 53.70 \sin^2\theta$ |
| $R$ ($R_w$) | 0.076 (0.052) |
| $S$ | 1.082 |
| Extinction coeff. | None |
| $(\Delta/\sigma)_{max}$ | 0.0005 |
| Min/max residual electron density/e Å$^{-3}$ | −0.92/2.03 |

coordinating through their carboxylate oxygens (O1.1 and O1.2), the bond angles of the distorted octahedron range from 87.6(1) to 92.4(1)°. The distance between the carboxylate oxygens of a coordinating methylmalonate ion is 2.690(3) Å, which is considerably shorter than the corresponding distance in methylmalonic acid, 3.03 Å.[12] It is evident that this difference, together with the enlargement of the bite angle, 92.4(1)°, is the result of an accommodation to fit the size of the aluminium(III) octahedron. For each ligand, the two Al–O bond lengths are 1.840(2) and 1.886(2) Å, an inequality which probably originates from crystal packing effects. The bonds to the water molecules are slightly longer, 1.935(2) Å. These bond angles and bond distances are all very similar to those previously found for the corresponding complex with malonate ions.[6] In turn, this implies that the methyl group in methylmalonate has an insignificant effect on the binding character in the $AlL_2(H_2O)_2^-$ complex.

The packing of the structure has a distinct layer character. Alternate rows of the $Al(H_2O)_6^{3+}$ and the $Al(C_4H_4O_4)_2(H_2O)_2^-$ complexes build up layers, parallel to the (010) plane (cf. Fig. 3). These layers are stacked in the [010] direction, with layers of chloride ions and water molecules in between. The chloride ions and water molecules are arranged in distorted trigonal anti-prisms between the $Al(H_2O)_6^{3+}$ complexes, cf. Fig. 4. A local pseudo-three-fold axis could be distinguished, running in the [010] direction through the $Al(H_2O)_6^{3+}$ complexes and the distorted trigonal anti-prisms (cf. Fig. 2). The structure is held together by a complicated pattern of electrostatic interactions and hydrogen bonds. In Table 4 some selected hydrogen bonds are listed, and these are also represented by dotted lines in Figs. 3 and 4. The interactions between the layers are mainly electrostatic, and the only sites possibly connected via hydrogen bonds are over 3.1 Å apart, which leads to the conclusion that these bonds, if they exist, are very weak. The weak interactions between the layers, due to sparsely populated

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

| Atom | *x/a* | *y/b* | *z/c* | $U_{eq}$/Å$^{2\,a}$ |
|---|---|---|---|---|
| Al1 | 0 | 0 | 0.5 | 0.0224(5) |
| O1.1 | 0.8330(3) | 0.0884(3) | 0.5866(2) | 0.0270(8) |
| O1.2 | 0.8351(3) | 0.0458(3) | 0.3388(2) | 0.0268(8) |
| O1.3 | 0.8424(3) | 0.7960(3) | 0.4894(2) | 0.0304(8) |
| O1.4 | 0.5514(3) | 0.1695(3) | 0.6071(2) | 0.0336(9) |
| O1.5 | 0.5808(3) | 0.1269(4) | 0.1885(2) | 0.39(1) |
| C1.1 | 0.6686(4) | 0.1497(4) | 0.5417(2) | 0.026(1) |
| C1.2 | 0.6780(4) | 0.1186(4) | 0.3033(3) | 0.028(1) |
| C1.3 | 0.5983(5) | 0.2027(4) | 0.4010(3) | 0.034(1) |
| C1.4 | 0.6660(8) | 0.3849(5) | 0.4028(4) | 0.049(2) |
| Al2 | 0 | 0 | 0 | 0.0233(5) |
| O2.1 | 0.7856(3) | 0.1118(3) | 0.0147(2) | 0.0297(8) |
| O2.2 | 0.0200(4) | 0.1308(3) | 0.8610(2) | 0.0322(9) |
| O2.3 | 0.1848(3) | 0.1457(3) | 0.1163(2) | 0.0323(9) |
| Cl | 0.0983(2) | 0.4143(1) | 0.2679(1) | 0.0453(4) |
| O1aq | 0.2583(6) | 0.3932(5) | 0.8957(4) | 0.063(2) |
| O2aq | 0.6275(5) | 0.3304(5) | 0.8480(4) | 0.061(2) |

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

*Table 3.* Selected inter-atomic distances (in Å) and bond angles (in ).

| | | | |
|---|---|---|---|
| Al1–O1.1 | 1.886(2) | C1.1–C1.3 | 1.526(4) |
| Al1–O1.2 | 1.840(2) | C1.2–C1.3 | 1.523(5) |
| Al1–O1.3 | 1.935(2) | C1.3–C1.4 | 1.560(6) |
| O1.1–C1.1 | 1.262(4) | Al2–O2.1 | 1.878(3) |
| O1.2–C1.2 | 1.263(4) | Al2–O2.2 | 1.883(2) |
| C1.1–O1.4 | 1.243(4) | Al2–O2.3 | 1.870(2) |
| C1.2–O1.5 | 1.227(3) | | |
| O1.1–Al1–O1.2 | 92.4(1) | C1.3–C1.2–O1.2 | 121.8(2) |
| O1.1–Al1–O1.2$^{I}$ | 87.6(1) | C1.3–C1.2–O1.5 | 115.9(3) |
| O1.1–Al1–O1.3$^{I}$ | 90.6(1) | O1.5–C1.2–O1.2 | 122.4(3) |
| O1.1–Al1–O1.3 | 89.4(1) | C1.2–O1.2–Al1 | 132.7(2) |
| O1.2–Al1–O1.3$^{I}$ | 91.1(1) | O2.1–Al2–O2.2$^{I}$ | 91.3(1) |
| O1.2–Al1–O1.3 | 88.9(1) | O2.1–Al2–O2.2 | 88.7(1) |
| Al1–O1.1–C1.1 | 130.4(2) | O2.1–Al2–O2.3 | 90.4(1) |
| O1.1–C1.1–C1.3 | 121.8(3) | O2.1–Al2–O2.3$^{I}$ | 89.6(1) |
| O1.1–C1.1–O1.4 | 123.0(2) | O2.2–Al2–O2.3$^{I}$ | 90.4(1) |
| O1.4–C1.1–C1.3 | 115.1(3) | O2.2–Al2–O2.3 | 89.6(1) |
| C1.1–C1.3–C1.2 | 116.6(3) | | |
| C1.1–C1.3–C1.4 | 106.6(2) | | |
| C1.4–C1.3–C1.2 | 108.5(3) | | |

Symmetry code: $^{I}$ $-x, -y, -z$.

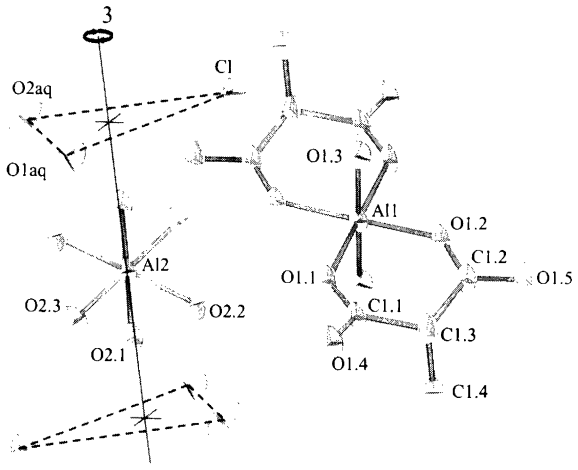


*Fig. 2.* The $Al(H_2O)_6^{3+}$ and the $Al(C_4H_4O_4)_2(H_2O)_2^-$ complex illustrated with the thermal displacement parameters scaled to include 50% probability. The figure also illustrates the pseudo-three-fold axis through the $Al(H_2O)_6^{3+}$ and the distorted trigonal anti-prism (cf. Fig. 4).

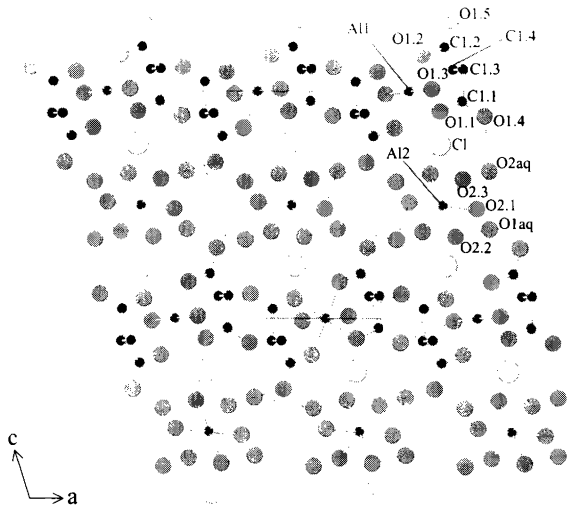


*Fig. 3.* The packing of the $Al(H_2O)_6^{3+}$ and the $Al(C_4H_4O_4)_2(H_2O)_2^-$ complexes in alternate rows viewed along the *b*-axis. The dotted lines represent possible hydrogen bonds.

*Table 4.* Hydrogen bond distances (in Å).

| | | | |
|---|---|---|---|
| O2.1···O1.5 | 2.665(4) | O1aq···O2.2 | 2.594(5) |
| O2.2···O1.1 | 2.862(3) | O1aq···O2aq | 2.854(6) |
| O2.3···O1.5 | 2.656(3) | O2aq···O1.4 | 2.809(5) |
| O2.3···Cl | 2.991(3) | O2aq···O2.1 | 2.649(5) |

$Cl^-/H_2O$ layers, are also reflected in the morphology of the crystals. The typical appearance is that of a thin lens of the proportion 250:1:150, where the shortest dimension coincides with the [010] crystallographic direction. Another indication of weak cohesive crystalline forces in general is the long time and the low temperature needed to crystallise the compound. Since such 'thin' crystals give rise to large X-ray absorption effects in certain directions, the crystal used for investigation ($0.39 \times 0.11 \times 0.22$ mm$^3$) was a fragment of a much larger lens-shaped crystal. It can finally be noted that since the aim was to synthesise the $AlL^+$ complex, an Al/L ratio of 1/1 was used in the crystallisation solution. However, since the resulting double salt also contains this overall ratio (2/2), the crystal formation can be viewed upon as a drainage from solution of two minor solution constituents (cf. Fig. 1) followed by redistribution of two $AlL^+$ complexes into one $Al^{3+}$ and one $AlL_2^-$ ion. The present structure determination therefore gives support for the aqueous speciation model presented by Marklund and Öhman.[5]

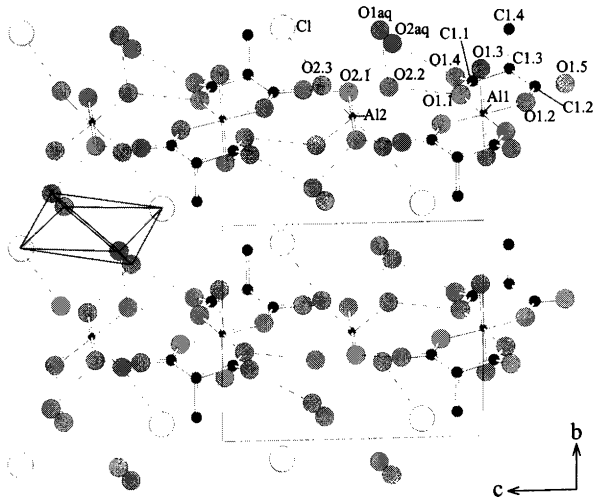


*Fig. 4.* The stacking of the $Cl^-/H_2O$ layers and the Al-containing layers viewed along the *a*-axis with the distorted trigonal anti-prism illustrated in the left part of the figure. The dotted lines represent possible hydrogen bonds.

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