An Unexpected Structural Principle for Crystalline $MgBr_2 \cdot OEt_2$: Chains of Trigonal Bipyramids

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Abstract: $MgBr_2 \cdot OEt_2$ (**1**), which is commercially available and has been examined by different methods in the past, was obtained in crystalline form as a by-product of the reaction of amine-stabilised AlCl solution with mesitylene magnesium bromide. The following unexpected structure was obtained by X-ray techniques: five-coordinate magnesium centres form trigonal bipyramids, which are connected by two common bromine atoms into chains. Structural details and especially the relationship with solid $MgBr_2$, $MgBr_2 \cdot (OEt_2)_2$ and $MgI_2 \cdot (OEt_2)_2$ (**2**) are discussed in order to illuminate the unusual bonding in **1**.

Keywords
coordination · crystal structure · halogen compounds · magnesium compounds · structure elucidation

Introduction

Diethyletherates of magnesium dibromide have been studied since the turn of the century. Not only are the solubility of the monoetherate,[1,2] the decomposition pressures of the mono-, di- and trietherates,[3,4] and the IR and NQR spectra known,[5–7] but also the structures have been determined—since 1967—by X-ray diffraction. These show isolated $MgBr_2 \cdot (OEt_2)_2$ units for the dietherates, though these results are imprecise.[8] In the case of the monoetherate **1**, photographs of the crystals were published in the literature,[4] but no X-ray structure analysis is available. Further successful structure determinations of the magnesium dibromide monoetherate **1** are unknown to us. However, a structural model for **1** based on vibrational spectroscopic analysis[5] exhibits four-coordinate magnesium centres. The lack of direct structural data for **1** is particularly surprising because this compound is commercially available (e.g., Aldrich, Fluka).[9]

Coordination of $MgBr_2$ with other ethers like THF or diglyme results in the formation of monomeric species ($MgBr_2 \cdot 4THF$,[10] $MgBr_2 \cdot diglyme \cdot THF$[11]), dimeric species ($(MgBr_2 \cdot diglyme)_2$[11]) and also chainlike structures ($(MgBr_2 \cdot 2THF)_\infty$[12]), according to X-ray structure analysis. The variety of different donor adducts for the dihalides clearly shows that the Schlenk equilibrium in reactions of Grignard compounds ($2RMgX \rightleftharpoons MgR_2 + MgX_2$) can easily be tuned by the donor strength of the solvent and the solubility of the products. In all these compounds magnesium is six-coordinate.

Compounds with five-coordinate magnesium are far less common. Species with square pyramidal geometry predominate over those exhibiting a trigonal bipyramidal structure. Examples of the latter type all contain soft ligating atoms and carbon, and in fact most of them are organometallic derivatives.[13] Only two examples with oxygen- and nitrogen-containing ligands have been published recently.[14] Therefore the observation of five-coordinate magnesium in the dihalide **1** is very surprising.

During our investigations of Al^I and Ga^I compounds we repeatedly used organomagnesium reagents. The magnesium halides formed as by-products crystallise easily under these conditions. Therefore we have recently been able to isolate crystals of $[Mg_3Cl_5(OEt_2)_6]^+[GaCl_4]^-$ as by-products of the reaction between Ga_2Cl_4 and $MgCp^*_2$. The geometry found in this compound, which exhibits three face-linked $MgCl_4(OEt_2)_2$ octahedrons, is analogous to the structure of $Cs_{11}O_3$ clusters.[15]

In the following discussion, we will focus on the structure of compound **1**, its synthesis from a solution of aluminium(I) chloride and mesitylene magnesium bromide and the comparison of **1** with the structures of $MgBr_2$ (solid and gas phase) and its etherates.

Results and Discussion

After co-condensing AlCl with Me_2NSiMe_3 and an excess of toluene, $AlCl_3$ and donor-stabilised Al_2Cl_4 were obtained as a result of a disproportionation reaction.[16] To get the tetraarylaluminium compound, mesitylene magnesium bromide in diethyl ether was added to this raw product. Instead of the desired Al_2R_4 compound, the product of the reaction was mes_3Al (mes = 2,4,6-trimethylphenyl).[17] In addition only the compound $MgBr_2 \cdot OEt_2$ (**1**) has been isolated as a crystalline species from the reaction solution up to now.

The formation of **1** may be explained on the grounds of the special crystallisation conditions during summertime. Indeed, according to the literature, the dietherate is transformed into the monoetherate at a temperature of 28 °C.[3] The habit of the crystals is that of the cubes depicted in the literature.[4] The X-ray structure analysis (Table 1) reveals an unexpected chain

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Table 1. Crystal structure data of **1** and **2** [21].

	1	**2**
empirical formula	$MgBr_2OC_4H_{10}$	$MgI_2O_2C_8H_{20}$
formula weight	258.25	426.35
crystal size (mm)	0.3 × 0.3 × 0.2	0.2 × 0.2 × 0.1
crystal colour and habit	colourless cubes	colourless square platelets
crystal system	monoclinic	triclinic
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
unit cell dimensions	$a = 6.900(15)$ Å	$a = 7.7110(15)$ Å
	$b = 8.192(10)$ Å	$b = 8.072(2)$ Å
	$c = 15.662(17)$ Å	$c = 12.790(3)$ Å
		$\alpha = 100.16(3)^\circ$
	$\beta = 90.88(17)^\circ$	$\beta = 96.54(3)^\circ$
		$\gamma = 93.22(3)^\circ$
V (Å^3)	885.2(19)	776.1(3)
Z	4	2
density (Mg/m^3, calculated)	1.938	1.824
absorption coefficient (mm^{-1})	9.151	4.070
$F(000)$	496	404
diffractometer	STOE STADI4	STOE STADI4
radiation, wavelength	$Mo_{K\alpha}$, $\lambda = 0.71073$ Å	$Mo_{K\alpha}$, $\lambda = 0.71073$ Å
scan mode	ω	ω
T (K)	210	200
2θ range for data collection	5.20–44.98°	5.14–39.94°
index ranges	$-7 \leq H \leq 7$ $-8 \leq K \leq 8$ $-16 \leq L \leq 16$	$-7 \leq H \leq 7$ $-8 \leq K \leq 8$ $-16 \leq L \leq 16$
reflections collected	2326	2884
independent reflections	1163 ($R_{int} = 0.1491$)	1442 ($R_{int} = 0.1213$)
observed reflections	583 ($F > 4\sigma(F)$)	863 ($F > 4\sigma(F)$)
scan time	variable; 0.5–2.0 s/step	variable; 0.5–2.5 s/step
scan range (ω)	2°	1.5°
structure solution	SHELXS (Sheldrick **1990**)	SHELXS (Sheldrick **1990**)
solution	direct	direct
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
hydrogen atoms	riding model, fixed isotr. U	riding model, fixed isotr. U
weighting scheme	$w^{-1} = \sigma^2 F_o^2 + (0.0924P)^2 + 0P$	$w^{-1} = \sigma^2 F_o^2 + (0.0562P)^2 + 0P$
	where $P = (F_o^2 + 2F_c^2)/3$	where $P = (F_o^2 + 2F_c^2)/3$
data/restraints/parameters	1163/0/75	1440/0/122
data:parameter ratio	15.5:1 (7.8:1 [$F > 4\sigma(F)$])	11.8:1 (7.1:1 [$F > 4\sigma(F)$])
final R indices [$F > 4\sigma(F)$]	$R1 = 0.0662$, $wR2 = 0.1642$	$R1 = 0.0540$, $wR2 = 0.1100$
R indices (all data)	$R1 = 0.1485$, $wR2 = 0.2013$	$R1 = 0.1235$, $wR2 = 0.1345$
goodness-of-fit on F^2	0.989	1.050
largest and mean Δ/σ	−0.003 0.001	−0.006 0.001
largest difference peak (e Å^{-3})	0.764	1.356
largest difference hole (e Å^{-3})	−0.576	−1.217
structure refinement	SHELXL (Sheldrick **1993**)	SHELXL (Sheldrick **1993**)

structure with trigonal bipyramids of $MgBr_2 \cdot OEt_2$ units linked by two common edges. The angles between the three equatorial atoms are nearly 120° (122.7, 120.8, 116.5°). The axial atoms form an angle of 178° with the central Mg atom, nearly ideal for a trigonal bipyramid. The principle of this chain structure for **1** is shown in Figure 1. In Table 2 distances and angles are listed and compared with those of solid $MgBr_2$ and $MgBr_2 \cdot (OEt_2)_2$. Unfortunately structural data for $MgBr_2 \cdot (OEt_2)_2$ are based on less accurate diffraction data; therefore they should be considered carefully. However, a more precise insight into the structure of a four-coordinate $MgX_2 \cdot (OEt_2)_2$ species is now possible from the structure of the homologue iodide **2**, which we were able to determine recently.

$MgI_2 \cdot (OEt_2)_2$ (**2**), characterised by X-ray diffraction techniques (Table 1), crystallises isotopically to $MgBr_2 \cdot (OEt_2)_2$ in the reaction between solid $\{(\eta^5\text{-}Cp^*)Mg(\mu\text{-}Cl) \cdot OEt_2\}_2$[19] and a solution of aluminium(I) iodide in OEt_2/toluene at −80 °C. The crystals, in the form of colourless square platelets, are soluble in the reaction solution at temperatures higher than −80 °C. The intermolecular angles of **2** (Table 2) confirm the geometry of $MgBr_2 \cdot (OEt_2)_2$, but in contrast to $MgBr_2 \cdot (OEt_2)_2$, all angles in **2** are close to tetrahedral ones.

The systematic structural tendency is convincing. With increasing donor activity the two-dimensional layer structure of $MgBr_2$ (CdI_2 type, hexagonal close-packing of the bromides) is reduced to the one-dimensional chain structure of $MgBr_2 \cdot OEt_2$ (**1**) and finally to separate units in solid $MgBr_2 \cdot (OEt_2)_2$. In the same sequence the coordination number decreases from 6 to 5 to 4. Consequently the MgBr bond strength increases with decreasing coordination number: $d(Mg-Br) = 270.1$ pm ($MgBr_2$) → $d(Mg-Br) = 256.3$ pm (**1**). The strongest bond, with a Mg–Br distance of 234 pm, is found in gaseous $MgBr_2$.[20]

The THF adducts follow the same trend. However, the lesser steric requirements of THF compared with diethyl ether lead to a different situation. While two diethyl ethers form a monomeric unit, four THF molecules are required for the generation of the isolated species $MgBr_2 \cdot 4THF$. In contrast $MgBr_2 \cdot 2THF$

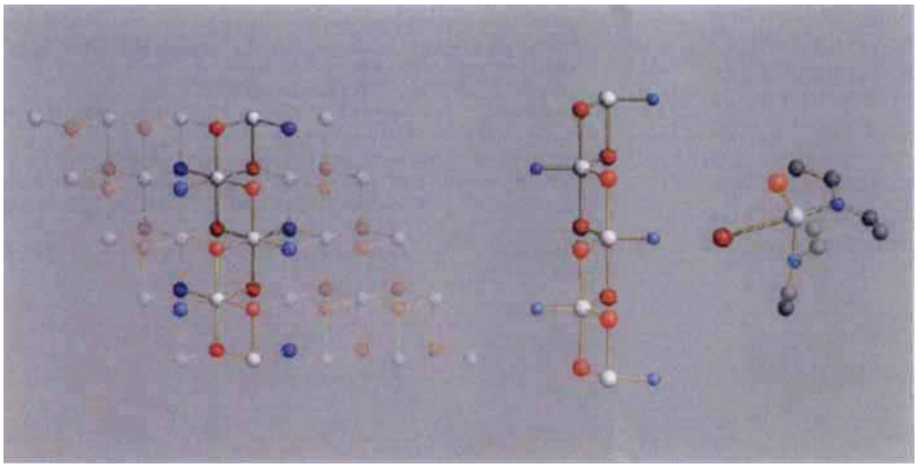

Fig. 1. Left to right: $MgBr_2$ [22], $(MgBr_2 \cdot OEt_2)_x$ (**1**), $MgBr_2 \cdot (OEt_2)_2$ [8]. Mg: white; Br: red (and also blue in $MgBr_2$); O: blue; C: grey; in **1** carbon and hydrogen, in **2** hydrogen atoms are omitted for clarity.

Table 2. Bond lengths (Å) and angles (°) of the crystalline compounds.

	$MgBr_2$ [22]	$MgBr_2 \cdot OEt_2$ (1)	$MgBr_2 \cdot (OEt_2)_2$ [8]	$MgI_2 \cdot (OEt_2)_2$ (2)
Mg–X	2.70	2.633(5) [a,c] 2.493(6) [a,b]	3.13 [a]	2.663(6) [a]
Mg–O	–	2.025(10)	2.13 [a]	1.99(2) [a]
X-Mg-X	90	122.7(2) [b] 90.3(2) [a,c] 178.5(2) [d]	76.4 [a]	117.0(2)
X-Mg-O	–	118.7(2) [a]	112.1 [a]	108.9(5) [a]
O-Mg-O	–	–	117.8 [a]	102.6(6)

[a] Mean values. [b] Equatorial. [c] Axial. [d] Apical.

exhibits chains of edge-linked deformed octahedrons, with THF in *trans* positions perpendicular to the chain direction. In the case of $MgBr_2 \cdot (OEt_2)_x$ compounds, no six-coordinate Mg centres are known and the coordination number of five can only be realised with one OEt_2 molecule per formula. In the case of the THF ligand only vague speculations about the possibility of pentacoordination exist.[12]

As well as chains and isolated molecules, intermediate cluster species are formed. One such species has been made by our group, the cation $[Mg_3Cl_5 \cdot (OEt_2)_6]^+$. Quantum-chemical calculations have shown that these cluster species are only stable under particular conditions,[15] so that the concentration as well as the strength of the Lewis base or acid used have to be carefully chosen. At one end of the spectrum the hexahydrate $MgBr_2 \cdot (H_2O)_6$ is the borderline case in which the Mg^{2+} cation is coordinated by six molecules of the strong donor H_2O. At the other end the one-dimensional structure described here can be formally regarded as the initial step in the decomposition of the two-dimensional structure in solid $MgBr_2$ by donor-containing solvents. Without electron donors solid $MgBr_2$ is thermodynamically stable. Therefore $MgBr_2$ should be precipitated in donor-free solvents during alkylations with organomagnesium compounds.

After these general remarks concerning the chain structure of $MgBr_2 \cdot OEt_2$, a detailed discussion of the chains and their relation to the layers in crystalline $MgBr_2$ may be informative. Chains of $MgBr_6$ octahedrons may be visualised in these layers, as emphasised in Figure 1. The principle of linking polyhedrons by two edges shows the analogy to 1. Substitution of two equatorial bromine atoms of an $MgBr_6$ octahedron by one oxygen atom from the donor molecule OEt_2 means a change of equatorial coordination from four, in $MgBr_2$, to three, in the chain of 1, and thus in the equatorial angles from 90° in the octahedron to 120° in the trigonal bipyramid. However, this consideration is rather formal, because the "chains" in the two-dimensional layers of $MgBr_2$ are linked by three-coordinate bromine atoms, while only two-coordinate bromine atoms are present in the "isolated" chains of 1.

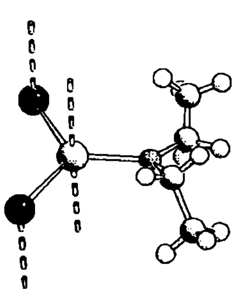

Fig. 2. Magnesium and bromine atoms in 1 stack together to form a chain.

In addition to the systematic structural interpretation of 1, an alternative kinetic view of the formation of 1 starting with monomeric $MgBr_2 \cdot (OEt_2)_2$ exists. Loss of an ether molecule would lead to trigonal planar units (Fig. 2), which could stack together to form 1. The driving force for this reaction is the increased coordination of the magnesium (4 → 5) and bromine (1 → 2) atoms.

Conclusion

This examination of the structure of 1 is an example of an important interdisciplinary view situated between molecular and solid-state chemistry. For a deeper understanding of molecular structures, the discussion of direct molecular bonding is often not sufficient.

In 1, the polyhedrons—trigonal bipyramids—form one-dimensional chains, which are packed in a three-dimensional network with their elliptical diameters like a stack of wood. Viewed similarly, the structure of solid $MgBr_2$ can be described as follows: $MgBr_6$ octahedrons are linked in two-dimensional layers, which are stacked to form the final three-dimensional structure.

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