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

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Redetermination of di-$\mu$-hydrido-hexahydridotetrakis(tetrahydrofuran)-
dialuminium(III)magnesium(II)

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The structure of the title compound, [Mg(AlH4)$_2$(C$_4$H$_8$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 Mg(AlH$_4$)$_2$·4THF, see: Ashby et al. (1970); Shen & Che (1991); Nöth et al. (1995). For the synthesis of AlH$_4$MgBH$_4$, see: Ashby & Goel (1977). For previous determinations of the crystal structure of Mg(AlH$_4$)$_2$·4THF, see: Noth et al. (1995); Fichtner & Fuhr (2002). For the thermal decomposition properties of Mg(AlH$_4$)$_2$·4THF, see: Dilts & Ashby (1972). For other alanate structures, see: Sklar & Post (1967); Lauher et al. (1979); Fichtner & Fuhr (2002); Fichtner et al. (2004).

Data collection

Nonius Kappa CCD diffractometer

5018 measured reflections

2687 independent reflections

1973 reflections with $I > 2\sigma(I)$

$R_{int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.119$

$S = 1.07$

2687 reflections

122 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta \rho_{\text{max}} = 0.30$ e Å$^{-3}$

$\Delta \rho_{\text{min}} = -0.30$ e Å$^{-3}$

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

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

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Comment

Mg(AlH$_4$)$_2$-4THF, (I), is a starting material for the synthesis of Mg(AlH$_4$)$_2$ 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 NaAlH$_4$ and MgCl$_2$. 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 NaAlH$_4$ and ClMgBH$_4$ where the product, AlH$_4$MgBH$_4$.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 AlH$_4^-$ 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 AlH$_4^-$ tetrahedral are 1.547 Å (at 8 K) for LiAlH$_4$ (Sklar & Post, 1967), 1.532 Å (at 296 K) for NaAlH$_4$ (Lauher et al., 1979), 1.55 Å (at 200 K) for Mg(AlH$_4$)$_2$.Et$_2$O (Fichtner & Fuhr, 2002) and 1.65 Å (at 230 K) for Ca(AlH$_4$)$_2$.4THF (Fichtner et al., 2004).

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 ClMgBH$_4$ was synthesized by ball milling MgCl$_2$ and Mg(BH$_4$)$_2$ in 1:1 mole ratio in a high energy ball mill for 1 h. AlH$_4$MgBH$_4$ was prepared by the procedure reported by Ashby & Goel (1977). In a typical procedure, a clear solution of NaAlH$_4$ in THF was added to a solution of ClMgBH$_4$ 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 AlH$_4$MgBH$_4$.THF powder was dissolved in benzene, filtered, concentrated, and aged for 2 days. AlH$_4$MgBH$_4$.THF slowly disproportionated to give colourless crystals of (I).
supplementary materials

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 $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

Fig. 1. The molecular structure of [Mg(AlH$_4$)$_2$(C$_4$H$_8$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-$\mu$-hydrido-hexahydridotetrakis(tetrahydrofuran)dialuminium(III)magnesium(II)

Crystal data

$\text{[Al}_2\text{MgH}_8\text{(C}_4\text{H}_8\text{O})_4]\n
F(000) = 824

M_r = 374.75

$D_x = 1.063 \text{ Mg m}^{-3}$

Orthorhombic, $Pcnb$

Hall symbol: -P 2b 2ac

$a = 10.161$ (2) Å

$\theta = 2.4–27.5^\circ$

$b = 14.027$ (3) Å

$\mu = 0.16 \text{ mm}^{-1}$

$c = 16.429$ (3) Å

$T = 150 \text{ K}$

$V = 2341.6$ (8) Å$^3$

Cube, colourless

$Z = 4$

$T_{min} = 0.940$, $T_{max} = 0.969$

$0.38 \times 0.31 \times 0.19 \text{ mm}$

Data collection

Nonius Kappa CCD
diffractometer

Radiation source: fine-focus sealed tube

graphite

$\varphi$ and $\omega$ scans

Absorption correction: multi-scan

(SCALEPACK; Otwinowski & Minor, 1997)

$\theta_{max} = 27.5^\circ$, $\theta_{min} = 2.4^\circ$

$h = -13 \rightarrow 13$

$1973$ reflections with $I > 2\sigma(I)$

$R_{int} = 0.017$

$5018$ measured reflections

$\mu = 0.16 \text{ mm}^{-1}$

$T = 150 \text{ K}$

$Z = 4$

$T_{min} = 0.940$, $T_{max} = 0.969$

$0.38 \times 0.31 \times 0.19 \text{ mm}$

Refinement

Refinement on $F^2$

Primary atom site location: structure-invariant direct methods
supplementary materials

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.041$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.119$

H atoms treated by a mixture of independent and constrained refinement

$S = 1.07$

2687 reflections (Δ/σ)_{max} = 0.001

122 parameters

0 restraints

$\Delta \rho_{\text{max}} = 0.30 \text{ e Å}^{-3}$

$\Delta \rho_{\text{min}} = -0.30 \text{ e Å}^{-3}$

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 ($Å^2$)

| Atom | $x$     | $y$     | $z$     | $U_{iso}/U_{eq}$ |
|------|---------|---------|---------|------------------|
| Al1  | 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* |
supplementary materials

|        |          |          |          |          |
|--------|----------|----------|----------|----------|
| 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)**

|        | U₁¹     | U₂²     | U₃³     | U₁₂     | U₁³     | U₂₃     |
|--------|---------|---------|---------|---------|---------|---------|
| 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)|          |          | 1.471 (3)|
| Al1—H2 | 1.55 (2)  |          |          | 0.99     |
| Al1—H3 | 1.52 (2)  |          |          | 0.99     |
| Al1—H4 | 1.50 (2)  |          |          | 1.505 (2)|
| Mg1—O1 | 2.0517 (11)|          |          | 0.99     |
| Mg1—O1 | 2.0518 (11)|          |          | 0.99     |
| Mg1—O3 | 2.0800 (15)|          |          | 0.99     |
| Mg1—O2 | 2.0804 (15)|          |          | 0.99     |
| Mg1—H1 | 1.977 (18)|          |          | 1.519 (4)|
| O1—C1  | 1.443 (2)  |          |          | 0.99     |
| O1—C4  | 1.4529 (19)|          |          | 0.99     |
| O3—C7  | 1.4537 (17)|          |          | 1.477 (3)|
| O3—C7  | 1.4537 (17)|          |          | 1.487 (3)|
| C8—C7  | 1.506 (2)  |          |          | 0.99     |
| C8—C8  | 1.517 (4)  |          |          | 0.99     |
| Bond | Dist. (Å) | Bond | Dist. (Å) |
|------|----------|------|----------|
| 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—Mg1—O1 | 179.65 (6) | O3—C7—C8 | 105.66 (13) |
| O1—Mg1—O3 | 90.18 (3) | O3—C7—H7A | 110.6 |
| O1—Mg1—O2 | 89.82 (3) | C8—C7—H7A | 110.6 |
| O1—Mg1—O2 | 89.82 (3) | C8—C7—H7B | 110.6 |
| O3—Mg1—O2 | 180.0 | H7A—C7—H7B | 108.7 |
| O1—Mg1—H1 | 91.4 (5) | C5—C6—C6i | 102.59 (11) |
| O1—Mg1—H1 | 88.6 (5) | C5—C6—H6A | 111.2 |
| O3—Mg1—H1 | 90.4 (4) | C6i—C6—H6A | 111.2 |
| O2—Mg1—H1 | 89.6 (4) | C5—C6—H6B | 111.2 |
| C1—O1—C4 | 109.08 (13) | C6i—C6—H6B | 111.2 |
| C1—O1—Mg1 | 125.75 (10) | C1—C2—H2A | 110.8 |
| C1—O1—Mg1 | 125.10 (10) | H6A—C6—C6i | 110.2 |
| C7—O3—C7 | 109.37 (16) | C3—C2—H2B | 110.8 |
| C7—O3—Mg1 | 125.32 (8) | C7—C8—H8A | 110.2 |
| C7—O3—Mg1 | 125.32 (8) | C2—C3—H3A | 110.7 |
| C5—O2—C5i | 109.39 (16) | C8—C8—H8A | 110.2 |
| C5—O2—Mg1 | 125.30 (8) | C4—C3—H3A | 110.7 |
| C5—O2—Mg1 | 125.30 (8) | H8A—C8—C8i | 110.2 |
| C7—C8—C8i | 102.78 (11) | C4—C3—H3A | 110.7 |
| C7—C8—H8A | 111.2 | C2—C3—H3A | 110.7 |
| C8—C8—H8A | 111.2 | C4—C3—H3B | 110.7 |
| C8—C8—H8B | 111.2 | C2—C3—H3B | 110.7 |
| H8A—C8—H8B | 109.1 | H3A—C3—H3B | 108.8 |
| O1—C4—C3 | 105.34 (15) | O1—C1—C2 | 106.93 (15) |
| O1—C4—H4A | 110.7 | O1—C1—H1A | 110.3 |
| C3—C4—H4A | 110.7 | C2—C1—H1A | 110.3 |
| O1—C4—H4B | 110.7 | O1—C1—H1B | 110.3 |
| C3—C4—H4B | 110.7 | C2—C1—H1B | 110.3 |
| H4A—C4—H4B | 108.8 | H1A—C1—H1B | 108.6 |

Symmetry codes: (i) −x, −y+1/2, z.
