

A twinned triclinic polymorph of dibromidotetrakis(tetrahydrofuran- κ O)magnesium(II)

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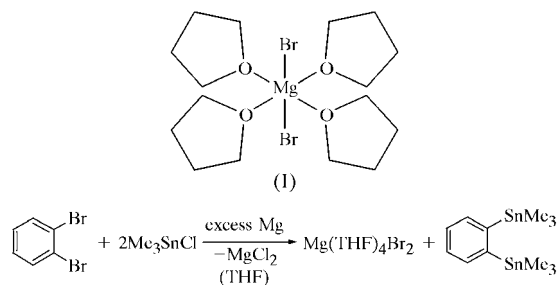
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The title compound, $[\text{MgBr}_2(\text{C}_4\text{H}_8\text{O})_4]$, forms crystals which appear to be monoclinic but are actually twinned triclinic. The current form is a new triclinic polymorph, with $Z' = 2$, in addition to the already known tetragonal polymorph. Although the geometric parameters of the two polymorphs agree well, their packing patterns are completely different.

Comment

Salt metathesis reactions of Grignard compounds and organohalides are common preparation routes. However, the disadvantage of this method is the separation of the organic compounds from MgX_2 , since most of these magnesium salts are soluble in organic solvents such as tetrahydrofuran. We report here the X-ray crystal structure analysis of the title adduct, (I), of MgBr_2 with four tetrahydrofuran molecules, which was obtained by the reaction of 1,2-dibromobenzene with Mg in the presence of Me_3SnCl , as shown in the scheme.



A perspective view of compound (I) is shown in Fig. 1. Geometric parameters are in the normal ranges [Cambridge Structural Database, Version 5.28, November 2006, updated January 2007 (Allen, 2002); *MOGUL*, Version 1.1 (Bruno *et al.*, 2004)].

Compound (I) is a new polymorph of dibromidotetrakis(tetrahydrofuran)magnesium, for which a tetragonal polymorph (space group $P4_22_12$) has already been described. Schroder & Spandau (1966) did not publish any coordinates,

but there are two structure determinations at room temperature (Metzler *et al.*, 1994; Heeg *et al.*, 1998). Since the quality of the structure of Heeg *et al.* [hereinafter (Ia)] is the higher, it will be used in the following comparison with (I).

The most important bond lengths (Table 1) of (Ia) ($\text{Mg}-\text{Br} = 2.652 \text{ \AA}$ and $\text{Mg}-\text{O} = 2.111 \text{ \AA}$) agree well with those of (I) (Table 2). The packing pattern of the two polymorphs, however, is completely different. Whereas (Ia) shows planes of molecules at $z = 0$ and $z = \frac{1}{2}$ being rotated by 90° and translated by $(\frac{1}{2}, \frac{1}{2}, 0)$ (Fig. 3), the molecules of (I) are almost located in the same plane (Table 2), but the $\text{Br}-\text{Br}$ vectors of two adjacent molecules are rotated by just 22.0° (Fig. 2).

It is interesting to note that for dichloridotetrakis(tetrahydrofuran)magnesium, two different polymorphs have also been found. One form (Handlir *et al.*, 1985) is isostructural with (Ia). The second polymorph, on the other hand, is

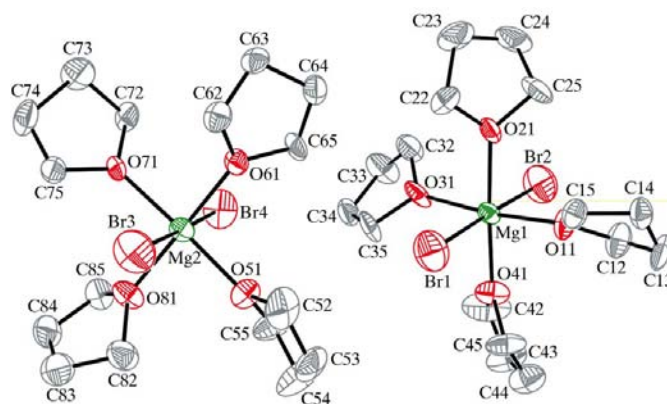


Figure 1

A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

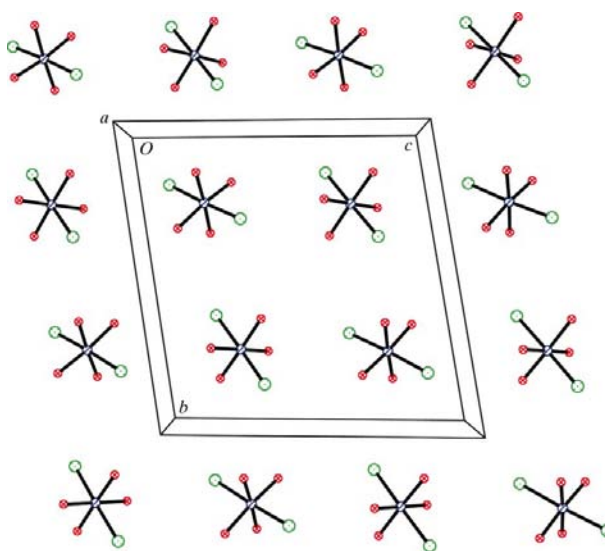


Figure 2

A packing diagram for (I), viewed in the bc plane. C and H atoms have been omitted for clarity. Key: Mg atoms are shaded, Br atoms are dotted and O atoms are cross-hatched.

monoclinic (space group $P2_1/c$). Its structure has been determined at room temperature (Huang *et al.*, 1987), at 173 K (Bolte *et al.*, 2002) and at 150 K (Parsons *et al.*, 2004).

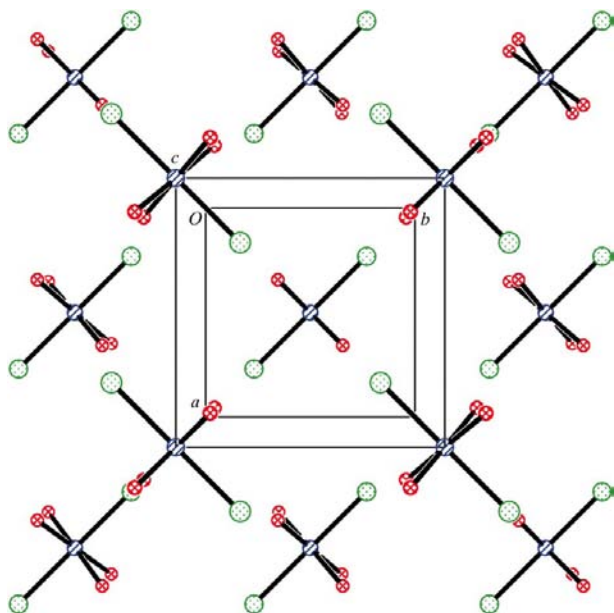


Figure 3
Packing diagram of the tetragonal polymorph of dibromidotetrakis(tetrahydrofuran)magnesium, (Ia), viewed in the ab plane. C and H atoms have been omitted for clarity. Key: Mg atoms are shaded, Br atoms are dotted and O atoms are cross-hatched.

Experimental

A solution of Me_3SnCl (26.08 g, 130.9 mmol) and 1,2-dibromobenzene (7.8 ml, 64 mmol) in tetrahydrofuran (THF) (100 ml) was added dropwise to a mixture of magnesium (7.45 g 306 mmol) and CH_3MgCl (0.6 mmol) in THF (100 ml). The reaction mixture was heated under reflux for 90 min. After cooling to ambient temperature, colourless crystals of $\text{Mg}(\text{THF})_4\text{Br}_2$ suitable for X-ray crystallographic analysis were obtained (yield 23%).

Crystal data

$[\text{MgBr}_2(\text{C}_4\text{H}_8\text{O})_4]$	$\gamma = 85.190$ (11) $^\circ$
$M_r = 472.55$	$V = 2089.3$ (3) \AA^3
Triclinic, $P\bar{1}$	$Z = 4$
$a = 8.6620$ (9) \AA	Mo $K\alpha$ radiation
$b = 15.6820$ (12) \AA	$\mu = 3.93$ mm^{-1}
$c = 15.6910$ (13) \AA	$T = 173$ (2) K
$\alpha = 80.501$ (9) $^\circ$	$0.27 \times 0.26 \times 0.24$ mm
$\beta = 85.131$ (11) $^\circ$	

Data collection

Stoe IPDSII two-circle diffractometer	22055 measured reflections
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	7347 independent reflections
$T_{\min} = 0.342$, $T_{\max} = 0.420$ (expected range = 0.318–0.390)	4969 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.080$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.087$	416 parameters
$wR(F^2) = 0.232$	H-atom parameters constrained
$S = 1.44$	$\Delta\rho_{\text{max}} = 0.97$ e \AA^{-3}
7347 reflections	$\Delta\rho_{\text{min}} = -1.11$ e \AA^{-3}

Table 1
Selected bond lengths (\AA).

Mg1—O31	2.099 (8)	Mg2—O51	2.087 (9)
Mg1—O41	2.105 (9)	Mg2—O71	2.096 (8)
Mg1—O21	2.105 (8)	Mg2—O81	2.128 (8)
Mg1—O11	2.106 (8)	Mg2—O61	2.138 (8)
Mg1—Br1	2.569 (3)	Mg2—Br4	2.562 (4)
Mg1—Br2	2.592 (3)	Mg2—Br3	2.605 (4)

Table 2
Coordinates of the Mg atoms in the unit cell of (I).

Atom	x	y	z
Mg1	0.5332 (4)	0.2517 (2)	0.2364 (2)
Mg2	0.5228 (4)	0.2559 (2)	0.7201 (2)
Mg1 ¹	0.4668 (4)	0.7483 (2)	0.7636 (2)
Mg2 ¹	0.4772 (4)	0.7441 (2)	0.2799 (2)

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

The frames collected during data collection did not show split reflections and there was no warning sign that the structure determination would be problematic. The cell parameters of (I) indicate a monoclinic C -centred cell ($a = 23.945$ \AA , $b = 20.271$ \AA , $c = 8.662$ \AA , $\alpha = 90.05^\circ$, $\beta = 96.35^\circ$, $\gamma = 89.97^\circ$ and $V = 4178.64$ \AA^3) and the R_{int} value for the monoclinic crystal system is 0.096 (compared with 0.080 for the triclinic crystal system). However, there are no systematic extinctions and the structure cannot be solved in any of the monoclinic space groups. Thus, the structure was solved in the triclinic space group $P\bar{1}$ by locating the heaviest atoms in a Patterson map and using successive Fourier syntheses to find the remaining atoms. After encountering severe problems during structure solution, anisotropic refinement remained stalled at $R_1 = 0.278$ and $wR_2 = 0.685$, with several atoms going nonpositive definite. It was therefore assumed that the crystal was twinned. The warning signs for twinning are, firstly, that $E^2 - 1$ is just 0.768, which is a little bit too small for a centrosymmetric structure and, secondly, that R_{int} for the higher-symmetry Laue group is only slightly higher than for the lower-symmetry Laue group. Nevertheless, the twin law is not a symmetry operation of the higher-symmetry Laue group, but a twofold rotation axis along the face diagonal of the bc plane interchanging b and c , which are almost equal in length, *i.e.* $(\bar{1}00/001/010)$. Applying this twin law ultimately provided success and R_1 dropped below 0.1. All H atoms could now be located by difference Fourier synthesis. They were refined using a riding model with fixed individual displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] and with $\text{C}—\text{H} = 0.99$ \AA . Finally, the ratio of the twin components refined to 0.534 (3):0.466 (3).

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3104). Services for accessing these data are described at the back of the journal.

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