

## Dibromotetra- $\mu_3$ -methoxy-di- $\mu_2$ -methoxy-hexakis(tetrahydrofuran-*d*<sub>8</sub>)tetramagnesium

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The crystal structure of the title compound,  $[\text{Mg}_4\text{Br}_2(\text{CH}_3\text{O})_6(\text{C}_4\text{D}_8\text{O})_6]$ , consists of discrete molecules with imposed symmetry  $C_i$ . The tetranuclear compound exhibits two crystallographically independent Mg atoms having distorted octahedral and trigonal-bipyramidal coordination spheres. The Mg atoms are bridged by two  $\mu_3$ -OMe and four  $\mu_2$ -OMe ligands, and their coordination is completed by two terminal Br and six tetrahydrofuran ligands.

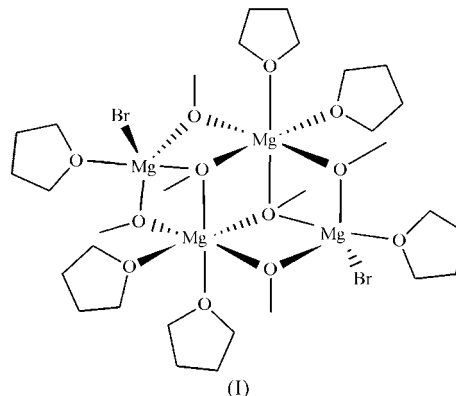
### Comment

Magnesium exhibits a rich coordination chemistry, ranging from mononuclear to polymeric species with linear two- to ten-coordinate Mg atoms. With typical bridging ligands, such as halides, alkoxides, amides and organyls, Mg tends to form cluster and cage compounds (Fenton, 1987; Holloway & Melnik, 1994). We report here the structure of the title methoxy-bridged tetranuclear complex, (I), having  $\mu_2$ - and  $\mu_3$ -methoxy ligands and also terminal Br and tetrahydrofuran (thf) ligands.

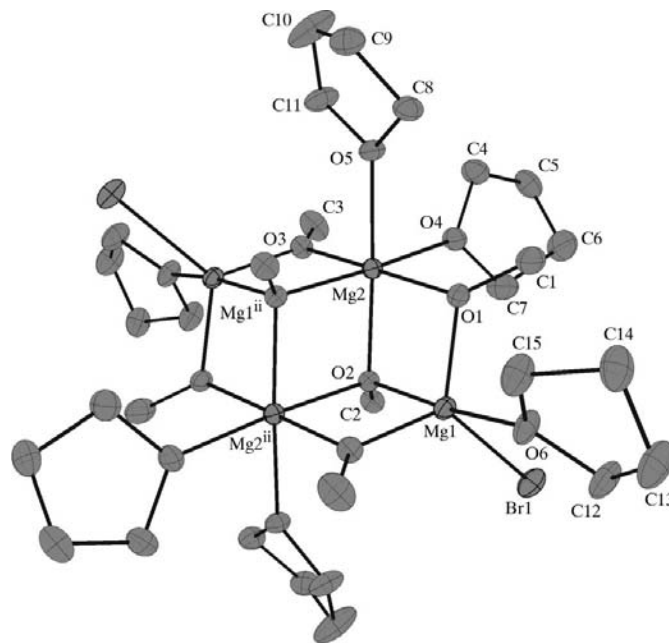
Complex (I) crystallizes as discrete molecules without unusual intermolecular contacts (Fig. 1); the smallest distance between non-H atoms is 3.596 (4) Å between atoms C7 and C15<sup>i</sup> [symmetry code: (i)  $x - 1, y, z$ ]. The molecule lies on a crystallographic inversion centre located at the centre of the  $\text{Mg}2-\text{Mg}2^{\text{ii}}-\text{O}2-\text{O}2^{\text{ii}}$  rhomboid [symmetry code: (ii)  $1 - x, 1 - y, 2 - z$ ].

The two independent Mg atoms exhibit six- (Mg2) or five-coordinate (Mg1). The six-coordinated Mg atoms have a distorted octahedral coordination sphere built up from two terminal thf ligands in mutually *cis* positions, and two  $\mu_2$ - and two  $\mu_3$ -methoxy ligands in mutually *trans* and *cis* positions, respectively. The angles of the coordination octahedron lie in the ranges 78.98 (6)–101.74 (6) or 170.12 (7)–175.86 (8)°. The five-coordinated Mg atoms exhibit a trigonal-bipyramidal

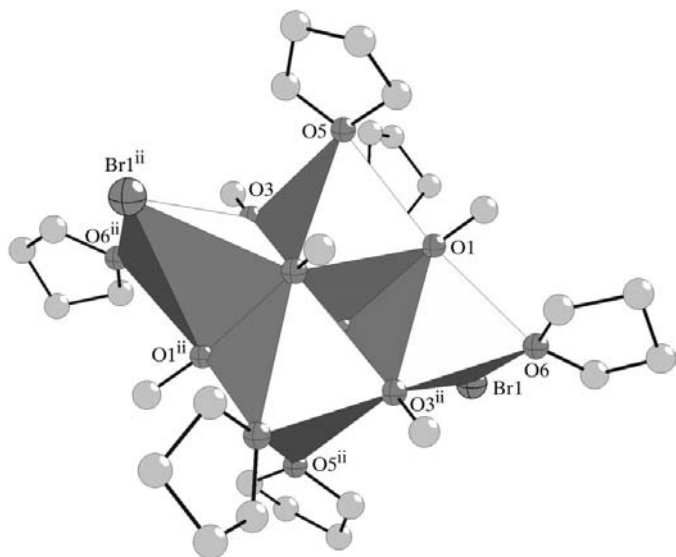
coordination sphere. The apical positions ( $L_{\text{ap}}$ ) are occupied by a  $\mu_3$ -OMe ligand (O2) and a terminal thf ligand (O6); the



$\text{O}2-\text{Mg}1-\text{O}6$  angle is 170.24 (7)°. The equatorial coordination sites ( $L_{\text{eq}}$ ) are occupied by a Br ligand and two  $\mu_2$ -OMe ligands. The angles between the equatorial ligands range from 114.70 (8) to 125.35 (6)° (sum of angles 359.82°). The  $L_{\text{eq}}-\text{Mg}1-L_{\text{ap}}$  angles lie between 82.97 (6) and 98.37 (5)°. The  $\text{Mg}-\mu\text{-OMe}$  distances are in the order  $\text{Mg}1/2-\mu_3\text{-OMe}$  [2.092 (2)–2.117 (2) Å] >  $\text{Mg}2-\mu_2\text{-OMe}$  [1.999 (2) and 2.015 (2) Å] >  $\text{Mg}1-\mu_2\text{-OMe}$  [1.950 (2) and 1.968 (2) Å], so that bonds to the  $\mu_3$ -methoxy ligands are longer than to the  $\mu_2$ -bound ligands. Furthermore, the five-coordinate Mg atoms bind the  $\mu_2$  ligands more tightly than the six-coordinate Mg atoms. On the other hand, the  $\text{Mg}-\text{O}$  bonds to  $\mu_3$ -OMe and to thf ligands do not exhibit statistically significant ( $3\sigma$  criterion) length dependence on coordination number (5 versus 6).



**Figure 1**  
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H and D atoms have been omitted for clarity. Only one of the two disordered positions of atom C10 is displayed. [Symmetry code: (ii)  $1 - x, 1 - y, 2 - z$ .]



**Figure 2**  
A drawing of the edge-sharing octahedra and trigonal bipyramids in the structure of (I). [Symmetry code: (ii)  $1 - x, 1 - y, 2 - z$ ]

As shown in Fig. 2, the tetranuclear complex (I) can be (formally) viewed as being built up from two octahedra and two trigonal bipyramids that are edge-shared. Thus, a tetranuclear cluster is formed with a core of two face-linked open cuboidal building blocks having the composition  $[\text{Mg}_4(\mu_2\text{-OME})_4(\mu_3\text{-OME})_2]^{2+}$ . Due to the crystallographically imposed inversion symmetry, the four Mg atoms define an exact plane. An analogous structural motif has also been found in other Mg clusters having  $[\text{Mg}_4(\mu_2\text{-X})_4(\mu_3\text{-X})_2]^{2+}$  cores with Cl bridges ( $X = \text{Cl}$ ) (Toney & Stucky, 1971; Casellato & Ossola, 1994) or with bridging deprotonated ether-alcohol ligands, such as 2-(hydroxymethyl)tetrahydrofuran, 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran (Sobota *et al.*, 1996; Sobota, Utoko, Sztajnowska *et al.*, 2000; Sobota, Utoko, Ejfler & Jerzykiewicz, 2000), and 1-methoxypropan-2-ol (Albaric *et al.*, 1997). All these structures exhibit crystallographically imposed inversion symmetry.

## Experimental

Dissolution of  $[\text{MgMeBr}(\text{diglyme})]$  (prepared by addition of diglyme to a concentrated solution of  $\text{MgMeBr}$  in diethyl ether) in tetrahydrofuran- $d_8$  resulted in a clear solution. Crystals of (I) appeared within several weeks as a result of slow decomposition of this solution at 233 K.

### Crystal data

$[\text{Mg}_4\text{Br}_2(\text{CH}_3\text{O})_6(\text{C}_4\text{D}_8\text{O})_6]$   
 $M_r = 924.18$   
 Monoclinic,  $P2_1/c$   
 $a = 8.4836$  (4) Å  
 $b = 18.9094$  (9) Å  
 $c = 12.8907$  (6) Å  
 $\beta = 97.4570$  (10)°  
 $V = 2050.43$  (17) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.497$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8574 reflections  
 $\theta = 2.4\text{--}28.3^\circ$   
 $\mu = 2.09$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Block, colourless  
 $0.4 \times 0.3 \times 0.2$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)  
 $T_{\text{min}} = 0.476, T_{\text{max}} = 0.658$   
 17 714 measured reflections  
 5081 independent reflections

4061 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$   
 $\theta_{\text{max}} = 28.3^\circ$   
 $h = -11 \rightarrow 11$   
 $k = 0 \rightarrow 25$   
 $l = 0 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.099$   
 $S = 1.03$   
 5081 reflections  
 230 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 1.3532P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.042$   
 $\Delta\rho_{\text{max}} = 0.92 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$

All H-atom positions were refined using a riding model starting from calculated positions. The D atoms of the tetrahydrofuran molecules were refined as H atoms. The formula weight and related parameters have been recalculated using values appropriate for deuterium. Atom C10 is disordered and was refined with a split occupancy of 0.34 (2):0.66 (2)

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1633). Services for accessing these data are described at the back of the journal.

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