Dative Metal–Nitrogen π-Bonding in Bis(dimethylamino)beryllium

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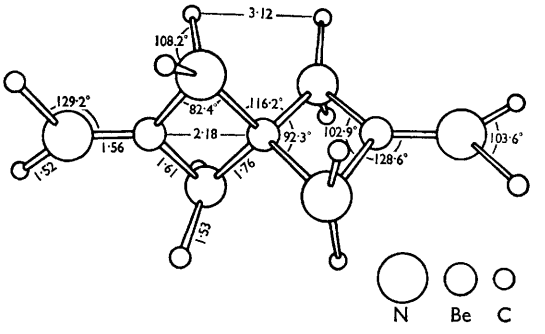
BIS(DIMETHYLAMINO)BERYLLIUM, $Be(NMe_2)_2$, was first prepared by Coates and Glocking,[1] who predicted the structure to be that of a cyclic trimer on the basis of molecular weight data. However, recent n.m.r. work by Fetter and Peters[2] has indicated that in benzene the complex is trimeric but not cyclic. A preliminary report of a crystallographic study and some additional n.m.r. data on bis(dimethylamino)beryllium are reported here.

Crude $Be(NMe_2)_2$,† which is a powdery mixture of orange and white materials, was sublimed at 50° and 10^{-5} mm Hg. The resulting clear, colourless crystals with needle and polyhedral habits were shown by precession photographs (Mo-K_α) to belong in the orthorhombic space group *Fddd*, with $a = 20{\cdot}60 \pm 0{\cdot}03$, $b = 14{\cdot}07 \pm 0{\cdot}02$, $c = 13{\cdot}33 \pm 0{\cdot}02$ Å, $U = 3818$ Å^3, $D_m = 0{\cdot}95$ g. cm.$^{-3}$ ($D_c = 1{\cdot}01$ g. cm.$^{-3}$ for $Z = 8$, $M = 297$). Visual estimation of $hk0$–$hk7$ Weissenberg photographs taken with Cu-K_α radiation gave 226 independent reflections. The structure was solved by a process of trial and error and Fourier syntheses and has been refined to an R value of 13·6%, without hydrogen-atom contributions. The molecule, shown in the Figure, lies at the intersection of three two-fold axes, and possesses D_{2d} symmetry.

A co-ordination number of three is postulated for a number of organoberyllium compounds.[3] However, the only previous verification of this geometry by *X*-ray diffraction techniques was



FIGURE

with Y_2BeO_4,[4] and $Ca_{12}Be_{17}O_{29}$.[5] (Both compounds were formed by quenching from the liquid state.) The fact that bis(dimethylamino)-beryllium does not form an infinite polymer of four co-ordinate beryllium atoms indicates that the differences between entropy and enthalpy factors for the two possible environments are quite small.

† Bis(dimethylamino)beryllium was kindly supplied by Dr. N. R. Fetter of the U.S. Naval Ordnance Laboratory, Corona, California.

In order to understand the nature of the bonding of the bridging and terminal dimethylamino-groups to the beryllium atoms, several factors must be considered. The n.m.r. work by Fetter has shown that there are two methyl resonances (τ 4·28 and τ 4·90 in benzene) in the ratio 1 : 2. Extension of this work to the measurement of the ^{13}C–H spin–spin coupling constants has led to interesting results. For the protons in the terminal dimethylamino-groups, $J(^{13}C–H) = 138$ c./sec. A coupling constant of this magnitude for a methyl group bonded to a three-co-ordinate nitrogen atom is indicative of a degree of π-bonding between the nitrogen and beryllium atoms.[6] π-Bonding is also substantiated by the geometry, since a terminal beryllium atom, the nitrogen atoms to which the beryllium atom is co-ordinated, and the carbon atoms of the methyl groups on the terminal nitrogen atom are coplanar. Essentially unhybridized *p*-orbitals on both the terminal nitrogen and beryllium atoms are then free to form a dative π-bond. In the terminal dimethylamino-group the observed C–N–C bond angle of 102° is much smaller than the expected angle if the nitrogen atom is assumed to exhibit sp^2 hybridization, but this may be accounted for, in part, by classical electrostatic repulsion arguments.[7] The Be(terminal)–N(terminal) bond length of 1·56 Å may be compared with distances of 1·61 Å for Be(terminal)–N(bridge), and 1·76 Å for Be(central)–N(bridge). This trend is in the expected direction if π-bonding effects are considered. However, further refinement is needed before a quantitative comparison of these distances can be made. The N–C bond lengths (1·52 Å) in the terminal dimethylamino-groups are not significantly different from those (1·53 Å) in the bridging dimethylamino-groups.

For the protons in the bridging dimethylamino-groups, the ^{13}C–H spin–spin coupling constant is also *ca.* 138 c./sec. However, this does not necessarily indicate π-bonding, since a coupling constant of this magnitude is normal for a methyl group bonded to a four-co-ordinate nitrogen atom.[6]

Further structural and n.m.r. experiments being undertaken at this time with $[Be(NMe_2)_2]_3$ and with $[Be(OBu^t)_2]_3$ should help to clarify the nature of the bonding in these complexes.

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