π-Bonding in Three-co-ordinate Beryllium Compounds. Structure of Tetra-μ-t-butoxydichlorotriberyllium

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The crystal structure of the title compound shows that the three beryllium atoms are collinear with adjacent beryllium atoms linked by two bridging t-butoxy groups, so that while the central beryllium is four-co-ordinate the terminal beryllium atoms are three-co-ordinate by also bonding to a terminal chlorine atom; the short bonds around the terminal beryllium atom are supportive of some degree of π-bonding and the co-planarity of beryllium and its three attached atoms will tend to maximise any such dative interaction.

Reaction of $LiOBu^t$ with $BeCl_2$ in diethyl ether yields colourless crystals of $(ClBeOBu^t{\cdot}OEt_2)_2$ which lose diethyl ether on gentle warming to form the tetramer $(ClBeOBu^t)_4$. However, on refluxing the diethyl ether adduct under reduced pressure in benzene solution colourless cubic crystals were obtained and these were subsequently shown by *X*-ray analysis to be $Cl_2Be_3(OBu^t)_4$ which differs from the tetramer by one $BeCl_2$ unit.[1]

Crystal data: $Cl_2Be_3(OBu^t)_4$, $C_{16}H_{36}Be_3Cl_2O_4$ orthorhombic, $a = 13.91(2)$, $b = 12.19(2)$, $c = 13.71(2)$ Å, space group *Cmcm*, $Z = 4$, $R = 0.054$ for 720 independent reflections having $I/\sigma(I) > 3.0$.‡

The molecule lies at the intersection of two perpendicular mirror planes in the unit cell. The two chlorine and three beryllium atoms lie along the intersection of these mirror planes and are collinear (Figure 1). Adjacent beryllium atoms are linked by two bridging t-butoxy groups and the two sets are at right angles to one another so that whereas the central beryllium atom is four-co-ordinate and has an approximately tetrahedral distribution of surrounding oxygen atoms, the terminal beryllium atoms are three-co-ordinate. Each terminal beryllium atom and its three attached groups are coplanar so that any π-bonding effects are maximised.

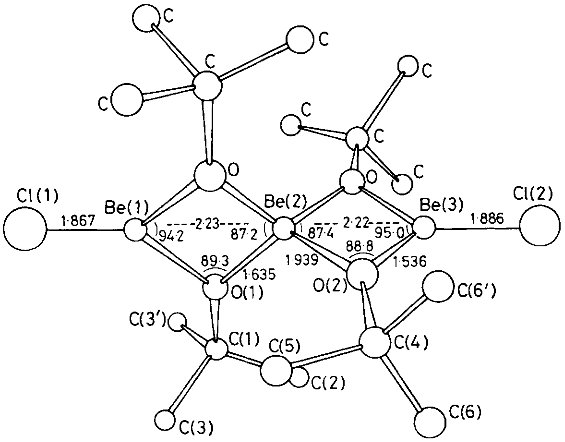

Figure 1. Structure of $Cl_2Be_3(OBu^t)_4$. Selected bond lengths (Å) and angles (°) are shown.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The molecular geometry thus closely resembles that found[2] for $[Be(NMe_2)_2]_3$ but is somewhat different from that of $(BH_4)_2Be_3(OBu^t)_4$ in which all the beryllium atoms are four-co-ordinate.[3]

Evidence for dative π-bonding to boron compounds is well documented (*e.g.* ref. 4 and refs. therein). In contrast, for beryllium discussions of structural features which are consistent with dative π-bonding ($Be \leftharpoons N$) are limited to $[Be(NMe_2)_2]_3$[2] and $[Be(NCBu^t_2)_2]_2$.[5] Unfortunately there are few Be–Cl distances known with which to compare those found herein. The Be–Cl distances, 1.87(1) and 1.89(1) Å, contrast sharply with that found[6] in polymeric beryllium chloride [2.02(3) Å] and the sum of the tetrahedral covalent radii 2.05 Å.[7] They are also significantly shorter than those found in $BeCl_2(OEt_2)_2$ [1.96(1) Å][8] and in $BeCl_2(NCMe)_2$ [1.970(4) and 1.985(4) Å],[9] but longer than in monomeric beryllium chloride [1.75(2) Å],[10] where the linear short bonding arrangement may be due to some degree of π-bonding. Two different Be–O distances are found involving the three- and four-co-ordinate beryllium atoms, their mean values being $Be(sp^2)$–O, 1.54(1) Å and $Be(sp^3)$–O, 1.64(1) Å, the latter value being close to the corresponding distances in $(BH_4)_2Be_3(OBu^t)_4$, [1.644(5) and 1.633(5) Å][3] and the $Be{-}OBu^t$ distance in $(Bu^tOBeBr{\cdot}OEt_2)_2$.[11]

Although some shortening of bond distances is to be expected around beryllium atoms having a lower co-ordination number compared to the four-co-ordinate compounds mentioned above, the extreme shortening of bond distances around the terminal beryllium atoms, together with the coplanarity of Be(1) and Be(3) and the three atoms surrounding each of them which will maximise π-interactions, are suggestive of filled p-orbitals on the terminal chlorine and bridging oxygen atoms interacting with the empty p-orbital on the three-co-ordinate beryllium atoms to form dative π-bonds.†

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† *Added in proof*: Recent M.O. calculations show a π-bond order of *ca.* 0.4 in each of the terminal Be–Cl bonds and *ca.* 0.15 in each of the terminal Be–μO bonds, ref. 12.