

Synthesis and Molecular Structure of the Cyclic Hexamer of 2,3-Dimethylbutene Aluminium Monochloride

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The compound $\text{cyclo-}\{\mu\text{-}[\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}_2]\}_6(\mu\text{-Cl})_6\text{Al}_6$, $(\text{AlCl}\cdot\text{DMB})_6$, prepared as a toluene solvate from a solution of AlCl_3 and dimethylbutadiene in toluene, has been characterized crystallographically.

Cryochemical methods enable the preparation of compounds which otherwise cannot be synthesized or cannot be synthesized easily.¹ In this respect, co-condensation of metal atoms or high-temperature species with unsaturated molecules has been applied in the past.² Recently we showed that the high-temperature molecule AlCl can also be successfully used in cryochemical preparations.^{3,4} The related SiF_2 and BF react under cryochemical conditions with dimethylbutadiene (DMB) to monomeric sila- and bora-cyclopentenes.² Using AlCl and DMB, an analogue Al species may form. As Al prefers the co-ordination number four and lower co-ordinated Al compounds are stable only in the presence of very bulky ligands, the new species will probably be oligomeric or polymeric. The preparative procedure is outlined as follows. After co-condensation of AlCl and DMB dissolved in toluene at 77 K in the ratio 1 : 1 and warming up to 273 K a clear yellow solution was obtained, from which air- and moisture-sensitive crystals precipitated after 3 days. The crystals hydrolysed to

2,3-dimethylbut-1- and -2-ene and were insoluble in all common solvents, thereby preventing reliable NMR spectroscopy.

Crystals of diffraction quality were isolated from the solution and transferred directly into a stream of cold nitrogen at the diffractometer. §

§ *Crystal data:* $\text{C}_{36}\text{H}_{60}\text{Al}_6\text{Cl}_6$, $M = 959.6$, monoclinic, $P2_1/a$, $a = 9.759(2)$, $b = 44.362(9)$, $c = 12.013(3)$ Å, $\beta = 93.19(2)^\circ$, $U = 5192.5(8)$ Å³, $Z = 4$, $D_c = 1.23$ g cm⁻³. Mo- K_α radiation, $\lambda = 0.71073$ Å, $\mu = 0.46$ mm⁻¹, $F(000) = 506$, crystal dimensions $0.3 \times 0.2 \times 0.15$ mm. Siemens-Nicolet R3 diffractometer. Data were collected at 140 K in the range $4 \leq 2\theta \leq 48^\circ$ with the ω - 2θ mode. 8141 Independent reflections were measured. Intensities were corrected for Lorentz and polarization effects. 6269 Absorption corrected data with $I \geq 1.96\sigma(I)$ were obtained. The structure was solved by direct methods (SHELXTL PLUS). Full matrix least squares refinement was used (non-hydrogen atoms anisotropic, hydrogen in idealized positions, $-\text{CH}_2-$ and $\text{Me}-$ refined as rigid groups with fixed isotropic temperature factors, $U = 0.08$ Å²). 532 Variables, weights $w^{-1} = \sigma^2(F_o) + 0.0003 F_o^2$, $R = 0.0723$, $R_w = 0.0684$. 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.

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‡ Molecular AlCl is formed in a high-temperature reaction (1200K) of $\text{Al}_{(l)}$ with $\text{HCl}_{(g)}$.

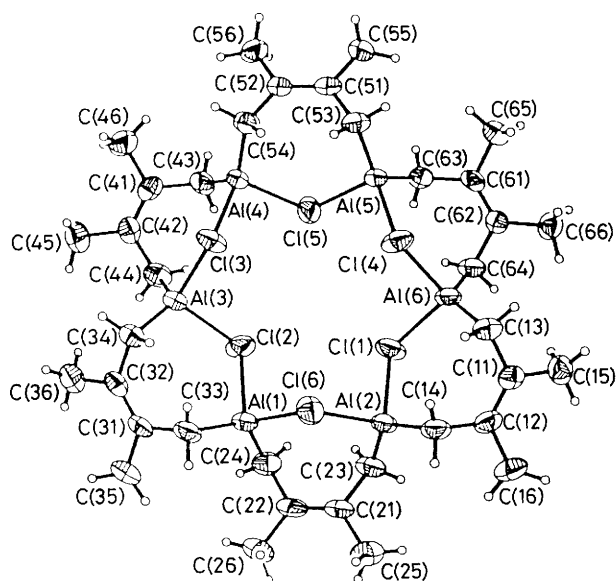


Figure 1. The $(\text{AlCl} \cdot \text{DMB})_6$ molecule. Principal mean distances (\AA) and angles ($^\circ$) are: Al–Cl 2.292(1); Al–C 1.952(7); C=C 1.347(6); C–C 1.509; Cl–Al–Cl 99.2(2); C–Al–C 128.1(3); Cl–Al–C 103.0(2)–109.1(2); Al–Cl–Al 114.7(1); C–C–Al 111.8(4).

A view of the molecular structure is presented in Figure 1, and a space filling molecular model plot is shown in Figure 2.

The $(\text{AlCl} \cdot \text{DMB})_6$ is a remarkably symmetrically and aesthetically appealing molecule. Its lens-shaped architecture deviates only slightly from D_{3h} -symmetry. The six Al atoms form a regular planar hexagon. They are bridged by six Cl atoms in a trigonal antiprismatic arrangement.

A similar twelve-membered ring structure $(\text{AlO})_6$ has been found in a tricalcium aluminate.⁵ The related dimethylaluminium fluoride forms tetrameric molecules with fluoro bridges.⁶ Chemically equivalent bonds only vary slightly from the mean values.

The mean Al–Cl distance in $(\text{AlCl} \cdot \text{DMB})_6$ is 2.292(1) \AA , approximately 0.08 \AA larger than the bridge bonds in dimeric Al_2Cl_6 .⁷ The Al–C bonds, 1.952(7) \AA , are in the usual range of terminal Al–C bonds.^{6,7} The bond angles at Al are considerably distorted. The C–Al–C angles are enlarged to 128.1(3) $^\circ$, the Cl–Al–Cl angles diminished to 99.2(2) $^\circ$. This seems to be inherent to the overall structure of the molecule: the central (Al, Cl)-core has to be spanned by the very rigid dimethylbutadiene moieties on the outside. Displacement of the Al atoms into the direction of the core-centre would relieve the

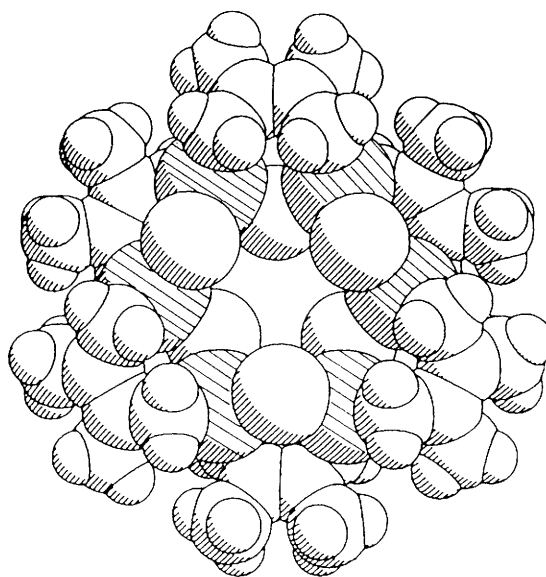


Figure 2. Space filling molecular model plot of $(\text{AlCl} \cdot \text{DMB})_6$.

strain in the Al co-ordination sphere, but simultaneously cause closer Cl \cdots Cl contacts, the smallest ones of which (3.47 \AA) are already less than the sum of the van der Waals radii. The dimensions within the dimethylbutadiene moieties are normal. In the unit cell the molecules are packed with their longest extension along the b axis, leaving holes for the toluene molecules.

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