The Crystal and Molecular Structure of an Oxo-bridged Aluminium Complex Containing Pentaco-ordinated Aluminium Atoms

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Summary A complex formed by the reaction of aluminium chloride and 2-methyl-8-quinolinol in a nonaqueous medium was found, by a single-crystal *X*-ray investigation, to be μ-oxo-di[bis(2-methyl-8-quinolinolato)aluminium(III)], containing two pentaco-ordinated aluminium atoms.

ALUMINIUM usually forms either four- or six-co-ordinated complexes, and the existence of five-co-ordinated complexes of aluminium has only recently been substantiated by single crystal *X*-ray studies.[1,2] Bis(trimethylamine)-alane, $H_3Al,2NMe_3$ was found to be a trigonal bipyramid in the solid state with the two nitrogen atoms occupying apical positions perpendicular to the plane formed by the aluminium and three hydrogen atoms.[1] A distorted trigonal bipyramidal or square pyramidal configuration around the aluminium atom was found in an aluminosiloxane in which the aluminium atom was co-ordinated to four oxygen atoms and one bromine atom.[2] To our knowledge, these are the only two compounds in which a five-co-ordinated aluminium atom has been unequivocally established.

We have described the preparation of several complexes of aluminium(III) and 2-methyl-8-quinolinol in nonaqueous

media, and postulated that the complexes were hydroxo-complexes and hydroxo-bridged dimers containing six-co-ordinated aluminium atoms.[3,4] We report here a preliminary account of the structure of one of the complexes which was assumed to be a hydroxo-bridged dimer of bis-(2-methyl-8-quinolinolato)aluminium(III).

Crystal data: $Al_2O(C_{10}H_8NO)_4$, space group *Pbca*, $a = 19{\cdot}09 \pm 0{\cdot}01$, $b = 17{\cdot}04 \pm 0{\cdot}01$, $c = 21{\cdot}08 \pm 0{\cdot}01$ Å; $D_m = 1{\cdot}363$ g. cm.$^{-3}$ (by flotation), $D_c = 1{\cdot}362$ g. cm.$^{-3}$, $Z = 8$. Multiple film equi-inclination Weissenberg data were collected with Cu-K_α radiation and the intensities of 5300 independent reflections, (*h*0*l*—*h*11*l*) were measured visually. The structure was solved by the symbolic addition method and refined by isotropic full-matrix least-squares analysis to $R = 14\%$ for 3700 non-zero terms, hydrogen atoms being excluded.

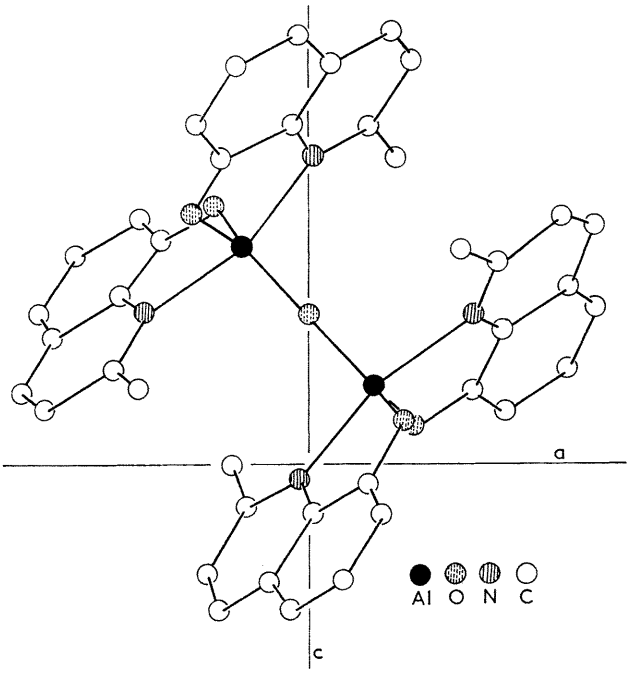

FIGURE 1

The structure consists of discrete molecules of $Al_2O(C_{10}H_8NO)_4$ as shown in Figure 1. Several unusual features are evident. The compound is not a hydroxo-bridged dimer as was first suspected. Each of the two aluminium atoms is co-ordinated to two molecules of 2-methyl-8-quinolinol which acts as a bidentate ligand. The two aluminium atoms in the molecule are also connected by an oxo-bridge and therefore both aluminium atoms are penta-co-ordinated. The molecule does not have a centre of symmetry; the two aluminium atoms and the oxygen lie on a two-fold axis of the molecule. The co-ordination around each of the aluminium atoms is trigonal bipyramidal; the three oxygen atoms and the aluminium atom are in a plane and the two nitrogen atoms occupy the apical positions. This is the first structure of a penta-co-ordinated aluminium(III) complex containing both oxygen and nitrogen donor atoms and an oxo-bridge connecting the two metal atoms.

The stability of the complex, at room temperature on exposure to air and to *X*-rays, was unexpectedly high. After 4 months of continuous exposure of a crystal to *X*-rays there was no noticeable change in the intensities in the zero-level Weissenberg photographs. This unusual stability of the compound can be attributed to the strong interaction of the two aluminium atoms with the bridging oxygen atom and to the proximity of the methyl groups to the π-electron cloud of the pyridine rings. The van der

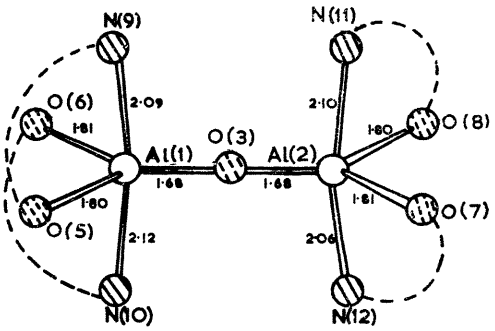

FIGURE 2

Waals contacts between the carbon atoms of the four methyl groups and the carbon atoms of the nearest pyridine rings are less than 3·6 Å.

The bond lengths between the aluminium atom and the oxygen and nitrogen atoms are shown in Figure 2. The average Al–N distance is 2·09 Å which is significantly shorter than the Al–N distance of 2·18 Å found in bis(trimethylamine)alane.[1] The average Al–O distance in the chelate ring is 1·80 Å and is normal, but the Al–O distance in the oxo-bridge is 1·68 Å. The standard deviation of the Al–O distance is 0·013 Å and that of the Al–N distance is 0·014 Å. The bond angles in the two trigonal bipyramids are Al(1)–O(3)–Al(2), 180°; N(9)–Al(1)–N(10) 163°; N(11)–Al(2)–N(12) 163°; O(5)–Al(1)–O(6) 118°; O(7)–Al(2)–O(8) 118°; O(3)–Al(1)–O(5) 121°; O(3)–Al(1)–O(6) 121°; O(3)–Al(2)–O(7) 119°; and O(3)–Al(2)–O(8) 123°. Their standard deviations are 0·5°. Therefore the three atoms in the oxo-bridge are linear and the nitrogen atoms at the apices of the trigonal bipyramids do not lie on a perpendicular, drawn through the aluminium atom, to the plane of the three oxygen atoms.

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