Acta Cryst. (1984). C**40**, 605–607

Dimeric *tert*-Butoxyberyllium Bromide–Diethyl Ether Adduct,* $[Be_2Br_2(C_4H_9O)_2(C_4H_{10}O)_2]$, and a Comparison with the Magnesium Analogue

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(*Received* 8 *September* 1983; *accepted* 25 *November* 1983)

Abstract. $M_r = 472{\cdot}3$, monoclinic, $P2_1/n$, $a = 9{\cdot}035\,(5)$, $b = 13{\cdot}180\,(5)$, $c = 9{\cdot}805\,(5)$ Å, $\beta = 96{\cdot}4\,(1)°$, $U = 1160{\cdot}3$ Å^3, $Z = 2$ (dimer units), $D_m = 1{\cdot}35\,(1)$, $D_x = 1{\cdot}35$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 3{\cdot}71$ mm^{-1}, $F(000) = 488$, $T = 293$ K. Final R is 0·0946 for 526 observed photographic data. The structure contains a centrosymmetric Be_2O_2 four-membered ring and each Be becomes four-coordinate by also bonding to a terminal Br atom and forming a coordinate bond to an ether O atom. The structure is thus similar to the Mg analogue but in this case the three metal—O distances are the same within experimental error.

Introduction. Be achieves four-coordination in a number of compounds ranging from species containing a single Be atom to polymers. The latter, including electron-deficient polymers, amply demonstrate this strong tendency towards attainment of maximum coordination (Bell, 1982). Solid $BeCl_2$ consists of a halogen-bridged polymer with Be four-coordinate and Cl two-coordinate (Rundle & Lewis, 1952) and solid Me_2Be has a similar structure with bridging C atoms, although in the latter case the bonding is electron-deficient (Snow & Rundle, 1951). O is a better bridging group to Group II elements than halogen, alkyl or aryl groups such that compounds of the type RBeOR' (Bell, 1982) are associated, the degree of association depending on the nature of R and R' and the presence of donor solvents. Crystal-structure analyses have authenticated bridging O in the cubane structures of $(MeZnOMe)_4$ (Shearer & Spencer, 1980) and $(MeBeOSiMe_3)_4$ (Mootz, Zinnius & Böttcher, 1969) and in the Grignard–ketone intermediate $(BrMgOBu^t.OEt_2)_2$ (Bell, Moseley & Shearer, 1984).

Although the X-ray investigation into $(BrMgOBu^t.OEt_2)_2$ was initially undertaken to provide information about the reaction of Grignard reagents with ketones, the emergence of previously unpredicted structural features provoked further interest in the stereochemistry of this molecule. The preference for trigonal geometry at the O atoms over a pyramidal alternative which would provide one direction free in space to accommodate a lone pair of electrons not used in bonding appears to contrast with general predictions (Gillespie & Nyholm, 1957) that have been made about atoms in this sort of environment. The μ-Bu^{t}O—Mg distances are much shorter than the Et_2O—Mg distance and are consistent with a bond order greater than one and a synergic bonding system can be envisaged which would also require trigonal O atoms. In order to clarify this situation, we have examined the structure of the Be analogue, for which there can be no possibility of d_π–p_π interactions.

Experimental. Compound prepared as described by Andersen, Bell & Coates (1972); D_m by flotation in benzene/bromobenzene; crystal 0·2 × 0·2 × 1·0 mm, sealed in Pyrex capillary tube in atmosphere of dry N_2; unit-cell dimensions from zero-level precession photographs, hkn (n = 0–4) and hnl (n = 0–5) reflections recorded photographically with Zr-filtered Mo radiation, intensities measured using a calibrated scale and corrected for Lorentz and polarization factors but not for absorption; index range $h \pm 9$, k 0/14, l 0/9; structure factors placed on the same scale by means of the common reflections. Br atoms located from the Patterson function and light atoms from successive Fourier syntheses; structure refined by least squares, block-diagonal approximation minimizing $\sum w\Delta^2$ ($\Delta = F_o - F_c$), Br, Be and O atoms refined anisotropically, C isotropically; R converged to 0·0946 for the 526 observed reflections, weighting scheme $w = 1{\cdot}0/(10{\cdot}0 + |F_o| + 0{\cdot}013|F_o|^2 + 0{\cdot}00007|F_o|^3)$; in the final cycle of refinement parameter shifts all $< \frac{1}{3}\sigma$, residual electron density in final $F_o - F_c$ synthesis within −0·4 and 0·6 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). Computer programs were supplied by Professor D. W. J. Cruickshank and Dr J. G. Sime of Glasgow University.

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* Di-μ-*tert*-butoxo-bis[bromo(diethyl ether)beryllium].

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0108-2701/84/040605-03$01.50

Table 1. *Fractional positional parameters* ($\times 10^4$) *and isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}/B(\text{Å}^2)$
Br	2665 (3)	1279 (2)	−432 (3)	5·9 (1)*
Be	1133 (27)	−10 (25)	−428 (37)	4·4 (13)*
O(1)	584 (13)	−236 (11)	1037 (14)	3·2 (6)*
O(2)	1852 (14)	−1008 (11)	−1131 (16)	4·2 (7)*
C(1)	1324 (25)	−551 (20)	2283 (27)	5·0 (5)
C(2)	2820 (48)	−701 (40)	2352 (50)	12·2 (13)
C(3)	1624 (53)	310 (39)	3111 (55)	12·7 (13)
C(4)	484 (45)	−1283 (40)	2957 (46)	11·0 (11)
C(5)	3307 (33)	−879 (25)	−3056 (34)	7·0 (7)
C(6)	3377 (30)	−1122 (26)	−1551 (31)	6·7 (7)
C(7)	911 (28)	−1914 (21)	−1517 (28)	5·4 (6)
C(8)	1356 (44)	−2800 (35)	−726 (43)	10·3 (11)

* B_{eq} values calculated by reference to Willis & Pryor (1975).

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry code: (i) $-x, -y, -z$.

Be—Br	2·19 (3)	O(2)—C(7)	1·49 (3)
Be—O(1)	1·60 (4)	C(1)—C(2)	1·36 (5)
Be—O(1^i)	1·63 (3)	C(1)—C(3)	1·40 (6)
Be—O(2)	1·65 (3)	C(1)—C(4)	1·43 (5)
O(1)—C(1)	1·39 (3)	C(5)—C(6)	1·50 (4)
O(2)—C(6)	1·49 (3)	C(7)—C(8)	1·44 (5)
Br—Be—O(1)	114 (2)	Be(1)—O(2)—C(7)	120 (2)
Br—Be—O(2)	110 (2)	C(6)—O(2)—C(7)	112 (2)
Br—Be—O(1^i)	115 (2)	O(1)—C(1)—C(2)	118 (3)
O(1)—Be—O(2)	114 (2)	O(1)—C(1)—C(3)	108 (3)
O(1)—Be—O(1^i)	89 (2)	O(1)—C(1)—C(4)	112 (3)
O(1^i)—Be—O(2)	114 (2)	C(2)—C(1)—C(3)	88 (3)
Be(1)—O(1)—Be(1^i)	91 (2)	C(2)—C(1)—C(4)	117 (3)
Be(1)—O(1)—C(1)	133 (2)	C(3)—C(1)—C(4)	111 (3)
Be(1^i)—O(1)—C(1)	137 (2)	O(2)—C(6)—C(5)	108 (2)
Be(1)—O(2)—C(6)	128 (2)	O(2)—C(7)—C(8)	113 (3)

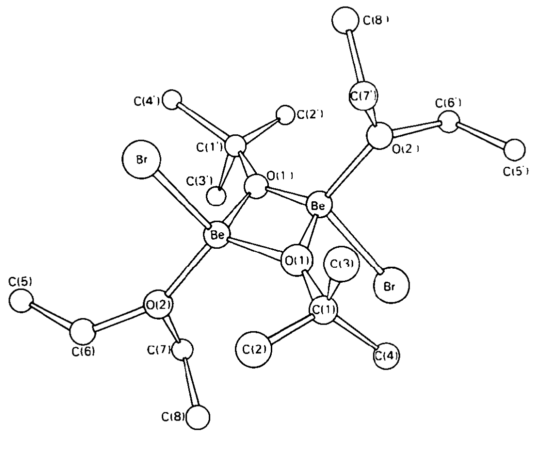

Fig. 1. Structure of ($Bu^tOBeBr.OEt_2$)$_2$.

Discussion. Final atomic parameters are given in Table 1.*

The molecule is a dimer by virtue of a four-membered square Be_2O_2 ring as shown in Fig. 1. The consequences of this are that Be is four-coordinate and adopts a distorted tetrahedral arrangement and the *tert*-butyl O atoms O(1) and O(1^i) are three-coordinate and adopt a trigonal arrangement as do the ether O(2) and O(2^i) attached to Be. The structure is therefore similar to the Mg analogue (Bell *et al.*, 1984) and, in both cases, the *tert*-butoxy O atom acts as a bridging group between two metal atoms due to its enhanced donor capability when attached to an electropositive metal so that the Br atoms and the OEt_2 groups occupy terminal sites.

Bond lengths and angles are in Table 2. The three Be—O distances are the same within experimental error [Be—O(1) 1·60 (4), Be—O(1^i) 1·63 (3), Be—O(2) 1·65 (3) Å], in contrast to the Mg analogue where the metal—ether O distance [2·01 (2) Å] is longer than the metal—ring O distances [1·91 (1), 1·91 (1) Å] (Bell *et al.*, 1984). The mean Be—O bond length [1·63 (3) Å] is in good agreement with values of 1·655 and 1·647 Å found in BeO (Jeffrey, Parry & Mozzi, 1956) and of 1·666 (4) and 1·624 (10) Å in beryllium oxyacetate (Tulinsky & Worthington, 1959). The Br atom completes the four-coordination of Be with a Be—Br bond length of 2·19 (3) Å which is close to the sum (2·17 Å) of the covalent radii (Pauling, 1960).

The ring angles at Be and O are 89 (2) and 91 (2)° respectively so that within experimental error the ring is square. For the metal, this means a distortion in the other bond angles at Be, making them all greater than the tetrahedral value. These distortions are not very large, a maximum angle of 115 (2)° being reached for Br—Be—O(1^i). The values of B for the methyl C atoms in the *tert*-butyl group are very large (~ 12 Å^2) and the difference maps calculated at the completion of the refinement showed that these atoms appear to be involved in large atomic librations. The values of bond lengths and angles obtained are a consequence of these effects. The Be$\cdots$Be^i distance across the ring [2·30 (4) Å] is close to the distance 2·225 Å found in the metal (*International Tables for X-ray Crystallography*, 1962) and is similar to the short Be$\cdots$Be distances found with other three-electron bridging ligands (O'Neill & Wade, 1982). Mean-plane data and non-bonding intramolecular contacts > 4 Å have been deposited.* The crystal packing is shown in Fig. 2.

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* Lists of structure factors, anisotropic thermal parameters, least-squares-planes' data and some intramolecular non-bonding contacts (<4 Å) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39071 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

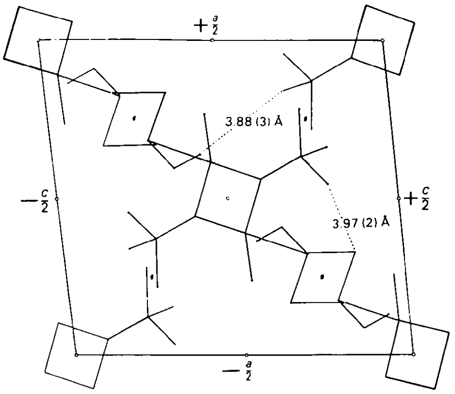

Fig. 2. $(Bu^tOBeBr.OEt_2)_2$–projection on (010).

Comparison of the beryllium and magnesium analogues

Both compounds adopt the same basic conformation with trigonal geometries for all the O atoms, so that the second pair of electrons on the O appears to be sterically unimportant. The existence in the Mg compound of the shorter Mg—O distance in the ring as compared to the Mg—O(ether) length indicated a bonding system involving empty $3d$ orbitals of Mg and doubly occupied $2p$ orbitals of the ring O which would require trigonal O atoms. Two factors mitigate against this as the chief cause of the trigonal geometry of the O atoms. First, a very approximate MO calculation performed on the four ring atoms alone indicated a very small $3d$–$2p$ interaction and, more significantly, the O atoms of the Be compound adopt the same configuration. In the latter case, d_π–p_π interactions are ruled out and in fact all the Be—O distances are equivalent. Thus any extra bonding in the Mg compound is envisaged as a secondary consequence of the relevant atoms finding themselves with suitable geometries. In both structures, but especially in the Be case, the molecular arrangement is extremely compact and it seems likely that steric interference plays a significant part in determining the actual configuration adopted.

The other main differences between the two compounds are those arising from the replacement of Mg by the smaller Be atom. The ring angle at Be, 89 (2)°, is much greater than at Mg, 83·3 (6)°. In consequence, the distortions in the other bond angles away from the tetrahedral value are much less pronounced at Be. However, the *tert*-butoxy O atoms in this compound are placed in a more strained environment, the angle at O being 91 (2)°, than their counterparts in the Mg compound, where the angle at the ring O is 96·7 (6)°. The smaller ring in the Be compound also means that intramolecular non-bonding contacts are shorter and this probably accounts for the more compact arrangement of the Be compound.

The authors thank Professor G. E. Coates for his interest, Dr I. W. Nowell for helpful discussions and the SERC for a research studentship (to JT).

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