

Co-operative Hydrogen Bonding with Short O...O Distances in a Binuclear Al^{III}-Glycolate Complex

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X-Ray structure analysis of tri(sodium hydrogen)bis[trisglycolato-aluminate(III)], Na₃H₃[Al(C₂H₂O₃)₃]₂, has revealed facial 1:3 Al^{III}-glycolate complexes that are connected into binuclear complexes by three short [O...O 2.425(4) Å] and symmetrical hydrogen bonds between the hydroxy moieties.

Hydrogen bonds with short O...O distances and symmetry about the hydrogen are essentially known from hydrated protons, hydrated hydroxide ions, the monobasic carboxylic acid salts, and the metal-dioxime complexes.^{1,2} The strong co-operative hydrogen bonds reported here for the tri(sodium hydrogen)bis[trisglycolato-aluminate(III)] complex, represent a rare type of hydrogen bonding in metal-ligand complexes. In the binuclear Al^{III}-glycolate complex, the metal is only indirectly involved in the formation of the strong hydrogen bond: the Al^{III} facilitates the ionisation of the hydroxy group of glycolate. To our knowledge, the only two other comparable examples of co-operative hydrogen bonding are found in a Co^{III}-amino-ethanol^{3,4} and a Sn^{IV}-1-hydroxybenzene-2-thiolato complex.⁵

Recently, the co-ordination of Al^{III} with glycolic acid in aqueous solution has been studied with the use of high-field multinuclear NMR spectroscopy.⁶ The results showed that the glycolate ligand co-ordinates *via* both the carboxylate and the hydroxy group to the Al^{III} ion. In solution, 1:1, 1:2, 1:3, and polynuclear Al^{III}-glycolate complexes were observed. Moreover, it was found that, in aqueous Al^{III} solutions, deprotonation of the hydroxy moiety of glycolate may occur at pH 4.

Single crystals of Na₃H₃[Al(C₂H₂O₃)₃]₂, isolated from an aqueous solution at pH 4, were used for ²⁷Al MAS and ¹³C CPMAS NMR experiments. The ²⁷Al MAS NMR spectrum shows, after correction for the second order quadrupole shift, a peak centred at about 30 ppm (referenced to external aqueous 1 M AlCl₃). This is at intermediate chemical shift with respect to 1:3 Al^{III}-glycolate complexes in aqueous solution with none and all hydroxy groups of the glycolate ligands deprotonated. The ¹³C CPMAS NMR spectrum shows only two peaks at δ 61 and 180 respectively, thus pointing to a facial geometry of the ligands. An X-ray structural analysis of this

solid Al^{III}-glycolate complex[†] was performed in order to obtain additional information. Excellent, octahedrally shaped, single crystals of Na₃H₃[Al(C₂H₂O₃)₃]₂ were obtained by liquid diffusion of ethanol into an aqueous solution of AlCl₃·6H₂O and glycolic acid, which was adjusted to pH 4 with NaOH.

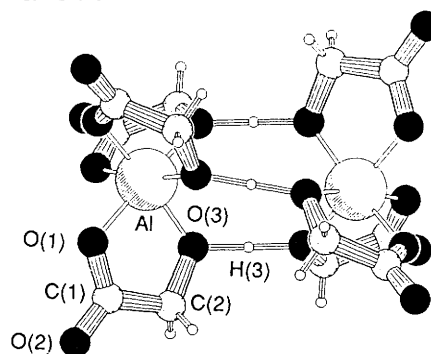


Figure 1. Molecular conformation of the binuclear Al^{III}-glycolate complex. Bond lengths: O(3)...O(3) 2.425(4), O(3)-H(3) 1.21(4) Å.

[†] Crystal data for Na₃H₃[Al(C₂H₂O₃)₃]₂: *M* = 570.2, cubic, *a* = 12.872(2) Å, *U* = 2133(1) Å³, λ(Mo-K_α) = 0.71073 Å, space group *P*4₁32, *Z* = 4, *D*_x = 1.782 g cm⁻³, transparent crystals, size 0.2 × 0.2 × 0.4 mm, μ = 3.0 cm⁻¹. Intensities were measured on an Enraf-Nonius CAD-4 diffractometer using Zr-filtered Mo-K_α radiation. *F*(000) = 1160, *T* = 295 K. The structure has been refined to *R* = 0.029 for 530 unique reflections with *I* ≥ 2.0 σ(*I*) and 64 variables. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Figure 1 shows the molecular conformation of the Al^{III} -glycolate complex. The Al atom occupies a position on the three-fold axis and is co-ordinated to six oxygen atoms from three facial (three-fold related) glycolate ligands, forming a (distorted) octahedron. Half the hydroxy sites are deprotonated, leading to a very short symmetrical hydrogen bond between two-fold related hydroxy sites with $\text{O} \cdots \text{O}$ 2.425(4) Å and the bridging H-atom at the two-fold axis. Three such hydrogen bonds connect two *fac*- Al^{III} -glycolate complexes into a binuclear complex along a common three-fold axis. The binuclear complexes are packed into three dimensions by $\text{O} \cdots \text{Na}$ interactions. The Na atom is co-ordinated to O(1) and O(2) atoms of the carboxylate group to give a highly distorted octahedron.

The *fac* geometry of the ligands, together with the half deprotonated hydroxy groups, is in accordance with the results obtained from the solid state NMR experiments, *vide supra*. Moreover, it shows that deprotonation of the glycolate hydroxy moiety may occur at pH 4, as was derived from ^{27}Al NMR experiments on aqueous Al^{III} solutions.

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