The Crystal Structures of Aluminium Borohydride–Trimethylamine: Low-temperature Study

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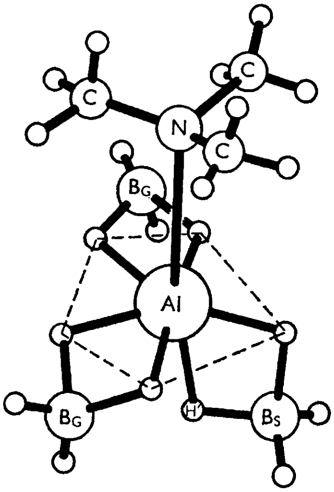
WE have recently described[1] the gross structure of aluminium borohydride–trimethylamine determined from room temperature (r.t.) X-ray data; we now report the detailed molecular structure as determined from X-ray data collected at −160°C.

The air-unstable compound crystallises in the orthorhombic space group *Pnam* (as at r.t.) with unit-cell dimensions a = 12·88, b = 7·15, c = 11·40 Å, z = 4 (*cf.* a = 13·016, b = 7·533, c = 11·325 Å at r.t.); the molecule possesses the strict mirror symmetry of the space group. A three-dimensional X-ray analysis (R = 0·108 for 617 independent reflexions) reveals that the essentially tetrahedral configuration at the aluminium atom (found in the r.t. analysis) is lost. The one boron atom lying in the mirror plane is distorted further away from the nitrogen atom (angle N·Al·B_S = 122°), whereas the other two (symmetry equivalent) boron atoms are bent back towards the nitrogen atom (N·Al·B_G = 100°). A difference synthesis based on the six unique atoms of the skeleton clearly revealed the positions of all twenty-one hydrogen atoms (twelve unique), showing the co-ordination around the aluminium atom to be a distorted pentagonal bipyramid, thereby explaining the deviation of the boron atoms from the tetrahedral configuration. The mean pentagonal plane, which contains the aluminium atom, is defined by five bridging hydrogen atoms, the root mean square deviations of these atoms from the plane being 0·22 Å. The two apical positions are filled by the second bridging hydrogen (H′) of the "special" borohydride group and by the nitrogen atom. The mean bond lengths and contacts are Al–N, 2·00 ± 0·01 Å; Al–B, 2·23 ± 0·01 Å; N–C, 1·53 ± 0·01 Å; Al–H, 1·97 ± 0·11 Å; B–H (bridging), 1·43 ± 0·11 Å; B–H (terminal), 1·19 ± 0·11 Å; and C–H, 1·11 ± 0·11 Å. In all cases estimated standard deviations are derived by inversion of the block-diagonal least-squares matrices. The sterochemistries of the nitrogen and carbon atoms are strictly tetrahedral, whilst at the boron atoms the tetrahedra are distorted.

The relationship between the r.t. and low-temperature (l.t.) structures may be understood by regarding the l.t. structure as a crystallographically symmetrical configuration; it is then possible to describe the r.t. structure in three ways. Firstly, as a static disordering (by three-fold rotation about the Al–N bond) of molecules with geometries illustrated by the l.t. structure. Secondly as a dynamic exchange of the asymmetric configuration around the aluminium atom between the borohydride groups, probably involving rigid-body motions of the borohydride groups about the Al–B directions. Thirdly, it would be possible to invoke a mechanism involving exchange of bridging and terminal hydrogen atoms within each borohydride group; which, if it persisted in solution, would be consistent with the previously reported interpretations of the proton nuclear magnetic resonance spectrum.[2,3]



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[1] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Chem. Comm.*, 1965, 438.

[2] P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 1965, 3923.

[3] J. K. Ruff, *Inorg. Chem.*, 1963, **2**, 515.