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Redetermination of di- μ -hydrido-hexahydridotetrakis(tetrahydrofuran)-dialuminium(III)magnesium(II)

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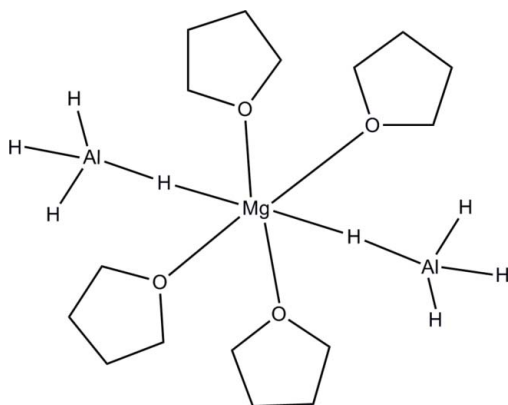
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.041; wR factor = 0.119; data-to-parameter ratio = 22.0.

The structure of the title compound, $[\text{Mg}(\text{AlH}_4)_2(\text{C}_4\text{H}_8\text{O})_4]$, has been redetermined at 150 K. The Mg^{II} ion is hexacoordinated to four tetrahydrofuran (THF) ligands, and two AlH_4^- anions through bridging H atoms. The Al—H distances are more precise compared to those previously determined [Nöth *et al.* (1995). *Chem. Ber.* **128**, 999–1006; Fichtner & Fuhr (2002). *J. Alloys Compd.* **345**, 386–396]. The molecule has twofold rotation symmetry.

Related literature

For the synthesis of $\text{Mg}(\text{AlH}_4)_2 \cdot 4\text{THF}$, see: Ashby *et al.* (1970); Shen & Che (1991); Nöth *et al.* (1995). For the synthesis of $\text{AlH}_4\text{MgBH}_4$, see: Ashby & Goel (1977). For previous determinations of the crystal structure of $\text{Mg}(\text{AlH}_4)_2 \cdot 4\text{THF}$, see: Noth *et al.* (1995); Fichtner & Fuhr (2002). For the thermal decomposition properties of $\text{Mg}(\text{AlH}_4)_2 \cdot 4\text{THF}$, see: Dilts & Ashby (1972). For other alanate structures, see: Sklar & Post (1967); Lauher *et al.* (1979); Fichtner & Fuhr (2002); Fichtner *et al.* (2004).



Experimental

Crystal data

$[\text{Al}_2\text{MgH}_8(\text{C}_4\text{H}_8\text{O})_4]$	$V = 2341.6$ (8) Å ³
$M_r = 374.75$	$Z = 4$
Orthorhombic, $Pcnb$	Mo $K\alpha$ radiation
$a = 10.161$ (2) Å	$\mu = 0.16$ mm ⁻¹
$b = 14.027$ (3) Å	$T = 150$ K
$c = 16.429$ (3) Å	$0.38 \times 0.31 \times 0.19$ mm

Data collection

Nonius Kappa CCD diffractometer	5018 measured reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	2687 independent reflections
$T_{\text{min}} = 0.940$, $T_{\text{max}} = 0.969$	1973 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.119$	$\Delta\rho_{\text{max}} = 0.30$ e Å ⁻³
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.30$ e Å ⁻³
2687 reflections	
122 parameters	

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5044).

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supporting information

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Redetermination of di- μ -hydrido-hexahydridotetrakis(tetrahydrofuran)-dialuminium(III)magnesium(II)

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S1. Comment

Mg(AlH₄)₂.4THF, (I), is a starting material for the synthesis of Mg(AlH₄)₂ which is an interesting candidate for hydrogen storage applications because of its high theoretical hydrogen storage capacity. Ashby *et al.* (1970) reported the synthesis of (I) by the metathesis reaction between NaAlH₄ and MgCl₂. Noth *et al.* (1995) and recently Fichtner & Fuhr (2002) reported the crystal structure of (I), but neither of the groups obtained high quality single crystal X-ray diffraction data. In the present work good quality single crystals were obtained from reaction between NaAlH₄ and ClMgBH₄ where the product, AlH₄MgBH₄.THF disproportionated to form (I). The crystal structure was determined using single crystal X-ray diffraction and compared with the previously reported data.

In general, the present crystal structure determination confirms the previous results. As previously described by Noth *et al.* (1995) and Fichtner & Fuhr (2002), the structure of (I) consists of discrete octahedral building blocks where four THF molecules and two tetrahedral AlH₄⁻ units are connected to a Mg central atom. Fichtner & Fuhr (2002) reported only lattice parameters without coordinates of the atoms. Noth *et al.* (1995) reported the Al—H(t) and Al—H(b) bond lengths as 1.214 and 1.528 Å, respectively, which are shorter than expected. Moreover, the structure was only refined to a final R value of 0.065. We have redetermined this crystal structure at 150 K, with a final R value of 0.040 to obtain more precise data. In the present work, the Al—H(t) and Al—H(b) bond lengths were found to be 1.524 and 1.573 Å, respectively, which are close to the Al—H bond distance in other alanates. Al—H distances reported in other alanates with AlH₄⁻ tetrahedral are 1.547 Å (at 8 K) for LiAlH₄ (Sklar & Post, 1967), 1.532 Å (at 296 K) for NaAlH₄ (Lauher *et al.*, 1979), 1.55 Å (at 200 K) for Mg(AlH₄)₂.Et₂O (Fichtner & Fuhr, 2002) and 1.65 Å (at 230 K) for Ca(AlH₄)₂.4THF (Fichtner *et al.*, 2004).

S2. Experimental

All the manipulations were carried out in high vacuum lines and an Ar filled glove box to avoid the compounds reacting with oxygen and moisture. Solvents were dried by vacuum distillation from sodium benzophenone ketyl. Precursor ClMgBH₄ was synthesized by ball milling MgCl₂ and Mg(BH₄)₂ in 1:1 mole ratio in a high energy ball mill for 1 h. AlH₄MgBH₄ was prepared by the procedure reported by Ashby & Goel (1977). In a typical procedure, a clear solution of NaAlH₄ in THF was added to a solution of ClMgBH₄ in THF with rapid stirring for 60 min at room temperature. After completion of reaction, NaCl was filtered out from the solution and the solvent was removed from the filtrate under dynamic vacuum. The obtained AlH₄MgBH₄.THF powder was dissolved in benzene, filtered, concentrated, and aged for 2 days. AlH₄MgBH₄.THF slowly disproportionated to give colourless crystals of (I).

S3. Refinement

H atoms bonded to aluminium atoms were located and refined isotropically. The range of refined Al–H distances is 1.50 (2)–1.573 (18) Å. The remaining H atoms were placed in calculated positions [C–H = 0.99 Å] and refined using a rigid model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

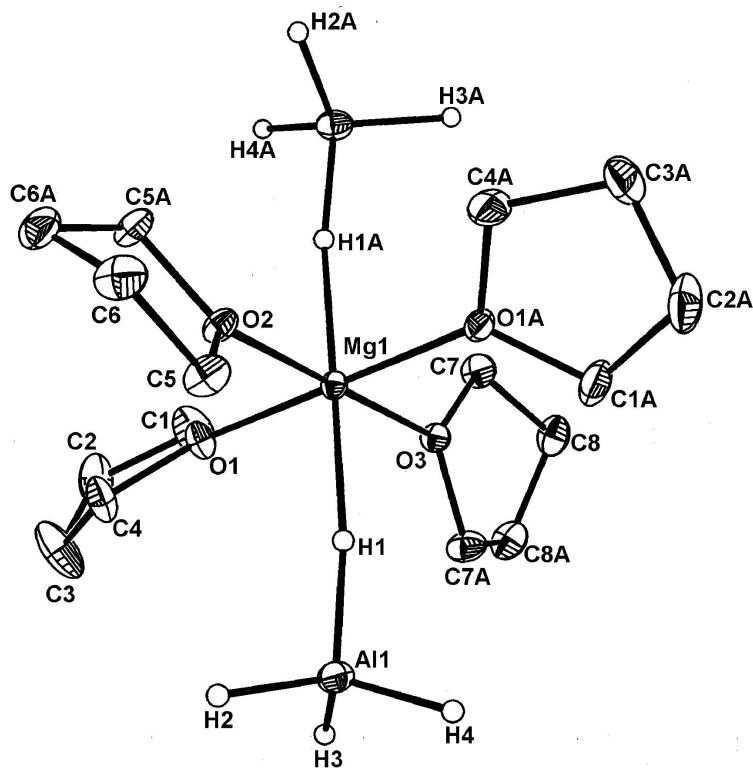


Figure 1

The molecular structure of $[\text{Mg}(\text{AlH}_4)_2(\text{C}_4\text{H}_8\text{O})_4]$, showing 50% probability displacement ellipsoids and the atomic numbering scheme. Atoms labelled with the suffix A are generated by the symmetry operation $(-x, 1/2-y, z)$.

Di- μ -hydrido-hexahydridotetrakis(tetrahydrofuran)dialuminium(III)magnesium(II)

Crystal data

$[\text{Al}_2\text{MgH}_8(\text{C}_4\text{H}_8\text{O})_4]$
 $M_r = 374.75$
 Orthorhombic, $Pcnb$
 Hall symbol: $-P\ 2b\ 2ac$
 $a = 10.161\ (2)\ \text{\AA}$
 $b = 14.027\ (3)\ \text{\AA}$
 $c = 16.429\ (3)\ \text{\AA}$
 $V = 2341.6\ (8)\ \text{\AA}^3$
 $Z = 4$

$F(000) = 824$
 $D_x = 1.063\ \text{Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$
 Cell parameters from 2687 reflections
 $\theta = 2.4\text{--}27.5^\circ$
 $\mu = 0.16\ \text{mm}^{-1}$
 $T = 150\ \text{K}$
 Cube, colourless
 $0.38 \times 0.31 \times 0.19\ \text{mm}$

Data collection

Nonius Kappa CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 φ and ω scans
Absorption correction: multi-scan
(SCALEPACK; Otwinowski & Minor, 1997)
 $T_{\min} = 0.940$, $T_{\max} = 0.969$

5018 measured reflections
2687 independent reflections
1973 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.4^\circ$
 $h = -13 \rightarrow 13$
 $k = -18 \rightarrow 18$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.119$
 $S = 1.07$
2687 reflections
122 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.6568P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
All	0.22387 (5)	0.44321 (4)	0.13620 (3)	0.03294 (17)
Mg1	0.0000	0.2500	0.13728 (4)	0.02116 (19)
O1	0.16625 (10)	0.16699 (8)	0.13767 (6)	0.0298 (3)
O3	0.0000	0.2500	0.01068 (8)	0.0269 (3)
O2	0.0000	0.2500	0.26391 (8)	0.0270 (3)
C8	-0.06993 (19)	0.23112 (14)	-0.12525 (9)	0.0429 (5)
H8A	-0.1341	0.2828	-0.1356	0.052*
H8B	-0.0815	0.1806	-0.1667	0.052*
C4	0.27768 (17)	0.17950 (14)	0.19205 (12)	0.0439 (5)
H4A	0.2588	0.1515	0.2461	0.053*
H4B	0.2982	0.2480	0.1991	0.053*
C5	0.02463 (19)	0.33286 (12)	0.31515 (9)	0.0370 (4)
H5A	-0.0285	0.3880	0.2967	0.044*
H5B	0.1189	0.3507	0.3136	0.044*
C7	-0.08466 (18)	0.19178 (13)	-0.04047 (9)	0.0382 (4)

H7A	-0.1773	0.1962	-0.0222	0.046*
H7B	-0.0570	0.1242	-0.0386	0.046*
C6	-0.0151 (2)	0.30305 (13)	0.39968 (10)	0.0445 (5)
H6A	-0.1098	0.3151	0.4094	0.053*
H6B	0.0373	0.3370	0.4415	0.053*
C2	0.3257 (2)	0.05289 (16)	0.10336 (13)	0.0573 (6)
H2A	0.3781	0.0396	0.0538	0.069*
H2B	0.3177	-0.0066	0.1354	0.069*
C3	0.3878 (2)	0.1296 (2)	0.15261 (16)	0.0763 (8)
H3A	0.4480	0.1022	0.1938	0.092*
H3B	0.4382	0.1737	0.1174	0.092*
C1	0.1945 (2)	0.09039 (16)	0.08170 (14)	0.0587 (6)
H1A	0.1945	0.1143	0.0250	0.070*
H1B	0.1272	0.0396	0.0865	0.070*
H1	0.1142 (17)	0.3641 (12)	0.1382 (9)	0.034 (5)*
H2	0.2892 (19)	0.4426 (13)	0.2215 (13)	0.055 (6)*
H3	0.3167 (19)	0.4126 (16)	0.0687 (13)	0.063 (6)*
H4	0.156 (2)	0.5361 (18)	0.1206 (14)	0.076 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Al1	0.0350 (3)	0.0315 (3)	0.0323 (3)	-0.0085 (2)	-0.0024 (2)	0.0047 (2)
Mg1	0.0227 (4)	0.0223 (4)	0.0184 (3)	0.0009 (3)	0.000	0.000
O1	0.0284 (6)	0.0313 (6)	0.0297 (6)	0.0073 (5)	-0.0075 (4)	-0.0111 (4)
O3	0.0292 (8)	0.0336 (8)	0.0178 (7)	-0.0037 (6)	0.000	0.000
O2	0.0401 (9)	0.0208 (7)	0.0200 (7)	-0.0038 (7)	0.000	0.000
C8	0.0587 (12)	0.0459 (11)	0.0243 (8)	0.0041 (9)	-0.0085 (8)	-0.0006 (7)
C4	0.0391 (10)	0.0438 (10)	0.0488 (11)	0.0098 (8)	-0.0215 (8)	-0.0096 (9)
C5	0.0550 (11)	0.0294 (9)	0.0268 (8)	-0.0089 (8)	0.0003 (7)	-0.0075 (7)
C7	0.0442 (10)	0.0455 (10)	0.0249 (8)	-0.0094 (8)	-0.0090 (7)	-0.0014 (7)
C6	0.0556 (12)	0.0522 (12)	0.0257 (8)	-0.0139 (9)	0.0049 (8)	-0.0098 (8)
C2	0.0657 (14)	0.0601 (14)	0.0462 (11)	0.0366 (11)	-0.0033 (10)	-0.0097 (10)
C3	0.0344 (12)	0.107 (2)	0.0876 (17)	0.0248 (12)	-0.0139 (11)	-0.0386 (16)
C1	0.0526 (12)	0.0554 (13)	0.0681 (14)	0.0211 (10)	-0.0125 (10)	-0.0379 (11)

Geometric parameters (Å, °)

Al1—H1	1.573 (18)	C4—C3	1.471 (3)
Al1—H2	1.55 (2)	C4—H4A	0.99
Al1—H3	1.52 (2)	C4—H4B	0.99
Al1—H4	1.50 (2)	C5—C6	1.505 (2)
Mg1—O1 ⁱ	2.0517 (11)	C5—H5A	0.99
Mg1—O1	2.0518 (11)	C5—H5B	0.99
Mg1—O3	2.0800 (15)	C7—H7A	0.99
Mg1—O2	2.0804 (15)	C7—H7B	0.99
Mg1—H1	1.977 (18)	C6—C6 ⁱ	1.519 (4)
O1—C1	1.443 (2)	C6—H6A	0.99

O1—C4	1.4529 (19)	C6—H6B	0.99
O3—C7 ⁱ	1.4537 (17)	C2—C1	1.477 (3)
O3—C7	1.4537 (17)	C2—C3	1.487 (3)
O2—C5	1.4567 (17)	C2—H2A	0.99
O2—C5 ⁱ	1.4567 (17)	C2—H2B	0.99
C8—C7	1.506 (2)	C3—H3A	0.99
C8—C8 ⁱ	1.517 (4)	C3—H3B	0.99
C8—H8A	0.99	C1—H1A	0.99
C8—H8B	0.99	C1—H1B	0.99
H1—Al1—H2	106.3 (9)	O2—C5—C6	105.40 (13)
H1—Al1—H3	104.8 (10)	O2—C5—H5A	110.7
H2—Al1—H3	113.1 (11)	C6—C5—H5A	110.7
H1—Al1—H4	107.0 (11)	O2—C5—H5B	110.7
H2—Al1—H4	110.9 (11)	C6—C5—H5B	110.7
H3—Al1—H4	114.0 (12)	H5A—C5—H5B	108.8
O1 ⁱ —Mg1—O1	179.65 (6)	O3—C7—C8	105.66 (13)
O1 ⁱ —Mg1—O3	90.18 (3)	O3—C7—H7A	110.6
O1—Mg1—O3	90.18 (3)	C8—C7—H7A	110.6
O1 ⁱ —Mg1—O2	89.82 (3)	O3—C7—H7B	110.6
O1—Mg1—O2	89.82 (3)	C8—C7—H7B	110.6
O3—Mg1—O2	180.0	H7A—C7—H7B	108.7
O1 ⁱ —Mg1—H1	91.4 (5)	C5—C6—C6 ⁱ	102.59 (11)
O1—Mg1—H1	88.6 (5)	C5—C6—H6A	111.2
O3—Mg1—H1	90.4 (4)	C6 ⁱ —C6—H6A	111.2
O2—Mg1—H1	89.6 (4)	C5—C6—H6B	111.2
C1—O1—C4	109.08 (13)	C6 ⁱ —C6—H6B	111.2
C1—O1—Mg1	125.75 (10)	H6A—C6—H6B	109.2
C4—O1—Mg1	125.10 (10)	C1—C2—C3	104.88 (16)
C7 ⁱ —O3—C7	109.37 (16)	C1—C2—H2A	110.8
C7 ⁱ —O3—Mg1	125.32 (8)	C3—C2—H2A	110.8
C7—O3—Mg1	125.32 (8)	C1—C2—H2B	110.8
C5—O2—C5 ⁱ	109.39 (16)	C3—C2—H2B	110.8
C5—O2—Mg1	125.30 (8)	H2A—C2—H2B	108.8
C5 ⁱ —O2—Mg1	125.30 (8)	C4—C3—C2	105.13 (18)
C7—C8—C8 ⁱ	102.78 (11)	C4—C3—H3A	110.7
C7—C8—H8A	111.2	C2—C3—H3A	110.7
C8 ⁱ —C8—H8A	111.2	C4—C3—H3B	110.7
C7—C8—H8B	111.2	C2—C3—H3B	110.7
C8 ⁱ —C8—H8B	111.2	H3A—C3—H3B	108.8
H8A—C8—H8B	109.1	O1—C1—C2	106.93 (15)
O1—C4—C3	105.34 (15)	O1—C1—H1A	110.3
O1—C4—H4A	110.7	C2—C1—H1A	110.3
C3—C4—H4A	110.7	O1—C1—H1B	110.3
O1—C4—H4B	110.7	C2—C1—H1B	110.3

C3—C4—H4B	110.7	H1A—C1—H1B	108.6
H4A—C4—H4B	108.8		

Symmetry code: (i) $-x, -y+1/2, z$.