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The low-temperature structure of diethyl ether magnesium oxybromide

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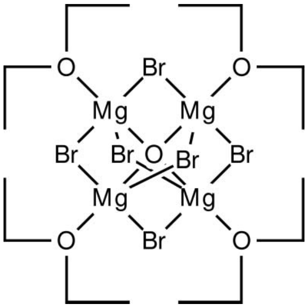
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.013 Å; R factor = 0.026; wR factor = 0.067; data-to-parameter ratio = 20.3.

The crystal structure of the title compound, hexa-μ_2-bromido-μ_4-oxido-tetrakis[(diethyl ether)magnesium], [$Mg_4Br_6O(C_4H_{10}O)_4$], 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 $I\overline{4}$, whereas the previously known structure crystallizes in a different tetragonal space group, namely $P\overline{4}2_1c$. Both molecules have crystallographic $\overline{4}$ 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

[$Mg_4Br_6O(C_4H_{10}O)_4$]
M_r = 889.18
Tetragonal, $I\overline{4}$
a = 10.4630 (13) Å
c = 15.276 (2) Å
V = 1672.3 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 7.30 mm^{-1}
T = 173 K
0.25 × 0.22 × 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_{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).

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supporting information

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The low-temperature structure of diethyl ether magnesium oxybromide

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S1. Comment

The solid-state structures of Mg–Br compounds feature coordination numbers of the Mg center from four as in $[\mathrm{MgBr(Si^{t}Bu_3)(THF)}]_2$ (Lerner *et al.*, 2003; Lerner, 2005) to six as in $[\mathrm{MgBr_2(THF)_4}]$ (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 $[(\mathrm{MgOEt_2})_4\mathrm{Br_6O}]$, which could be isolated from a solution of $\mathrm{C_6F_5MgBr}$ in $\mathrm{Et_2O}$.

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.

S2. Experimental

To a suspension of Mg turnings (0.5 g, 20.2 mmol) in 25 ml $\mathrm{Et_2O}$, 2.3 ml $\mathrm{C_6F_5Br}$ is added dropwise. The reaction starts when 0.3 ml of $\mathrm{C_6F_5Br}$ have been added. The rest of $\mathrm{C_6F_5Br}$ 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.

S3. Refinement

H atoms could be located in a difference Fourier map, but they were refined using a riding model with isotropic displacement parameters $U_{\mathrm{iso}}(\mathrm{H})$ set to $1.2U_{\mathrm{eq}}(\mathrm{C_{methylene}})$ and C—H = 0.99 Å or $U_{\mathrm{iso}}(\mathrm{H})$ set to $1.5U_{\mathrm{eq}}(\mathrm{C_{methyl}})$ 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).

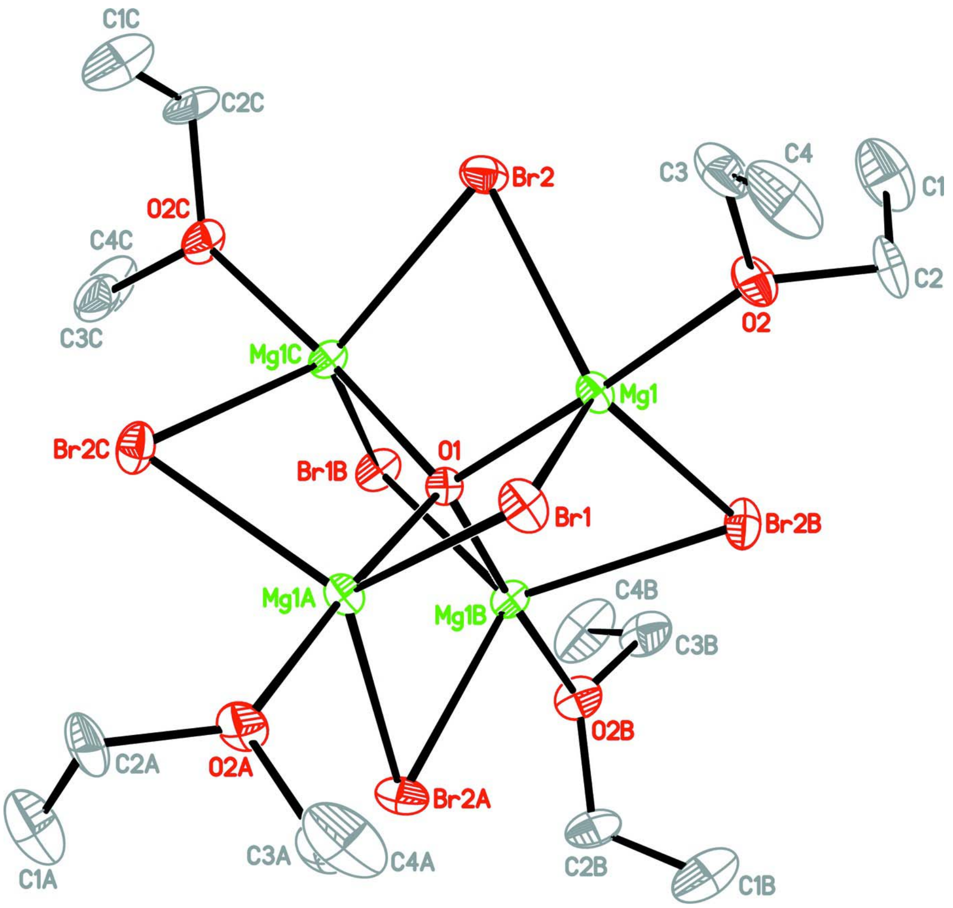

Figure 1

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

$[Mg_4Br_6O(C_4H_{10}O)_4]$
$M_r = 889.18$
Tetragonal, $I\bar{4}$
Hall symbol: I -4
$a = 10.4630$ (13) Å
$c = 15.276$ (2) Å
$V = 1672.3$ (4) Å^3
$Z = 2$
$F(000) = 868$
$D_x = 1.766$ 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 × 0.22 × 0.18 mm

Data collection

Stoe IPDS II two-circle diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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 $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\rm max} = 25.3°$, $\theta_{\rm min} = 3.8°$
$h = -12 \rightarrow 12$
$k = -8 \rightarrow 12$
$l = -13 \rightarrow 18$

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
73 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.284P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.62$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.56$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0036 (4)
Absolute structure: Flack (1983), with 689 Friedel pairs
Absolute structure parameter: −0.02 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
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 (Å²)

	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 (Å, º)

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