

The low-temperature structure of diethyl ether magnesium oxybromide

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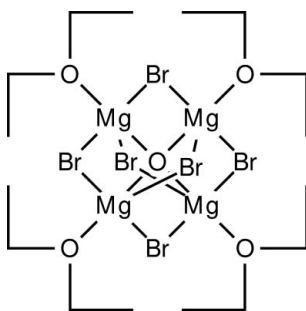
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.013$ Å; R factor = 0.026; wR factor = 0.067; data-to-parameter ratio = 20.3.

The crystal structure of the title compound, hexa- μ_2 -bromido- μ_4 -oxido-tetrakis[(diethyl ether)magnesium], $[\text{Mg}_4\text{Br}_6\text{O}(\text{C}_4\text{H}_{10}\text{O})_4]$, determined from data measured at 173 K, differs from the previously known structure of diethyl ether magnesium oxybromide, which was determined from room-temperature data [Stucky & Rundle (1964). *J. Am. Chem. Soc.* **86**, 4821–4825]. The title compound crystallizes in the tetragonal space group $I\bar{4}$, whereas the previously known structure crystallizes in a different tetragonal space group, namely $P\bar{4}2_1c$. Both molecules have crystallographic $\bar{4}$ symmetry and show almost identical geometric parameters for the Mg, Br and O atoms. The crystal of the title compound turned out to be a merohedral twin emulating a structure with apparent Laue symmetry $4/mmm$, whereas the correct Laue group is just $4/m$. The fractional contribution of the minor twin component converged to 0.462 (1).

Related literature

For Mg–Br complexes, see: Lerner (2005); Lerner *et al.* (2003); Metzler *et al.* (1994). For a polymorph of the title compound, see: Stucky & Rundle (1964). For the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$[\text{Mg}_4\text{Br}_6\text{O}(\text{C}_4\text{H}_{10}\text{O})_4]$
 $M_r = 889.18$
 Tetragonal, $I\bar{4}$
 $a = 10.4630$ (13) Å
 $c = 15.276$ (2) Å
 $V = 1672.3$ (4) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 7.30$ mm⁻¹
 $T = 173$ K
 $0.25 \times 0.22 \times 0.18$ mm

Data collection

Stoe IPDS II two-circle diffractometer
 Absorption correction: multi-scan [*MULABS* (Spek, 2009; Blessing, 1995)]
 $T_{\min} = 0.169$, $T_{\max} = 0.269$

3746 measured reflections
 1479 independent reflections
 1455 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.067$
 $S = 1.08$
 1479 reflections
 73 parameters
 H-atom parameters constrained

$\Delta\rho_{\max} = 0.62$ e Å⁻³
 $\Delta\rho_{\min} = -0.56$ e Å⁻³
 Absolute structure: Flack (1983), 689 Friedel pairs
 Flack parameter: -0.02 (2)

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2385).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Lerner, H.-W. (2005). *Coord. Chem. Rev.* **249**, 781–798.
 Lerner, H.-W., Scholz, S., Bolte, M., Wiberg, N., Nöth, H. & Krossing, I. (2003). *Eur. J. Inorg. Chem.* pp. 666–670.
 Metzler, N., Nöth, H., Schmidt, M. & Treitl, A. (1994). *Z. Naturforsch. Teil B*, **49**, 1448–1451.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
 Stucky, G. & Rundle, R. E. (1964). *J. Am. Chem. Soc.* **86**, 4821–4825.

supplementary materials

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Comment

The solid-state structures of Mg–Br compounds feature coordination numbers of the Mg center from four as in [MgBr(Si^{*t*}Bu₃)(THF)]₂ (Lerner *et al.*, 2003; Lerner, 2005) to six as in [MgBr₂(THF)₄] (Metzler *et al.*, 1994). Most of the Mg–Br compounds possess an octahedral coordination sphere which surrounds the Mg cation whereas only a few compounds are found in the Cambridge Structural Database (Allen, 2002) with five-coordinated Mg centers as found in the solid-state structure of the title compound. We report here the X-ray crystal structure analysis of [(MgOEt₂)₄Br₆O], which could be isolated from a solution of C₆F₅MgBr in Et₂O.

Data for the crystal structure of the title compound were collected at 173 K. It crystallizes in the tetragonal space group $I\bar{4}$ with crystallographic $\bar{4}$ symmetry. The previously known polymorph (Stucky & Rundle, 1964) for which data were collected at room temperature crystallizes in the space group $P\bar{4}2_1c$ and has crystallographic $\bar{4}$ symmetry, too. However, in the latter structure there is severe disorder of the C atoms, whereas in the title compound, no disorder was found. The geometric parameters involving Mg, Br and O atoms agree well in both structures.

Since the structures show striking similarities and were measured at different temperatures, a phase transition between them cannot be excluded.

Experimental

To a suspension of Mg turnings (0.5 g, 20.2 mmol) in 25 ml Et₂O, 2.3 ml C₆F₅Br is added dropwise. The reaction starts when 0.3 ml of C₆F₅Br have been added. The rest of C₆F₅Br is added dropwise at such a rate that the reaction mixture remains at its boiling point and refluxing is continued for 1 h until the magnesium turnings have dissolved completely. During the storing of this solution for 3 weeks, colorless crystals of the title compound were grown at room temperature.

Refinement

H atoms could be located in a difference Fourier map, but they were refined using a riding model with isotropic displacement parameters $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C}_{\text{methylene}})$ and C—H = 0.99 Å or $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ and C—H = 0.98 Å. The crystal turned out to be a merohedral twin emulating a structure with Laue symmetry $4/mmm$. The twin law (0 1 0/1 0 0/0 0 1) is a twofold rotation about the diagonal between the *a* and *b* axis and the fractional contribution of the minor twin component refined to 0.462 (1).

Figures

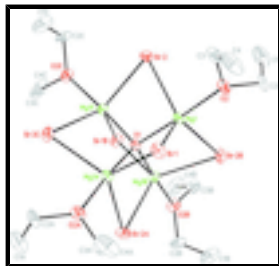


Fig. 1. Perspective view of the title compound with displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity. Symmetry operators for generating equivalent atoms: (A): $1 - x, -y, z$; (B): $1/2 + y, 1/2 - x, 1/2 - z$; (C): $1/2 - y, -1/2 + x, 1/2 - z$.

hexa- μ_2 -bromido- μ_4 -oxido-tetrakis[(diethyl ether)magnesium]

Crystal data

$[\text{Mg}_4\text{Br}_6\text{O}(\text{C}_4\text{H}_{10}\text{O})_4]$

$M_r = 889.18$

Tetragonal, $I\bar{4}$

Hall symbol: I -4

$a = 10.4630$ (13) Å

$c = 15.276$ (2) Å

$V = 1672.3$ (4) Å³

$Z = 2$

$F(000) = 868$

$D_x = 1.766$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3746 reflections

$\theta = 3.8$ – 25.6°

$\mu = 7.30$ mm⁻¹

$T = 173$ K

Block, colourless

$0.25 \times 0.22 \times 0.18$ mm

Data collection

Stoe IPDS II two-circle diffractometer

Radiation source: fine-focus sealed tube graphite

ω scans

Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)

$T_{\min} = 0.169$, $T_{\max} = 0.269$

3746 measured reflections

1479 independent reflections

1455 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 25.3^\circ$, $\theta_{\min} = 3.8^\circ$

$h = -12 \rightarrow 12$

$k = -8 \rightarrow 12$

$l = -13 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.067$

$S = 1.08$

1479 reflections

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.284P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.62$ e Å⁻³

$\Delta\rho_{\min} = -0.56$ e Å⁻³

73 parameters
 0 restraints
 0 constraints
 Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map

Extinction correction: *SHELXL97* (Sheldrick, 2008),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0036 (4)
 Absolute structure: Flack (1983), with 689 Friedel pairs
 Flack parameter: -0.02 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Mg1	0.40713 (19)	0.12350 (19)	0.32357 (13)	0.0135 (5)
Br1	0.5000	0.0000	0.45892 (4)	0.01815 (19)
Br2	0.19607 (5)	0.04477 (5)	0.24533 (6)	0.02114 (18)
O1	0.5000	0.0000	0.2500	0.0120 (13)
C1	0.2012 (10)	0.4180 (8)	0.3236 (7)	0.044 (2)
H1A	0.1953	0.5113	0.3196	0.065*
H1B	0.1161	0.3823	0.3348	0.065*
H1C	0.2345	0.3836	0.2685	0.065*
C2	0.2906 (8)	0.3818 (7)	0.3982 (6)	0.0286 (17)
H2A	0.3759	0.4195	0.3875	0.034*
H2B	0.2573	0.4174	0.4538	0.034*
O2	0.3026 (5)	0.2433 (5)	0.4064 (3)	0.0210 (10)
C3	0.2032 (8)	0.1864 (7)	0.4613 (5)	0.0289 (16)
H3A	0.1932	0.0953	0.4453	0.035*
H3B	0.1210	0.2299	0.4495	0.035*
C4	0.2326 (9)	0.1958 (10)	0.5579 (5)	0.040 (2)
H4A	0.1629	0.1570	0.5915	0.061*
H4B	0.2413	0.2859	0.5744	0.061*
H4C	0.3126	0.1507	0.5704	0.061*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0173 (10)	0.0158 (10)	0.0075 (9)	0.0031 (8)	0.0010 (8)	-0.0015 (8)
Br1	0.0265 (7)	0.0226 (6)	0.0054 (3)	0.0057 (6)	0.000	0.000
Br2	0.0149 (3)	0.0285 (3)	0.0200 (3)	0.0026 (2)	-0.0018 (4)	-0.0064 (4)
O1	0.0150 (18)	0.0150 (18)	0.006 (3)	0.000	0.000	0.000
C1	0.056 (5)	0.035 (4)	0.040 (5)	0.020 (4)	-0.001 (5)	0.002 (4)
C2	0.038 (4)	0.015 (3)	0.032 (4)	0.010 (3)	0.004 (3)	-0.008 (3)
O2	0.024 (2)	0.023 (2)	0.015 (2)	0.005 (2)	0.008 (2)	-0.0037 (19)
C3	0.029 (4)	0.027 (4)	0.031 (4)	0.009 (3)	0.013 (3)	0.001 (4)
C4	0.051 (6)	0.056 (6)	0.014 (4)	0.027 (5)	0.009 (3)	-0.004 (4)

Geometric parameters (\AA , $^\circ$)

Mg1—O1	1.969 (2)	C1—H1A	0.9800
Mg1—O2	2.090 (5)	C1—H1B	0.9800

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Mg1—Br2 ⁱ	2.597 (2)	C1—H1C	0.9800
Mg1—Br1	2.625 (2)	C2—O2	1.460 (8)
Mg1—Br2	2.643 (2)	C2—H2A	0.9900
Mg1—Mg1 ⁱ	3.206 (3)	C2—H2B	0.9900
Mg1—Mg1 ⁱⁱ	3.206 (3)	O2—C3	1.463 (9)
Mg1—Mg1 ⁱⁱⁱ	3.233 (4)	C3—C4	1.510 (11)
Br1—Mg1 ⁱⁱⁱ	2.625 (2)	C3—H3A	0.9900
Br2—Mg1 ⁱⁱ	2.597 (2)	C3—H3B	0.9900
O1—Mg1 ⁱⁱⁱ	1.9689 (19)	C4—H4A	0.9800
O1—Mg1 ⁱ	1.969 (2)	C4—H4B	0.9800
O1—Mg1 ⁱⁱ	1.969 (2)	C4—H4C	0.9800
C1—C2	1.523 (12)		
O1—Mg1—O2	175.84 (18)	Mg1—O1—Mg1 ⁱ	109.01 (6)
O1—Mg1—Br2 ⁱ	88.40 (7)	Mg1 ⁱⁱⁱ —O1—Mg1 ⁱⁱ	109.01 (6)
O2—Mg1—Br2 ⁱ	95.71 (15)	Mg1—O1—Mg1 ⁱⁱ	109.01 (6)
O1—Mg1—Br1	86.78 (7)	Mg1 ⁱ —O1—Mg1 ⁱⁱ	110.39 (12)
O2—Mg1—Br1	90.70 (16)	C2—C1—H1A	109.5
Br2 ⁱ —Mg1—Br1	118.15 (8)	C2—C1—H1B	109.5
O1—Mg1—Br2	87.12 (7)	H1A—C1—H1B	109.5
O2—Mg1—Br2	91.33 (16)	C2—C1—H1C	109.5
Br2 ⁱ —Mg1—Br2	120.44 (8)	H1A—C1—H1C	109.5
Br1—Mg1—Br2	120.81 (8)	H1B—C1—H1C	109.5
O1—Mg1—Mg1 ⁱ	35.49 (3)	O2—C2—C1	111.3 (6)
O2—Mg1—Mg1 ⁱ	148.63 (17)	O2—C2—H2A	109.4
Br2 ⁱ —Mg1—Mg1 ⁱ	52.92 (7)	C1—C2—H2A	109.4
Br1—Mg1—Mg1 ⁱ	103.98 (7)	O2—C2—H2B	109.4
Br2—Mg1—Mg1 ⁱ	103.99 (9)	C1—C2—H2B	109.4
O1—Mg1—Mg1 ⁱⁱ	35.49 (3)	H2A—C2—H2B	108.0
O2—Mg1—Mg1 ⁱⁱ	142.70 (17)	C2—O2—C3	113.0 (6)
Br2 ⁱ —Mg1—Mg1 ⁱⁱ	106.54 (9)	C2—O2—Mg1	126.1 (5)
Br1—Mg1—Mg1 ⁱⁱ	103.98 (7)	C3—O2—Mg1	118.4 (4)
Br2—Mg1—Mg1 ⁱⁱ	51.63 (7)	O2—C3—C4	112.9 (7)
Mg1 ⁱ —Mg1—Mg1 ⁱⁱ	60.57 (7)	O2—C3—H3A	109.0
O1—Mg1—Mg1 ⁱⁱⁱ	34.80 (6)	C4—C3—H3A	109.0
O2—Mg1—Mg1 ⁱⁱⁱ	142.56 (16)	O2—C3—H3B	109.0
Br2 ⁱ —Mg1—Mg1 ⁱⁱⁱ	104.34 (9)	C4—C3—H3B	109.0
Br1—Mg1—Mg1 ⁱⁱⁱ	51.98 (4)	H3A—C3—H3B	107.8
Br2—Mg1—Mg1 ⁱⁱⁱ	104.66 (9)	C3—C4—H4A	109.5
Mg1 ⁱ —Mg1—Mg1 ⁱⁱⁱ	59.72 (4)	C3—C4—H4B	109.5
Mg1 ⁱⁱ —Mg1—Mg1 ⁱⁱⁱ	59.72 (4)	H4A—C4—H4B	109.5
Mg1 ⁱⁱⁱ —Br1—Mg1	76.05 (9)	C3—C4—H4C	109.5
Mg1 ⁱⁱ —Br2—Mg1	75.45 (9)	H4A—C4—H4C	109.5

Mg1 ⁱⁱⁱ —O1—Mg1	110.39 (12)	H4B—C4—H4C	109.5
Mg1 ⁱⁱⁱ —O1—Mg1 ⁱ	109.01 (6)		
O1—Mg1—Br1—Mg1 ⁱⁱⁱ	0.0	Br2 ⁱ —Mg1—O1—Mg1 ⁱⁱ	-121.97 (10)
O2—Mg1—Br1—Mg1 ⁱⁱⁱ	176.68 (18)	Br1—Mg1—O1—Mg1 ⁱⁱ	119.72 (9)
Br2 ⁱ —Mg1—Br1—Mg1 ⁱⁱⁱ	-86.46 (9)	Br2—Mg1—O1—Mg1 ⁱⁱ	-1.38 (7)
Br2—Mg1—Br1—Mg1 ⁱⁱⁱ	84.71 (9)	Mg1 ⁱ —Mg1—O1—Mg1 ⁱⁱ	-120.57 (8)
Mg1 ⁱ —Mg1—Br1—Mg1 ⁱⁱⁱ	-31.31 (7)	Mg1 ⁱⁱⁱ —Mg1—O1—Mg1 ⁱⁱ	119.72 (9)
Mg1 ⁱⁱ —Mg1—Br1—Mg1 ⁱⁱⁱ	31.31 (7)	C1—C2—O2—C3	-86.8 (8)
O1—Mg1—Br2—Mg1 ⁱⁱ	1.02 (5)	C1—C2—O2—Mg1	74.9 (8)
O2—Mg1—Br2—Mg1 ⁱⁱ	-175.11 (18)	Br2 ⁱ —Mg1—O2—C2	17.5 (6)
Br2 ⁱ —Mg1—Br2—Mg1 ⁱⁱ	87.47 (9)	Br1—Mg1—O2—C2	135.9 (6)
Br1—Mg1—Br2—Mg1 ⁱⁱ	-83.50 (9)	Br2—Mg1—O2—C2	-103.3 (6)
Mg1 ⁱ —Mg1—Br2—Mg1 ⁱⁱ	32.52 (7)	Mg1 ⁱ —Mg1—O2—C2	16.9 (8)
Mg1 ⁱⁱⁱ —Mg1—Br2—Mg1 ⁱⁱ	-29.32 (7)	Mg1 ⁱⁱ —Mg1—O2—C2	-109.6 (6)
Br2 ⁱ —Mg1—O1—Mg1 ⁱⁱⁱ	118.31 (8)	Mg1 ⁱⁱⁱ —Mg1—O2—C2	140.2 (5)
Br1—Mg1—O1—Mg1 ⁱⁱⁱ	0.0	Br2 ⁱ —Mg1—O2—C3	178.3 (5)
Br2—Mg1—O1—Mg1 ⁱⁱⁱ	-121.10 (8)	Br1—Mg1—O2—C3	-63.3 (5)
Mg1 ⁱ —Mg1—O1—Mg1 ⁱⁱⁱ	119.72 (9)	Br2—Mg1—O2—C3	57.5 (5)
Mg1 ⁱⁱ —Mg1—O1—Mg1 ⁱⁱⁱ	-119.72 (9)	Mg1 ⁱ —Mg1—O2—C3	177.7 (4)
Br2 ⁱ —Mg1—O1—Mg1 ⁱ	-1.40 (7)	Mg1 ⁱⁱ —Mg1—O2—C3	51.2 (6)
Br1—Mg1—O1—Mg1 ⁱ	-119.72 (4)	Mg1 ⁱⁱⁱ —Mg1—O2—C3	-59.0 (6)
Br2—Mg1—O1—Mg1 ⁱ	119.19 (10)	C2—O2—C3—C4	-82.1 (8)
Mg1 ⁱⁱ —Mg1—O1—Mg1 ⁱ	120.57 (8)	Mg1—O2—C3—C4	114.7 (6)
Mg1 ⁱⁱⁱ —Mg1—O1—Mg1 ⁱ	-119.72 (9)		

Symmetry codes: (i) $y+1/2, -x+1/2, -z+1/2$; (ii) $-y+1/2, x-1/2, -z+1/2$; (iii) $-x+1, -y, z$.

Fig. 1

