Stereochemistry of 1 : 1 Adducts of Aluminium Compounds: Crystal Structure of Aluminium Borohydride–Trimethylamine

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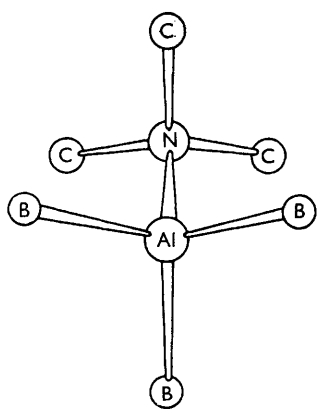
ALUMINIUM compounds of the type AlX_3 (or Al_2X_6) where X = halogen, alkyl, H, BH_4, *etc.*, react with a variety of Lewis bases to form, initially, a 1 : 1 adduct, $L \rightarrow AlX_3$, where L = ligand. *X*-Ray data[1] for the adduct $C_6H_5C(Cl)O \rightarrow AlCl_3$ have shown the presence of an O–Al bond, and of a tetrahedrally co-ordinated aluminium atom. We now present further evidence supporting the general occurrence of such stereochemistry in 1 : 1 complexes.

Aluminium borohydride–trimethylamine, Me_3N,-$Al(BH_4)_3$, was prepared as previously described,[2] and the colourless crystals purified by sublimation *in vacuo*. The crystals are orthorhombic with unit cell dimensions $a = 13{\cdot}016 \pm 0{\cdot}010$, $b = 7{\cdot}533 \pm 0{\cdot}005$, $c = 11{\cdot}325 \pm 0{\cdot}018$ Å, $z = 4$, corresponding to a density of $\rho_{calc} = 0{\cdot}781$ g. cm.$^{-3}$ The space group, determined from systematic absences, is either *Pnam*, or $Pna2_1$. A three-dimensional, room-temperature, *X*-ray analysis ($R = 0{\cdot}101$ for 388 independent reflexions) shows that, within standard errors, the molecular skeleton (C_3N, AlB_3, shown in the Figure) possesses the crystallographic mirror symmetry of space group *Pnam*. A difference Fourier synthesis shows strong indications of methyl-group hydrogen atoms, and of both bridging and terminal hydrogen atoms in the borohydride groups, but suggests that the latter do not conform with the higher symmetry, and that the true space group is probably $Pna2_1$. A further *X*-ray investigation, at 95°K, is in progress to determine more precisely the positions of the hydrogen atoms.



The atomic arrangements around the aluminium and nitrogen atoms are essentially tetrahedral (to within ± 1·5°), with the two tetrahedra adopting a staggered configuration. The calculated bond lengths, based on eight heavy atoms only, are C–N,

[1] S. E. Rasmussen and N. C. Broch, *Chem. Comm.*, 1965, 289.
[2] P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 1965, 3923.

1·58 ± 0·03 Å, and Al–N, 2·01 Å, while the Al–B distance is 2·19 ± 0·03 Å. Some shortening is to be expected when all hydrogens are included. However, the Al–N co-ordinate bond length is significant in that it is slightly greater than that predicted from the sum of covalent radii[3] (1·96 Å), a result which is to be compared with the abnormally short Al–O co-ordinate bond (1·84 Å) in $C_6H_5C(Cl)O$, $AlCl_3$.[1]

The re-hybridisation of the aluminium atom from planar (found for the AlB_3 atoms in aluminium borohydride[4]) to tetrahedral configuration, is in agreement with that expected for Group III acceptor atoms on the formation of 1 : 1 complexes.

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[3] L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, 1960.
[4] S. H. Bauer, *J. Amer. Chem. Soc.*, 1950, **72**, 622.