Polymorphism of Dibromo-tetrakis(tetrahydrofuran-κO)magnesium(II)

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Z. Naturforsch. 2010, 65b, 719 – 724; received February 24, 2010

The title compound, [MgBr₂(C₄H₈O)₄] (1a), forms twinned four-component monoclinic crystals as a new polymorph, space group P2₁/n with Z' = 2, in addition to the already known tetragonal polymorph (1b). Although the molecular parameters in the two polymorphs match very well, the packing patterns are significantly different. Furthermore, the correct constitution of the mixed halide bromo-chloro-tetrakis(tetrahydrofuran-κO)magnesium(II) (2) could be determined.

Key words: Polymorphism, Crystal Structure, Magnesium Halides, Schlenk Equilibrium, Grignard Reaction

Introduction

Since the first reports on organomagnesium compounds by Barbier [1] and Grignard [2] these highly reactive intermediates have become key reagents in synthetic chemistry [3 – 6]. Although the stoichiometry of a Grignard reagent can be expressed by the simple empirical formula RMgX (R = organic substituent, X = halide), the real composition is far more complex, both in solution and in the solid state. It can be described by the fundamental Schlenk equilibrium [7] (Scheme 1) where solvated MgX₂ (X = Cl, Br, I) is also present.

The position of the Schlenk equilibrium depends on the solvent, the concentration of the solution, the nature of the organic group and the halide, as well as the temperature. The most important factors are the solvent and the concentration [8]. Therefore, the isolation of the Grignard reagent (RMgX) itself can be exceedingly difficult and is typically hampered by the precipitation of either the magnesium dialkyl or, more frequently, the magnesium dihalide. Hence, for X-ray structural analyses the precise and reliable knowledge of the cell parameters of all possible magnesium halide complexes helps to avoid wasting valuable time.

Herein we report the crystal structures of monoclinic [MgBr₂(C₄H₈O)₄] (1a), which is a polymorph of the already known tetragonal structure 1b [9 – 11]. Both polymorphs could be transformed into each other by slow cooling or heating while they undergo a non-destructive phase transition which was detected by DSC and X-ray crystal structure analysis. Furthermore, we describe the structure of the mixed magnesium halide complex [Mg(Br,Cl)(C₄H₈O)₄] (2), which was erroneously published to be a triclinic polymorph (1c) of 1b [12].

Scheme 1. Formation of solvated magnesium dihalide from organomagnesium reagents in tetrahydrofuran.
Results and Discussion

The crystals analyzed were repeatedly obtained by preparing anthrylmagnesium bromides (1a), treating MeMgBr with S(N\text{t}Bu)\textsubscript{3} (1b) or 2-thiophenylmagnesium bromide with phosphanyl chlorides (2) in THF but can of course also be prepared much more easily by reacting magnesium turnings with elemental halogens in THF [13].

Magnesium dibromide crystallizes from THF solution as dibromido-tetrakis(tetrahydrofuran)magnesium in the tetragonal space group \(P4_2\text{2}_1\text{2}\) (1b) which was first described by Schröder and Spandau [9]. Redeterminations (all at room temperature) of this structure were described by Le Bihan and coworkers [10], Metzler et al. [11] and later by Heeg et al. [14]. Another supposed polymorph (triclinic space group \(P\bar{1}\)) 1c was published by Bolte et al. [12].

The shock cooling of a single crystal of 1b from r. t. to 100 K results in a sample showing a multicomponent diffractrogram caused by a destructive phase transition. At an elevated data collection temperature of 170 K the integrity of the single crystal is maintained, and the structure analysis shows it to be the known tetragonal polymorph 1b. This behavior indicates a phase transition from one crystalline state to another. Fig. 1A presents the DSC curves in the temperature window of \(-90\) to \(-145\) °C, obtained from a microcrystalline sample of 1a cooled at a rate \((\nu_c)\) of 10 °C min\(^{-1}\),
Table 1. Comparison of the crystallographic data and structure refinement parameters for the two polymorphs of [MgBr$_2$(C$_4$H$_8$O)$_4$] (1a and 1b), the published erroneous polymorph 1c and [MgBrCl(C$_4$H$_8$O)$_4$] [12] (2), identical to 1c.

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<tr>
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<th>1a</th>
<th>1b</th>
<th>1c</th>
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<td>Y = Br</td>
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<td>CSD</td>
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<td>$P$</td>
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<td>173(2)</td>
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<td>MgBr$_2$(C$_4$H$_8$O)$_4$</td>
<td>MgBr$_2$(C$_4$H$_8$O)$_4$</td>
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<td>2</td>
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<td>896</td>
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<td>0.0228</td>
<td>0.0804</td>
<td>0.0289</td>
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<td>0.0405, 0.0676</td>
<td>0.0782, 0.1163</td>
<td>0.0215, 0.0528</td>
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<tr>
<td>$R_1$, wR$_2$ (all data)</td>
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<td>0.0499, 0.0702</td>
<td>0.2321, 0.2211</td>
<td>0.0232, 0.0535</td>
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<td>0.091/ -</td>
<td>0.253/0.6804</td>
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<td>1.12</td>
<td>1.044</td>
<td>1.438</td>
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<td>0.27 / -0.26</td>
<td>0.97 / -1.11</td>
<td>0.33 / -0.29</td>
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<td>2.6552(3)</td>
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<td>av. Mg–O, Å</td>
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<td>2.108(9)</td>
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<tr>
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<td>Mg1 = 0.0160(8)</td>
<td>Mg1 = 0.0292(3)</td>
<td>Mg1 = 0.0296(9)</td>
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<td>Br1 = 0.0209(2)</td>
<td>Br1 = 0.04351(15)</td>
<td>Br2 = 0.0814(7)</td>
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</table>

$^a$ $R_1 = \Sigma|I|/\Sigma|F|$, $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2)^{1/2}$; $b = [\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P]^2 - 1$, where $P = (Max(F_o^2, 0) + 2F_c^2)/3$; $c$ $\text{GoF} = (\Sigma w(F_o^2 - F_c^2)^2/n_{param} - n_{param})^{1/2}$.

Fig. 4 (color online). Molecular graph of 1a (left) and 2 (right) showing the atom numbering scheme. Anisotropic displacement parameters are depicted at the 50% probability level. H atoms are omitted for clarity (symmetry code: (i) $-x+1$, $-y+1$, $-z+1$).

The structure determination revealed a monoclinic unit cell with almost identical parameters as for 1a (see Table 1). A molecular graph of 1b is given in Fig. 1b showing the central magnesium cation octahedrally coordinated by four equatorial THF molecules and the two bromide ions at the apical positions. The comparison of the data of our monoclinic polymorph with the five available datasets of 1b suggests that the

and then heated at a constant warming rate ($\nu$) of 10 °C min$^{-1}$. The thermogram of the subsequent cooling shows one exothermic (~120 to ~135 °C) signal that corresponds to a solid-solid transformation from the crystalline form 1a to 1b. Cooling down a single crystal of 1b slowly to 100 K ($\nu_c$ = 10 K min$^{-1}$) leads to a crystalline sample of polymorph 1a suitable for X-ray structure determination.
Presently no triclinic polymorph of \([\text{MgBr}_2(\text{C}_4\text{H}_8\text{O})_4]\) halogen magnesium salt complex is known. The erroneous ‘triclinic polymorph’ 1c published by Bolte et al. [12] is not made up exclusively by MgBr_2 but rather by a mixture of magnesium salts where the bromine atoms share their sites with the chlorine atoms. The packing pattern also differs completely from that for the tetragonal polymorph and the monoclinic polymorph described here.

The published structure of 1c shows too large displacement ellipsoids of the bromine atoms compared to the other atoms (e.g. \(U_{\text{iso}}(\text{Br2})/U_{\text{iso}}(\text{Mg1}) = 2.75\)). The \(R\) values are too high (\(wR_2 = 0.232, R_1 = 0.087\)), and the goodness-of-fit value (1.44) is not close to 1.0. A redetermination of the structure of this ‘polymorph’ confirmed our assumption, revealing the compound to be the complex \([\text{Mg}(\text{Br},\text{Cl})(\text{C}_4\text{H}_8\text{O})_4]\) (2). Table 1 contains crystallographic data, Fig. 2 shows the packing diagram of the incorrect (1c) and the correctly assigned structure of 2. All structural quality features clearly indicate the new \([\text{Mg}(\text{Br},\text{Cl})(\text{C}_4\text{H}_8\text{O})_4]\) refinement to be correct.

Unfortunately, the published crystal structures of the tetragonal polymorph could not be employed in the comparison to the new monoclinic polymorph because Schröder and Spandau published only the cell constants but not the atom coordinates. Moreover, the previous structures were determined at r.t. Therefore we re-determined the structure of the tetragonal polymorph 1b at 170 K.

The packing pattern of the two polymorphs, monoclinic 1a and tetragonal 1b (Fig. 3), is slightly different. In both cases the Mg atoms are placed at the corners and in the center of the unit cell, leading to planes of molecules at \(z = 0\) and \(z = \frac{1}{2}\) (Fig. 3, left). For 1b the different planes of molecules have to be rotated by 90° and translated by \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) to fit each other, but due to an additional rotational symmetry element along the \(a\) axis this operation fails for 1a.

A comparison of 1a and 2 is given in Fig. 4. 1a is a new polymorph of dibromido-tetrakis(tetrahydrofuran) magnesium, showing a destructive phase transition resulting in multiple domains. In Table 1 the basic crystallographic data of both polymorphs 1a and b, the erroneous ‘triclinic polymorph’ 1c and the mixed halogen magnesium salt complex 2 are compared. Presently no triclinic polymorph of \([\text{MgBr}_2(\text{C}_4\text{H}_8\text{O})_4]\) is known.

In \([\text{MgX},\text{Y}(\text{C}_4\text{H}_8\text{O})_4]\) (1a and b: \(X = Y = \text{Br}\), 1c and 2: \(X = \text{Cl}, Y = \text{Br}\)) the magnesium atoms show octahedral coordination geometry with the two halogen atoms axially oriented. In the polymorphs 1a and 1b the magnesium and bromine atoms are located at special positions. Therefore the Br–Mg–Br angle is exactly 180° by symmetry requirements. However, that angle in the mixed halide complexes 1c and 2 is marginally different (3–6°) from 180°. The characteristic bond lengths (Table 1) Mg–Br and Mg–O of 1a agree well with those of 1b.

A remarkably similar polymorphism has been described for the complex \([\text{MgCl}_2(\text{C}_4\text{H}_8\text{O})_4]\) (3). Handle et al. determined a tetragonal polymorph (space group \(\text{P}4_212\)) by powder diffraction [15], and additionally two monoclinic polymorphs (both space group \(\text{P}2_1/c\)) have been found.

The determination of the two monoclinic structures, carried out at r.t. (Huang et al. [16]), at 173 K (Bolte et al. [17]) and at 150 K (Parsons et al. [18]), which differ only in the choice of the unit cell, presented all massive problems indicated by large unit cells, unresolved disorder, isotropic displacement parameters and a large number of molecules in the asymmetric unit.

**Twinning of 1a, 1b and 2**

The twinning of 1a was quite obvious and could be easily seen on the diffraction images. The data had to be collected because no untwinned crystals could be found in the batch. The cell determination with CELL_NOW [19] resulted in four twin domains with the major cell (1) and three twin cells (2–4):

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1 \\
\end{pmatrix} \times \begin{pmatrix}
a \\
b \\
c \\
\end{pmatrix} = \begin{pmatrix}
a \\
-b \\
-c \\
\end{pmatrix}
\]

(a) 180° rotation of cell (1) about \(a_0\) produces cell (2)

\[
\begin{pmatrix}
0 & 1 & 0 \\
-1 & 0 & 0 \\
0 & 0 & 1 \\
\end{pmatrix} \times \begin{pmatrix}
a \\
b \\
c \\
\end{pmatrix} = \begin{pmatrix}
b \\
-a \\
c \\
\end{pmatrix}
\]

(b) 90° rotation of cell (1) about \(c_0\) produces cell (3)

\[
\begin{pmatrix}
0 & -1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1 \\
\end{pmatrix} \times \begin{pmatrix}
a \\
b \\
c \\
\end{pmatrix} = \begin{pmatrix}
-b \\
a \\
c \\
\end{pmatrix}
\]

(c) −90° rotation of cell (1) about \(c_0\) produces cell (4)

The respective twin cells could be related to the original monoclinic cell by rotating the first domain about a two-fold axis parallel to \(a\) and about a four-fold axis parallel to \(c\) (\(2||a_0, 4||c_0\)). Data reduction with
Experimental Section

The syntheses were performed under an inert gas atmosphere of dry nitrogen with Schlenk techniques. All solvents were dried and purified according to standard procedures and stored under nitrogen.

Dibromido-tetrakis(tetrahydrofuran)magnesium (1a)

A solution of 9-bromoanthracene (3.00 g, 11.67 mmol) in diethyl ether (40 mL) was added dropwise to magnesium turnings (0.44 g, 12.84 mmol) previously activated with iodine. The reaction mixture was stirred for 24 h under reflux. After cooling to ambient temperature the formed precipitate was filtered off, washed with Et₂O (10 mL) and dissolved in dry tetrahydrofuran. After cooling to −30 °C colorless crystals of [MgBr₂(thf)₄] suitable for X-ray crystallographic analysis were obtained.

Dibromido-tetrakis(tetrahydrofuran)magnesium (1b) [25]

S(N²Bu)₃ (1.25 g, 5.0 mmol) was dissolved in THF (20 mL), and MeMgBr (5.0 mmol) dissolved in tetrahydrofuran (20 mL) was added to this solution at −78 °C over a period of 15 min. The mixture was allowed to warm to r.t. and stirred overnight. The solvent was removed in vacuo, the residual solid was re-dissolved in a n-hexane/tetrahydrofuran mixture, and insoluble particles were filtered off. The resulting solution was stored at 24 °C and yielded colorless crystals suitable for X-ray crystallographic analysis after 1 – 3 d.

Bromido-chlorido-tetrakis(tetrahydrofuran)magnesium (2) [26]

A solution of 2-bromothiophene (25.00 g, 153 mmol) in tetrahydrofuran (50 mL) was added dropwise to magnesium turnings (4.2 g, 172 mmol) previously activated with iodide, to maintain a gentle reflux. After the addition was complete, the reaction mixture was stirred for 1 h at r.t. and cooled down to 0 °C before diethylphosphoramidous dichloride (12.0 g, 76.5 mmol) was added. The reaction was allowed to warm to room temperature and was stirred over night. The precipitate was filtered off through Celite, and most of the solvent was removed in vacuo. The resulting solution was stored at 4 °C and yielded colorless crystals suitable for X-ray crystallographic analysis after one week.

Structure determination of 1a, 1b and 2

The data for 1a and 2 were collected from shock-cooled crystals at 100(2) K, and 1b at 170(2) K [27]. The data of 1a were collected on an INCOATEC Mo Microsource [28] with Quazar mirror optics and an APEX II detector with D8 goniometer. The data of 1b and 2 were measured on a Bruker TXS-Mo rotating anode with Helios mirror optics.
and APEX II detector with D8 goniometer. Both diffractometers were equipped with a low-temperature device [29] and used MoKα radiation, λ = 7.1073 pm. All data were integrated with SAINT [20], and an empirical absorption correction was applied (SADABS [24]). The structures were solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares methods against F² (SHELXTL/SHELXL-97) [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their Ueq of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond length restraints and isotropic displacement parameter restraints.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in Table 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft. The authors gratefully acknowledge support of Chemetall GmbH, Frankfurt/Main and Langelsheim, and are grateful for the superb X-ray facilities supplied by the Volkswagenstiftung and the Land Niedersachsen.