Crystal and molecular structure of an aluminium clathrate exhibiting an unusual tertiary arrangement and an extraordinary degree of solvation

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In the course of our study of aluminium complexes, a new complex with *N*-salicylidene-*o*-aminophenol (H_2L) is isolated, which is unique because of its stereochemistry, degree of solvation, the manner of tertiary arrangement and by the crystal packing; the crystal and molecular structure of this complex is established by X-ray structure analysis.

Adverse effects of elevated aluminium concentration in the environment[1] attract attention to its coordination chemistry in biological systems. Among others, the Schiff bases as typical 'hard donor ligands' exhibit some similarity with ligands present in biological systems. Thus they can serve as a suitable *in vitro* model mimicking the coordination chemistry of Al *in vivo*.

The source material was obtained from *N*-salicylidene-*o*-aminophenol (6 mmol), NaOH (6 mmol), $AlCl_3{\cdot}6H_2O$ (6 mmol) in methanol–water (55 ml, 10 : 1) precipitated with sodium acetate (5% m/v in water, 25 ml). The yellow needles of the complex were obtained in 30–40% yield by the slow diffusion of diethyl ether into the solution containing the crude precipitate (50 mg), acetone (2 ml) and water (50 μl). The fact that the crystals immediately decompose upon removing them from the mother-liquor indicated that appropriate guests are necessary to stabilize the three-dimensional framework structure. Hence, a single crystal was adjusted in a glass capillary filled with diethyl ether for the X-ray analysis.†

Since the discovery of crown ethers a considerable number of various classes of host–guest compounds have been described,[2] including clathrates, framework silicates, Zintl phases, polycations and others. The new aluminium clathrate exhibits a combination of several new structural features. The primary structure of the complex is composed of two independent polynuclear moieties A and B. Moiety A is the binuclear complex $[(H_2O)LAl(\mu\text{-}MeCO_2)(\mu\text{-}OH)AlL(H_2O)]$ (Fig. 1), while moiety B consists of the $[\{LAl(H_2O)(OH_2)\}_2Al(\mu\text{-}OH)_2Al\{LAl(H_2O)(OH)_2\}_2]$ hexanuclear unit which is symmetrical along the twofold crystallographic axis (Fig. 2). Thus, in contrast to many other clathrates of cadmium[3] or nickel[4] cyanides or framework silicates,[2] bridging anions do not create the infinite network, and the structure consists of independent neutral polynuclear coordination compounds. The repeating of hydrogen-bond networks including the A_2B cyclic tertiary arrangement and four methanol molecules leads to infinite channels parallel to the *c* crystallographic axis (Fig. 3). The quite unusual cavity dimension (18 × 15 Å) and degree of solvation have some analogy with pore-forming proteins,[5] but

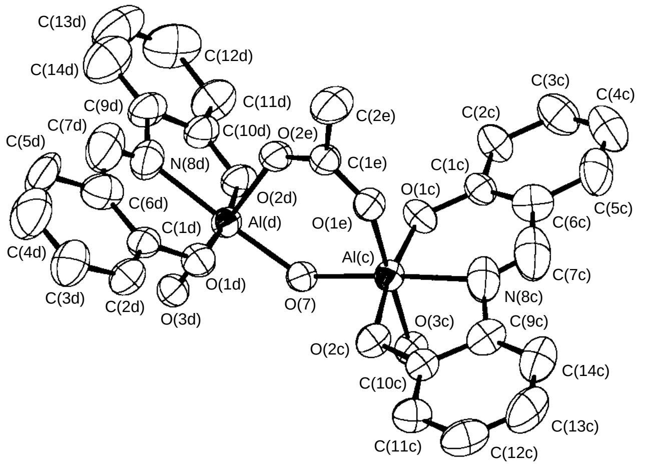

Fig. 1 Structure of the binuclear $[(H_2O)LAl(\mu\text{-}MeCO_2)(\mu\text{-}OH)AlL(H_2O)]$ complex

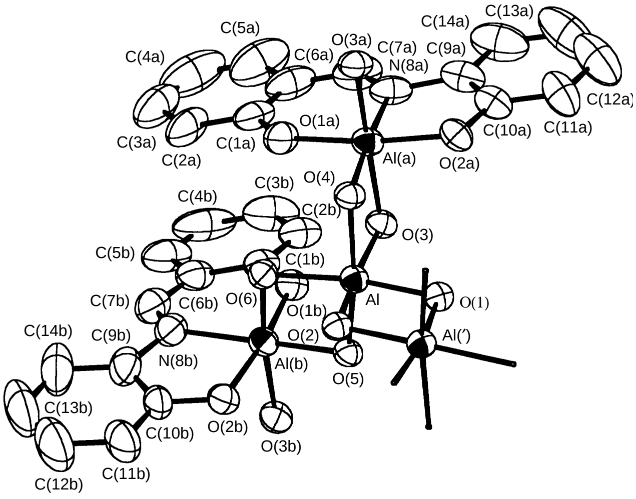

Fig. 2 Structure of the hexanuclear $[\{LAl(H_2O)(OH)_2\}_2Al(\mu\text{-}OH)_2Al\{LAl(H_2O)(OH)_2\}_2]$ complex [half of the molecule with the bridging $Al(\mu\text{-}OH)_2Al'$ moiety]

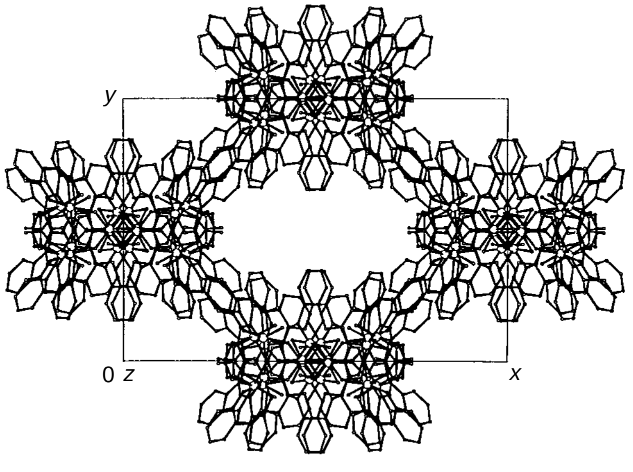

Fig. 3 Crystal packing of $2[(H_2O)LAl(\mu\text{-}MeCO_2)(\mu\text{-}OH)AlL(H_2O)]{\cdot}[\{LAl(H_2O)(OH)_2\}_2Al(\mu\text{-}OH)_2Al\{LAl(H_2O)(OH)_2\}_2]{\cdot}4MeOH{\cdot}nEt_2O$

on the other hand, is quite unexpected among coordination compounds. Another unusual feature of the present compound is the high degree of solvation. Since inclusion compounds of highly volatile guests are often unstable,[6] it is quite unexpected, that a compound containing approximately 45% of disordered diethyl ether molecules forms mechanically stable crystals at ambient temperature. In conclusion, the stereochemistry of this complex indicates that the ability of aluminium to create structures mimicking some structures typical of living systems should be considered for the evaluation of its *in vivo* toxicity.

Footnotes

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† *Crystal data*: $C_{52}H_{54}Al_6N_4O_{22}\cdot 2C_{28}H_{26}Al_2N_2O_9\cdot 4CH_4O\cdot nC_2H_6O$, $M = 2554.038$ (without diethyl ether), monoclinic, space group $C2/c$, $a = 29.143(7)$, $b = 18.302(4)$, $c = 32.631(8)$ Å, $\beta = 115.19(2)°$, $U = 15749.4(13)$ Å^3, $Z = 4$, $D_c = 1.0771$ g cm^{-3}, $\mu = 11.965$ cm^{-1}. The intensity data were collected through a glass capillary containing diethyl ether on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu-Kα radiation ($\lambda = 1.540\,56$ Å) with $R_{int} = 0.019$, and the structure was solved by direct methods with SHELXS-86.[7] All the non-hydrogen atoms were refined anisotropically with the exception of methanol atoms using SHELXL-93.[8] The final cycle of full-matrix least-squares refinement was based on 6761 observed reflections [$I > 2\sigma(I)$] and 661 variable parameters with $R(wR_2) = 0.120$ (0.394). Due to the high content of solvated molecules, the structure was refined by methods commonly used for proteins with SWAT parameter $g = 3.70(21)$ for $U = 4.00$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/435.

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