The N—Be—N angles in the four-membered Be_2N_2 rings in $[Be(NMe_2)_2]_3$ are 91·2 (2)° for the four-coordinate Be and 101·0 (3)° for the three-coordinate Be atoms (Atwood & Stucky, 1969). In the structure described herein, although Be is four-coordinate, the $N(1)—Be—N(1^i)$ angle lies intermediate [96·9 (4)°] between these two values. The trimethylethylenediamine moiety has bond lengths and angles similar to those found in the hydridozinc analogue (Bell *et al.*, 1980) and the C—C and C—N bond distances are essentially the same in the two compounds and show many features in common. The $Be—Be^i$ non-bonding contact of 2·316 (3) Å is similar to the short Be···Be distances found with other three-electron bridging ligands (O'Neill & Wade, 1982).

There is no evidence of any significant interdimer interactions, the only contacts less than 4 Å being C(2)···C(3) and C(3)···C(5) of 3·816 (10) and 3·815 (10) Å respectively and thus there can be no question of H acting as a bridging group between Be atoms in this compound.

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π-Bonding Around Three-Coordinate Beryllium in Tetra-μ-*tert*-butoxo-dichlorotriberyllium, $[Be_3Cl_2(C_4H_9O)_4]$

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Abstract. $M_r = 390·4$, orthorhombic, *Cmcm*, $a = 13·91\,(2)$, $b = 12·19\,(2)$, $c = 13·71\,(2)$ Å, $U = 2324·7$ Å^3, $Z = 4$, $D_m = 1·12\,(1)$, $D_x = 1·11$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0·7107$ Å, $\mu = 0·304$ mm^{-1}, $F(000) = 840$, $T = 293$ K. Final $R = 0·054$ for 720 observed reflections. The molecule lies at the intersection of two perpendicular mirror planes in the unit cell. The two Cl and three Be atoms lie along the intersection of these mirror planes and are collinear. Adjacent Be atoms are linked by two bridging *tert*-butoxy groups and the two $Be(\mu\text{-}OBu^t)_2Be$ units are at right angles to one another so that the central Be atom is four-coordinate and has an approximately tetrahedral distribution of surrounding O atoms. The terminal Be atoms are trigonal planar and involved in π-bonding to the surrounding O and Cl atoms.

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Introduction. When beryllium chloride reacts with lithium *tert*-butoxide colourless crystals of $(ClBeOBu^t.OEt_2)_2$ form on evaporation of the filtrate after removal of precipitated lithium chloride. On gentle warming the crystals lose ether to form the ether-free compound $(ClBeOBu^t)_4$ which is tetrameric in benzene solution (Andersen, Bell & Coates, 1972). Although $(BrBeOBu^t.OEt_2)_2$ (Bell, Shearer & Twiss, 1984) and $(MeBeOSiMe_3)_4$ (Mootz, Zinnius & Böttcher, 1969) have oxygen as bridging atoms, chlorine is a better bridging group to beryllium than either bromine or methyl. Attempts to obtain crystals for X-ray analysis of the tetramer $(ClBeOBu^t)_4$ resulted in the formation of the compound described herein $[Cl_2Be_3(OBu^t)_4]$ (Andersen *et al.*, 1972), which differs from the tetramer by one $BeCl_2$ unit. A preliminary report of this structure has been published (Bell, Coates, Shearer & Twiss, 1983).

Experimental. Prepared from $(ClBeOBu^t.OEt_2)_2$ on refluxing in benzene with pumping; D_m by flotation in fluorobenzene/pentafluorobenzene; the crystal used was a cube with edge *ca* 0·2 mm sealed in a Pyrex capillary tube under dry N_2; cell dimensions and intensities measured on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation, recording an octant of the sphere of reflection up to $\theta = 30°$, Lorentz and polarization corrections but no absorption corrections; 1841 independent reflections, 720 observed with $I \geq 3\sigma(I)$, index range h 0/18, k 0/16, l 0/19. Non-H atoms located from Patterson function; refinement by least squares using block-diagonal approximation, anisotropic temperature factors for all atoms, H atoms located from a difference map, included with $B_{iso} = 10$ Å^2 but not refined, in final LS cycle all shifts $<0{\cdot}3\,\sigma$, $\sum w(F_o^2 - F_c^2)^2$ minimized, $w = 1{\cdot}0/(20{\cdot}0 + |F_o| + 0{\cdot}005|F_o|^2 + 0{\cdot}000001|F_o|^3)$, $R = 0{\cdot}054$. 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.

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

The molecular geometry (Fig. 1) very closely resembles that found in $[Be(NMe_2)_2]_3$ (Atwood & Stucky, 1969) and in $[(BH_4)_2Be_3(OBu^t)_4]$ where all the Be atoms are four-coordinate with no planarity round the terminal Be atoms, though the *tert*-butoxy O atoms are coplanar with their three bonded atoms (Morosin & Howatson, 1979).

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

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

	x	y	z	B_{eq}(Å^2)
Cl(1)	0	−5 (2)	2500	4·9 (1)
Cl(2)	0	6727 (2)	2500	4·9 (1)
Be(1)	0	1527 (9)	2500	3·4 (5)
Be(2)	0	3357 (9)	2500	2·9 (4)
Be(3)	0	5180 (9)	2500	3·6 (5)
O(1)	0	2387 (3)	1677 (3)	3·3 (2)
O(2)	814 (3)	4329 (3)	2500	3·3 (2)
C(1)	0	2339 (5)	608 (4)	3·9 (3)
C(2)	0	3510 (7)	236 (5)	7·3 (5)
C(3)	902 (5)	1739 (6)	282 (4)	7·3 (4)
C(4)	1861 (5)	4425 (6)	2500	4·2 (3)
C(5)	2282 (5)	3286 (7)	2500	6·5 (5)
C(6)	2155 (4)	5048 (6)	1589 (5)	7·3 (4)

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

Symmetry code: (i) $x, y, \frac{1}{2} - z$; (ii) $-x, y, z$.

Cl(1)–Be(1)	1·87 (1)	O(1)–C(1)	1·47 (1)
Cl(2)–Be(3)	1·89 (1)	O(2)–C(4)	1·46 (1)
O(1)–Be(1)	1·54 (1)	C(1)–C(2)	1·52 (1)
O(2)–Be(3)	1·54 (1)	C(1)–C(3)	1·52 (1)
O(1)–Be(2)	1·64 (1)	C(4)–C(5)	1·51 (1)
O(2)–Be(2)	1·64 (1)	C(4)–C(6)	1·52 (1)
Cl(1)–Be(1)–O(1)	132·9 (4)	Be(2)–O(2)–C(4)	138·3 (4)
Cl(2)–Be(3)–O(2)	132·5 (4)	Be(3)–O(2)–C(4)	133·0 (4)
O(1)–Be(2)–O(2)	121·5 (4)	O(1)–C(1)–C(2)	107·4 (4)
O(1)–Be(2)–O(1^i)	87·2 (5)	O(1)–C(1)–C(3)	108·2 (4)
O(2)–Be(2)–O(2^{ii})	87·4 (5)	C(2)–C(1)–C(3)	110·8 (5)
O(1)–Be(1)–O(1^i)	94·2 (5)	C(3)–C(1)–C(3^{ii})	111·2 (5)
O(2)–Be(3)–O(2^{ii})	95·0 (5)	O(2)–C(4)–C(5)	108·3 (4)
Be(1)–O(1)–Be(2)	89·3 (4)	O(2)–C(4)–C(6)	108·0 (5)
Be(1)–O(1)–C(1)	134·8 (4)	C(5)–C(4)–C(6)	110·9 (5)
Be(2)–O(1)–C(1)	135·9 (4)	C(6)–C(4)–C(6′)	110·7 (5)
Be(2)–O(2)–Be(3)	88·8 (4)		

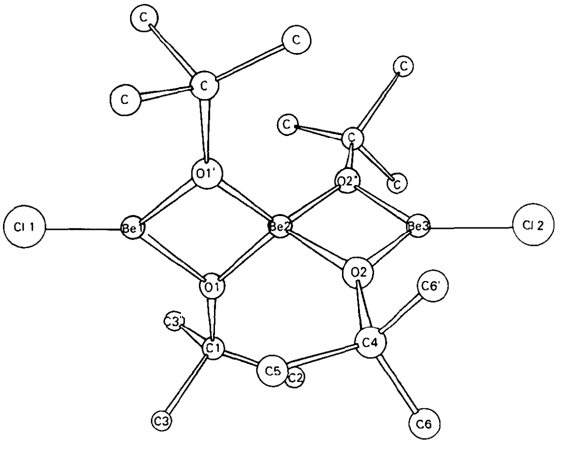

Fig. 1. Structure of $[Cl_2Be_3(OBu^t)_4]$.

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* Lists of structure factors, anisotropic thermal parameters, intramolecular non-bonded distances and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39058 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Bond lengths and angles with e.s.d.'s are listed in Table 2. The Be(1)—Cl(1) and Be(3)—Cl(2) distances of 1·87 (1) and 1·89 (1) Å contrast sharply with that found in solid polymeric $\mathrm{BeCl_2}$ (Rundle & Lewis, 1952) where Be is four coordinate and the Be—Cl distance [2·02 (3) Å] is close to the sum of the tetrahedral covalent radii (2·05 Å) (Pauling, 1960). In $[\mathrm{Cl_2Be_3(OBu^{\mathit{t}})_4}]$, both Be(1) and Be(3) are three-coordinate and can reduce the coordinative unsaturation using empty 2*p* orbitals to form dative π-bonding, resulting in shortening of the bonds around these two atoms.

Structural features which are consistent with dative π-bonding to Be are limited to Be ⇌ N π-bonding (Atwood & Stucky, 1969; Hall, Farmer, Shearer, Sowerby & Wade, 1979). In assessing the importance of any bond shortening it is important to realise that the change from sp^3 to sp^2 hybridization will lead to a reduction in bond length. For C, shortening of the order of 0·04 Å is indicated for the change from $\mathrm{C}(sp^3)$—$\mathrm{C}(sp^2)$ to $\mathrm{C}(sp^2)$—$\mathrm{C}(sp^2)$. In $[\mathrm{Be(NMe_2)_2}]_3$ distances around the four-coordinate Be atom are $\mathrm{Be}(sp^2)$—$\mathrm{N}(sp^3)$ 1·653 (7) Å and $\mathrm{Be}(sp^2)$—$\mathrm{N}(sp^2)$ 1·573 (11) Å (Atwood & Stucky, 1969), and similarly in $[\mathrm{Be(N{=}CBu^{\mathit{t}}_2)_2}]_2$ (Hall *et al.*, 1979) $\mathrm{Be}(sp^2)$—$\mathrm{N}(sp^2)$ are 1·682 (15) and 1·674 (14) Å whereas $\mathrm{Be}(sp^2)$—$\mathrm{N}(sp)$* is 1·502 (13) Å. Thus the short Be—N distances are appropriate for bonds involving atoms of low coordination numbers and a substantial degree of $p{\rightarrow}p$ N ⇌ Be dative π-bonding.

Unfortunately there have been few structural studies of compounds containing Be—Cl bonds for comparison with $[\mathrm{Cl_2Be_3(OBu^{\mathit{t}})_4}]$. However, the Be—Cl distances herein are shorter than in $[\mathrm{BeCl_2(OEt_2)_2}]$ [1·96 (1) Å] (Semenenko, Lobkovskii, Simonov & Shumakov, 1976) and in $[\mathrm{BeCl_2(NCMe)_2}]$ [1·970 (4), 1·985 (4) Å] (Chavant, Daran, Jeannin, Kaufmann & MacCordick, 1975) but longer than in the $\mathrm{BeCl_2}$ monomer [1·75 (2) Å] (Akishin & Spiridonov, 1957) where the linear short bonds may be due to some degree of Be—Cl π-bonding. Likewise $[\eta^5\text{-}\mathrm{C_5H_5BeCl}]$ is linear and although the authors (Drew & Haaland, 1972) believe that Be—Cl π-bonding is minimal as the *p* orbitals on Be are already involved in bonding to the cyclopentadienyl ring, this may not be entirely the case as the Be—Cl distance [1·837 (6) Å] is close to that found herein.

Two different Be—O distances are found involving the three- and four-coordinate Be atoms, their mean values being $\mathrm{Be}(sp^2)$—O 1·54 Å and $\mathrm{Be}(sp^3)$—O 1·64 Å, the latter value being close to the corresponding distances in $[\mathrm{(BH_4)_2Be_3(OBu^{\mathit{t}})_4}]$, 1·644 (5), 1·633 (5) Å (Morosin & Howatson, 1979), and the $\mathrm{Be{-}OBu^{\mathit{t}}}$ distances, 1·60 (4), 1·63 (3) Å, in $(\mathrm{BrBeOBu^{\mathit{t}}.OEt_2})_2$ (Bell, Shearer & Twiss, 1984) in all of which the butoxy O and its three attached atoms are coplanar. Thus the trend is in the expected direction if π-bonding effects are considered and this shortening of bond distances around the terminal Be atoms, together with the planarity of the three atoms surrounding Be(1), Be(3), O(1) and O(2) which will maximize π-interactions, permits filled *p* orbitals on the terminal Cl atoms and on the bridging O atoms to form dative π-bonds with the empty *p* orbitals of the three-coordinate Be atoms. Such π-bonding is supported by recent MO calculations (Snaith, unpublished results).

In $(\mathrm{BrBeOBu^{\mathit{t}}.OEt_2})_2$ the two Be atoms have the same environment and the central $\mathrm{Be_2O_2}$ ring is approximately square (Bell, Shearer & Twiss, 1984). The two such rings in $[\mathrm{Cl_2Be_3(OBu^{\mathit{t}})_4}]$ are not square owing to the differences in coordination and bonding of the constituent Be atoms. The significantly shorter Be—O bonds involving three-coordinate Be as compared to those involving four-coordinate Be result in the angles at Be(2) being smaller than those at Be(1) and Be(3) while those at O(1) and O(2) are the same within experimental error and are intermediate between the angles at Be. The greatest distortions in the ring angles are found at the O atoms and the terminal Be atoms. These atoms are all three-coordinate and could formally be regarded as sp^2-hybridized, the undistorted angles between the three valency lobes being therefore 120°. The angles at Be(2) do not represent distortions quite as large since being four-coordinate this atom would be expected to have a tetrahedral environment.

The C(1)—O(1) and C(4)—O(2) bond lengths of 1·47 (1) and 1·46 (1) Å respectively are longer than the corresponding distances in $(\mathrm{Bu^{\mathit{t}}OBeBr.OEt_2})_2$, 1·39 (3) Å (Bell, Shearer & Twiss, 1984), and in $(\mathrm{Bu^{\mathit{t}}OMgBr.OEt_2})_2$, 1·45 (2) Å (Bell, Moseley & Shearer, 1984). The Be—O—C angles are much greater than 120° but whereas those round O(1) are similar, those at O(2) differ significantly from each other [Be(2)—O(2)—C(4) 138·3 (4), Be(3)—O(2)—C(4) 133·0 (4)°] implying a movement of the C atoms of the *tert*-butoxy groups bridging Be(2) and Be(3) away from the four-coordinate Be.

A list of intramolecular non-bonded distances has been deposited.* No intermolecular contact distance is significantly shorter than the sum of the van der Waals radii.

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* Although formally *sp*-hybrid orbitals are used, the C—N—Be angle is only 160·5 (9)°.

* See deposition footnote.

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Tetrameric Methylzinc Acetoximate,* $[Zn_4(CH_3)_4(C_3H_6NO)_4]$

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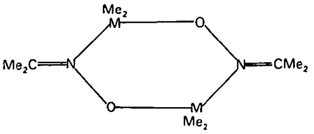
Abstract. $M_r = 610{\cdot}0$, monoclinic, $P2_1/c$, $a = 9{\cdot}258\ (6)$, $b = 13{\cdot}58\ (3)$, $c = 24{\cdot}10\ (5)$ Å, $\beta = 105{\cdot}4\ (2)°$, $U = 2921$ Å^3, $Z = 4$, $D_m = 1{\cdot}40\ (2)$, $D_x = 1{\cdot}39$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 4{\cdot}1$ mm^{-1}, $F(000) = 1248$, $T = 293$ K. Final $R = 0{\cdot}101$ for 3081 observed reflection intensities estimated visually. The molecule exists in the crystal as discrete tetramers in agreement with the solution data. The four Zn atoms lie at the corners of a slightly distorted tetrahedron and above each face is an acetoximate group in which the O atom is attached to two Zn atoms and the N to a third. A cage structure results which has four five-membered rings and two adjacent six-membered rings but no four-membered rings so that the four Zn atoms are in three different environments.

Introduction. The title compound was prepared as described by Coates & Ridley (1966). Though dimeric compounds ($Me_2C{=}NOMMe_2)_2$ (M = Al, Ga, In) have been prepared and are considered to have the cyclic structure (I) (Jennings & Wade, 1967), methylzinc acetoximate is tetrameric in benzene solution (Coates & Ridley, 1966). The present structure analysis was undertaken to establish the degree of association in the solid state and to investigate the manner by which association takes place, whether nitrogen is involved in coordination or whether the cubane structure found for $(MeZnOMe)_4$ (Shearer & Spencer, 1980) results.



(I)

Experimental. Recrystallized from pentane as air-sensitive colourless needles, elongated along **a**, rectangular cross-section, sealed in Pyrex capillaries under dry N_2; unit-cell dimensions from zero-level precession photographs using Mo $K\alpha$ radiation; D_m by flotation in *o*-bromotoluene/bromobenzene; intensity data recorded on layers $0kl$–$8kl$ using Ni-filtered Cu $K\alpha$ radiation by the equi-inclination Weissenberg multiple-film technique. There was a marked deterioration in the shape of the reflections after about five days exposure and subsequently the crystals turned from colourless through yellow to dark brown after an exposure time of about a fortnight. Three crystals of approximate dimensions 0·13 × 0·13 × 0·9 mm (for nets h = 0–2), 0·15 × 0·24 × 0·8 mm (h = 3–6) and 0·21 × 0·21 × 1·0 mm (h = 7–8) used for data collection, intensities estimated visually, Lorentz and polarization corrections applied with spot-length corrections (Phillips, 1956) for upper-level reflections; in view of the uncertainty in recognizing the individual crystal faces, together with

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