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Crystal and Molecular Structure of Magnesium Bromide–Tetrahydrofuran Complexes: $MgBr_2(C_4H_8O)_2$, Orthorhombic, and $MgBr_2(C_4H_8O)_4(H_2O)_2$, Triclinic

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Abstract: The structure of the magnesium bromide–tetrahydrofuran complex, $MgBr_2(C_4H_8O)_4(H_2O)_2$, has been determined by single-crystal x-ray diffraction. The crystals are *triclinic*, space group $P\bar{1}$, $a = 7.77$ (±0.01), $b = 9.26$ (±0.01), $c = 9.27$ (±0.01) Å, $\alpha = 84.9$ (±0.03), $\beta = 71.2$ (±0.03), $\gamma = 69.1$ (±0.03)°, $Z = 1$, $\rho_{calcd} = 1.44$ g cm^{-3}, $\rho_{obsd} = 1.43$ g cm^{-3}. The structure of $MgBr_2(C_4H_8O)_2$ has also been determined. The crystals are *orthorhombic*, space group $P2nn$, $a = 4.01$ (±0.01), $b = 7.52$ (±0.01), $c = 18.20$ (±0.01) Å, $Z = 2$, $\rho_{calcd} = 1.99$ g cm^{-3}, $\rho_{obsd} = 1.99$ g cm^{-3}. Intensity data were collected on a computer controlled CAD4 automatic diffractometer; 2050 and 626 independent reflections were collected using (θ–2θ) scan, with a scan width of 1.0°, for the trinclinic and orthorhombic crystals, respectively. The structures were solved by Patterson methods and refined to final R factors of 7.9% (triclinic, 2043 reflections), and 8.6% (orthorhombic, 618 reflections), by least-squares methods. The structure of diaquotetrakis(tetrahydrofuran)magnesium bromide consists of independent molecules with regular octahedral six-coordinate magnesium; two trans water molecules, Mg–O = 2.042 Å, and two pairs of trans THF molecules, Mg–O = 2.117 and 2.164 Å, respectively; the bromine atoms are in the outer sphere, Mg–Br = 4.651 Å. The structure of bis(tetrahydrofuran)magnesium bromide is polymeric with distorted octahedral six-coordinate magnesium: two trans THF molecules, Mg–O = 2.126 Å, two cis bromine atoms from the same formula unit, Mg–Br = 2.633 Å, and two cis bridging bromine atoms from an adjacent formula unit, Mg···Br = 2.799 Å. A third complex, $MgBr_2(C_4H_8O)_3$, which could have trigonal bipyramidal five-coordinate magnesium, has been isolated only as a microcrystalline powder. A *tetragonal* complex, $MgBr_2(C_4H_8O)_4$, has been reported by Pérucaud and LeBihan and by Schröder and Spandau. The interconversions among these complexes in aprotic solvents are discussed as examples of elimination and substitution reactions. All the complexes easily form $MgBr_2(H_2O)_6$ in water.

Much of the research on the structure of magnesium compounds, as revealed by single-crystal x-ray diffraction techniques, has been motivated by the problem of the constitution of the Grignard reagent.[2] The literature on this subject was reviewed by Toney and Stucky,[3] in connection with their study of the product of the reaction of ethyl chloride with magnesium in tetrahydrofuran (THF). These authors described a tetrameric Grignard reagent, $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$, consisting of two $MgCl_2(C_4H_8O)_2$ units associated with two $C_2H_5MgCl(C_4H_8O)$ units in such a way as to allow the six coordination of the former magnesium atoms and the five coordination of the latter magnesium atoms, with two- and three-coordinate chlorine atoms functioning as bridges. This beautiful structure brings out one of the interesting features of magnesium chemistry, namely, the ability of the metal to adjust its coordination number according to the demands of a particular constitution. Vallino[4] reported trigonal bipyramidal five coordination for the complex $CH_3MgBr(C_4H_8O)_3$. Moseley and Shearer[5] found four coordination for the magnesium in the dimer $[(CH_3)_3COMgBrO(C_2H_5)_2]_2$. Manning and co-workers[6] ascribed five coordination to the metal in the dimer $[(C_6H_5)_2NMgBr(C_4H_8O)]_2$.

In other types of magnesium compounds, six coordination prevails, as in diaquobis(acetylacetonato)magnesium(II),[7] and in a related tris(hexafluoroacetylacetonate) salt.[8] Other significant aspects of the crystal and molecular structure of magnesium compounds have been discussed in previous papers.[9-13]

This investigation focused on the structure of complexes of magnesium bromide with THF. In a previous paper[14] we described the isolation of four complexes with formulas $MgBr_2(C_4H_8O)_4$ (**1**), $MgBr_2(C_4H_8O)_3$ (**2**), $MgBr_2(C_4H_8O)_4(H_2O)_2$ (**3**), and $MgBr_2(C_4H_8O)_2$ (**4**) from the reaction of magnesium with mercuric bromide in THF solution, under various experimental conditions. Complex **1** was obtained as tetragonal crystals, which proved to have the same unit cell dimensions as those reported by Schröder and Spandau[15] and by Pérucaud and LeBihan.[16] Complex **2** has been obtained only as a microcrystalline powder; it has a remarkable solubility in aprotic solvents such as dichloromethane, and constitutes a new reagent to make *anhydrous* magnesium phosphodiester salts by the reaction: $(R^1O)(R^2O)P(O)OCH_3 + MgBr_2(C_4H_8O)_3 \rightarrow [(R^1O)(R^2O)P(O)O]_2Mg + 2CH_3Br + 3C_4H_8O$.

The other two complexes in this series, **3** and **4**, were obtained as single crystals of excellent quality for x-ray diffraction analyses. The results of such a study are described in this paper.

Experimental Section

The samples of diaquotetrakis(tetrahydrofuran)magnesium bromide (**3**, triclinic), and bis(tetrahydrofuran)magnesium bromide (**4**,

Table I. Crystal Data For Complexes of Magnesium Bromide With Tetrahydrofuran (THF) and Water

Crystal data	**1**[a]	**3**[b]	**4**[b]
Solvent	Anhydrous THF	Moist THF	Dichloromethane-hexane
Habit	Plates	Plates	Needles
System	Tetragonal	Triclinic	Orthorhombic
Unit cell dimensions; Å, deg, Å^3	$a = b = 7.79$ (±0.03); $c = 17.32$ (±0.03); $\alpha = \beta = \gamma = 90.0$; $V = 1051.0$	$a = 7.77$ (±0.01); $b = 9.26$ (±0.01); $c = 9.27$ (±0.01); $\alpha = 84.9$ (±0.03); $\beta = 71.2$ (±0.03); $\gamma = 69.1$ (±0.03); $V = 589.0$	$a = 4.01$ (±0.01); $b = 7.52$ (±0.01); $c = 18.20$ (±0.01); $\alpha = \beta = \gamma = 90.0$; $V = 548.0$
ρ_{obsd}, g cm^{-3}	1.50	1.426[c]	1.994[d]
Space group	$P4_22_12$	$P\bar{1}$	$P2nn$
Asymmetric units per unit cell	8	2	4
Unit cell content	$2Mg\cdot 4Br\cdot 8(C_4H_8O)$	$1Mg\cdot 2Br\cdot 4(C_4H_8O)\cdot 2(H_2O)$	$2Mg\cdot 4Br\cdot 4(C_4H_8O)$
Formula units per unit cell (Z)	2	1	2
Formula unit	$MgBr_2(C_4H_8O)_4$	$MgBr_2(C_4H_8O)_4(H_2O)_2$	$MgBr_2(C_4H_8O)_2$
Formula unit weight	472	508	328
Composition of asymmetric unit	$\frac{1}{4}Mg\cdot\frac{1}{2}Br\cdot 1(C_4H_8O)$	$\frac{1}{2}Mg\cdot 1Br\cdot 2(C_4H_8O)\cdot 1(H_2O)$	$\frac{1}{2}Mg\cdot 1Br\cdot 1(C_4H_8O)$
ρ_{calcd}, g cm^{-3}	1.484	1.440	1.997
$R_f[\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|]$	18%	7.9%	8.6%

[a] Reference 16. The preparation of these crystals and the unit cell dimensions were confirmed in the present investigation. [b] Present investigation. [c] Flotation in carbon tetrachloride-hexane. [d] Flotation in carbon tetrachloride-bromoform.

Table II. Results of the Statistical Test for Two Magnesium Bromide-Tetrahydrofuran Complexes

	Experimental		Theoretical	
	Triclinic	Orthorhombic	Centric	Noncentric
$\langle\|E\|\rangle$	0.850	0.817	0.798	0.886
$\langle\|E^2 - 1\|\rangle$	0.826	0.844	0.968	0.736
$\langle\|E\|^2\rangle$	0.984	0.984	1.000	1.000
$\|E\| > 3$	0.1%	0.0%	0.3%	0.01%
$\|E\| > 2$	3.0%	2.2%	4.5%	1.8%
$\|E\| > 1$	34.6%	34.9%	32.0%	37.0%

orthorhombic) used for the x-ray analysis were described in the previous paper.[14] The sample of tetrakis(tetrahydrofuran)magnesium bromide (**1**, tetragonal) on which the previously reported[15,16] unit cell dimensions were confirmed (Table I) was also described in ref 14.

Crystal Data. The crystal data for the triclinic (**3**) and the orthorhombic (**4**) crystals are given in Table I.

Data Collection and Structure Determination. The diffraction data for the triclinic and the orthorhombic crystals were collected using a computer controlled CAD4 automatic diffractometer with Cu Kα (1.542 Å) radiation. The crystals of both compounds were sensitive to atmospheric moisture and to prevent decomposition during data collection they were sealed in capillary tubes. Approximately 2050 independent reflections from the triclinic crystals and about 626 independent reflections from the orthorhombic crystals up to $\theta = 65°$ were measured. A (θ-2θ) scan was used in both cases with a scan width of 1.0° and a scan speed of 1.5°/min. Four reflections with each compound were measured periodically to monitor any crystal deterioration. No such effects were observed with either of the crystals. Since the crystals were sealed inside a capillary tube, an empirical absorption correction was applied[17] for each crystal. The correction was determined in each case by performing an azimuth scan of a reflection occurring at a χ value of approximately 90°. The intensity variation with the azimuth angle is dependent on the thickness of the crystal traversed by the incident and the reflected beams and this variation is used to calculate the transmission factor for all other reflections. The structure analysis of the two compounds was performed as described below. All structure factor least-squares calculations were performed using a set of programs provided by Dr. Finger (NBS technical note No. 854) on the UNIVAC-1110. The function minimized was $\Sigma\omega(\Delta F)^2$ with weights derived from $\sigma(I)$ through $\omega = 1/\sigma^2(F)$. The observed and calculated structure factors for the triclinic and the orthorhombic crystals are given as supplementary material; see paragraph at end of paper.

(a) **Triclinic (3).** The unit cell volume indicated a unit cell content of at least $1Mg{:}2Br{:}4(C_4H_8O)$. The system being triclinic, the space group is $P1$ or $P\bar{1}$. The statistical tests (Table II) were not unambiguous although they favored the centrosymmetric space group $P\bar{1}$. The Patterson synthesis showed two strong nonorigin peaks, one at (u, v, w) and the second one at ($2u$, $2v$, $2w$). This is possible only if the magnesium atom occupies a center of inversion and the two bromine atoms are related across this center of inversion. A Fourier synthesis performed with the phase angles calculated with the two bromines and one magnesium showed three oxygens in the vicinity of the magnesium related to three others across the center of inversion. Two of the three oxygen atoms formed part of a ring structure and the third oxygen was isolated. This last oxygen forms part of a water molecule coordinating with the magnesium. This chemical composition was confirmed by an elemental analysis of the compound. Several cycles of structure factors followed by least squares, initially with isotropic temperature factors for all the atoms, and subsequently with anisotropic temperature factors for all the atoms, gave a final reliability index (R, as defined in Table I) of 7.9% for 2043 reflections. The maximum electron density in the final ($\rho_{\mathrm{obsd}} - \rho_{\mathrm{calcd}}$) difference Fourier map is <1 e/A^3, indicating that no atoms other than hydrogen atoms remain to be located. The final positional and thermal parameters are given in Table III.

(b) **Orthorhombic (4).** The crystals showed the following systematic absences in the diffraction pattern:

$$hol \quad h + l = 2n + 1$$

$$hko \quad h + k = 2n + 1$$

This was consistent with either the centrosymmetric space group $Pmnn$ or the noncentrosymmetric space group $P2nn$. The statistical test was again not unambiguous, although it seemed to favor the noncentrosymmetric space group $P2nn$. The unit cell volume and the crystal density indicated that one unit cell contained 2Mg, 4Br, and 4THF molecules. Thus, if the space group is the centrosymmetric one, $Pmnn$, all atoms should lie on the mirror plane perpendicular to the x axis. If the space group is the noncentrosymmetric $P2nn$, then only the magnesium atoms occupy special positions and all the remaining atoms occupy general positions. The Patterson synthesis indicated unambiguously the y and z coordinates of the bromine atom. A heavy atom phased Fourier with bromine and the magnesium revealed the positions of the oxygen and the carbon atoms of the THF ring. The

Table III. Final Atomic Coordinates and Their Standard Deviations (×10^4, in parentheses) for all Atoms in One Formula Unit of Triclinic $MgBr_2(C_4H_8O)_4(H_2O)_2$

Atom	*x*	*y*	*z*	Atom related by inversion, Figure 1
Mg	0.0	0.0	0.0	Mg
Br(1)	0.5444 (2)	−0.2422 (2)	0.1565 (2)	Br(2)
O(5)	0.2207 (8)	0.0329 (7)	0.0506 (7)	O(6)
O(1)	0.0412 (9)	−0.2035 (7)	0.1282 (9)	O(3)
C(14)	0.1234 (20)	−0.3650 (12)	0.0577 (14)	C(34)
C(13)	0.1134 (32)	−0.4619 (17)	0.1985 (20)	C(33)
C(12)	0.0476 (25)	−0.3761 (16)	0.3324 (18)	C(32)
C(11)	−0.0080 (19)	−0.2046 (13)	0.2918 (13)	C(31)
O(2)	−0.2016 (10)	0.1330 (7)	0.2043 (8)	O(4)
C(24)	−0.4082 (16)	0.1574 (14)	0.2429 (14)	C(44)
C(23)	−0.4893 (23)	0.2548 (18)	0.3940 (16)	C(43)
C(22)	−0.3377 (27)	0.3164 (19)	0.3999 (20)	C(42)
C(21)	−0.1504 (20)	0.2043 (14)	0.3078 (14)	C(41)

Anisotropic Thermal Parameters[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg	0.0105	0.0097	0.0136	−0.0022	−0.0035	−0.0001
Br(1)	0.0227	0.0230	0.0340	−0.0109	−0.0145	0.0088
O(5)	0.0122	0.0127	0.0153	−0.0027	−0.0032	−0.0035
O(1)	0.0156	0.0138	0.0218	−0.0057	−0.0086	0.0015
C(14)	0.0466	0.0072	0.0192	0.0030	−0.0023	−0.0051
C(13)	0.1053	0.0187	0.0294	−0.0135	−0.0294	0.0108
C(12)	0.0571	0.0141	0.0272	0.0003	−0.0052	0.0053
C(11)	0.0370	0.0196	0.0098	−0.0026	0.0014	0.0010
O(2)	0.0163	0.0132	0.0155	−0.0019	−0.0027	−0.0033
C(24)	0.0136	0.0261	0.0192	−0.0042	0.0034	−0.0089
C(23)	0.0340	0.0330	0.0190	0.0039	0.0024	−0.0121
C(22)	0.0457	0.0309	0.0364	−0.0122	−0.0103	−0.0116
C(21)	0.0352	0.0220	0.0198	−0.0005	−0.0075	−0.0183

[a] Thermal parameter is defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Final Atomic Coordinates and Their Standard Deviations (×10^4, in parentheses) for all Atoms in One Formula Unit of Orthorhombic $MgBr_2(C_4H_8O)_2$

Atom	*x*	*y*	*z*	Atom related by a diad axis, Figure 3
Mg	0.0	0.5	0.5	Mg
Br(1)[a]	0.4720 (46)	0.6919 (2)	0.5619 (1)	Br(3)
O(1)	−0.0671 (76)	0.6727 (18)	0.4087 (6)	O(2)
C(11)	0.0255 (138)	0.6153 (26)	0.3339 (11)	C(21)
C(12)	0.0166 (103)	0.7727 (24)	0.2881 (11)	C(22)
C(13)	−0.0046 (152)	0.9318 (25)	0.3348 (11)	C(23)
C(14)	−0.0783 (123)	0.865 (24)	0.4150 (11)	C(24)

Anisotropic Thermal Parameters[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg	Isotropic value of 0.98 for *B*					
Br(1)	0.0448	0.0054	0.0012	0.0014	−0.0009	0.0004
O(1)	0.0374	0.0070	0.0004	0.0028	0.0030	0.0001
C(11)	0.0836	0.0074	0.0006	0.0078	0.0110	0.0001
C(12)	0.0641	0.0070	0.0013	0.0032	−0.0098	0.0001
C(13)	0.0847	0.0069	0.0017	−0.0079	0.0124	0.0008
C(14)	0.0043	0.0028	0.0018	0.0013	0.0019	−0.0001

[a] In Figures 3 and 4, Br(2) and Br(4) belong to an adjacent formula unit and are related to Br(3) and Br(1), respectively, by unit translation along the *a* axis. [b] Thermal parameters defined in Table III.

oxygen and the THF ring were on a plane that would have coincided with the mirror plane for the centrosymmetric space group *Pmnn*. However, the atoms were moved out of this plane and the structure factor least-squares refinement was carried out on all the positional and thermal parameters for the noncentrosymmetric space group *P2nn*. The *x* coordinates of all the atoms oscillated on either side of the plane in the initial stages and eventually settled at their final positions given in Table IV. These coordinates gave an *R* value of 8.6% for 618 independent reflections. A ripple of approximately ±2 electrons along the *y* and *z* directions in the vicinity of bromine atoms was observed in the final difference Fourier map.

Results

The main interatomic distances[18,19] and angles in the two new complexes of magnesium bromide and tetrahydrofuran are summarized in Table V (triclinic crystals, **3**) and Table VI (orthorhombic crystals, **4**). Figure 1 shows the atoms that are required to describe one formula unit in complex **3**; Figure 2 illustrates the packing in the crystal. Figure 3 gives the atoms in the formula unit, plus those that are necessary to complete the coordination sphere of the metal, in complex **4**; Figure 4 illustrates the packing in that crystal. All the atoms are numbered for the sake of clarity, and the corresponding symmetry equivalencies defined by the respective asymmetric units (cf. Table I) are explicitly indicated in Tables III and IV.

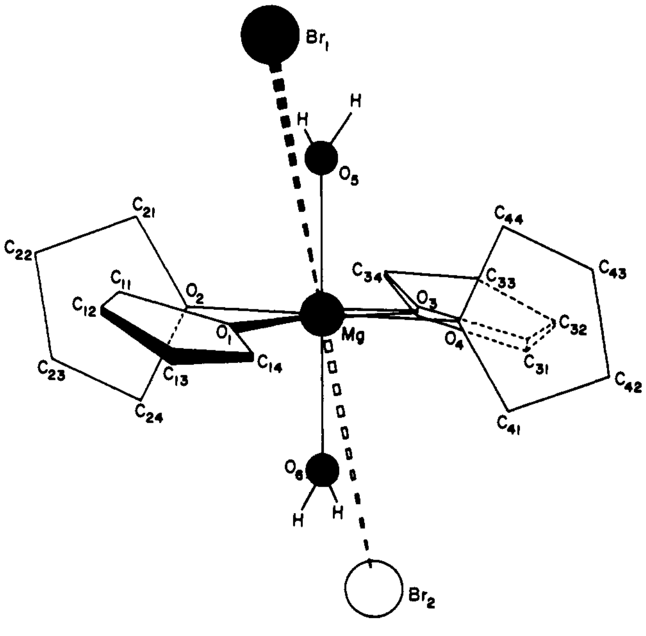


Figure 1. Computer generated drawing of the formula unit of triclinic $MgBr_2(C_4H_8O)_4(H_2O)_2$ (**3**).

The magnesium atom in the triclinic complex **3** is six-coordinate, with the oxygen atoms from four THF rings and two water molecules providing the ligands to the metal. The skeletal geometry about the magnesium is that of a nearly perfect octahedron, as can be deduced from the fact that the magnesium occupies the center of inversion and relates all the oxygens at the vertices of the octahedron. The formula units in this crystal are distinct molecules, and their relationship to the unit cell content as well as to the composition of the asymmetric unit are brought out in Table I. The two bromines may be regarded as outer-sphere atoms, although they are part of the formula unit, i.e., they are separated from the metal by an intramolecular interatomic distance.

The magnesium atom in the orthorhombic complex **4** is also six-coordinate, but the structure is quite different from the previous one. Oxygen atoms from two THF rings of a formula unit, two bromine atoms of the same formula unit, and two

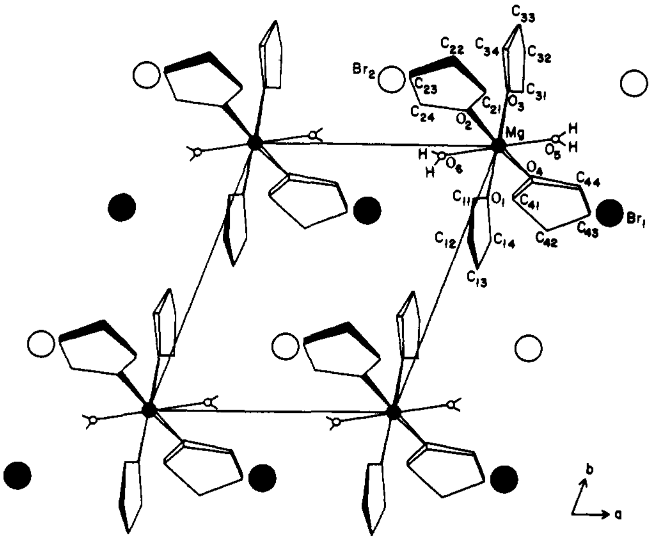


Figure 2. Projection of the unit cell contents of the triclinic crystals 3 viewed along the perpendicular to the *ab* plane.

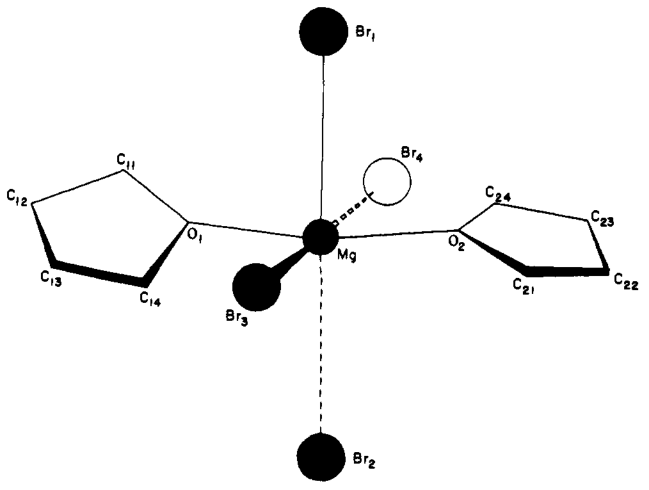


Figure 3. Computer generated drawing of the formula unit plus bridging bromines of orthorhombic $MgBr_2(C_4H_8O)_2$ (**4**).

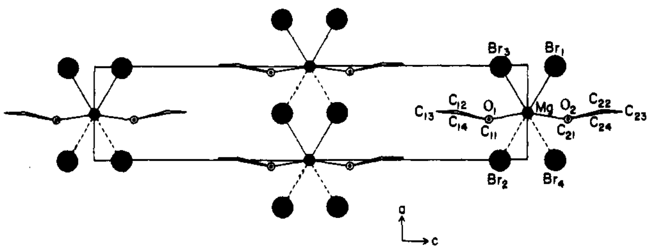


Figure 4. Orthorhombic **4** unit cell viewed along the perpendicular to the *ac* plane.

Table V. Some Interatomic Distances (Å) and Angles (deg), and Their Standard Deviations (×10^3, in parentheses),[a] for Triclinic $MgBr_2(C_4H_8O)_4(H_2O)_2$.

(i) Distances within One Formula Unit			
Mg-O(5)	2.042 (10)	Mg-O(1)	2.117 (7)
Mg-O(6)		Mg-O(3)	
		Mg-O(2)	2.164 (7)
Mg-Br(1)[b]	4.651 (3)	Mg-O(4)	
Mg-C(24)	3.152 (16)	Mg-C(22)	4.403 (17)
Mg-C(11)	3.158 (11)	Mg-C(13)	4.406 (15)
Mg-C(21)	3.212 (13)	Mg-C(23)	4.421 (18)
Mg-C(14)	3.213 (10)	Mg-C(12)	4.435 (15)
Br(1)-O(5)	3.218 (8)	Br(1)-O(1)	3.890 (12)
		Br(1)-O(4)	4.746 (10)
Br(1)-C(11)	3.957 (22)	Br(1)-C(14)	4.196 (23)
Br(1)-C(44)	4.106 (15)	Br(1)-C(12)	4.254 (28)
		Br(1)-C(13)	4.403 (33)
O(5)-O(1)	2.917 (12)	O(1)-O(2)	3.017 (9)
O(5)-O(2)	2.951 (15)	O(2)-O(3)	3.037 (11)
O(5)-O(3)	2.966 (13)	O(5)-O(6)	4.084 (15)
O(5)-O(4)	3.000 (11)	O(1)-O(3)	4.234 (9)
		O(2)-O(4)	4.328 (10)
O(1)-C(11)	1.440 (14)	O(2)-C(21)	1.436 (21)
O(1)-C(14)	1.515 (12)	O(2)-C(24)	1.463 (24)
C(11)-C(12)	1.536 (17)	C(21)-C(22)	1.484 (28)
C(12)-C(13)	1.382 (23)	C(22)-C(23)	1.497 (42)
C(13)-C(14)	1.514 (20)	C(23)-C(24)	1.557 (19)
(ii) Distances between Atoms in Adjacent Formula Units			
O(6)···Br(1)	3.221 (8)	C(11)···Br(1)	4.188 (22)
O(1)···Br(1)	3.926 (12)	C(13)···Br(1)	4.288 (33)
C(24)···Br(1)	4.019 (15)	Mg···Br(1)	4.631 (3)
C(14)···Br(1)	4.031 (23)	O(2)···Br(1)	4.679 (10)
		C(12)···Br(1)	4.447 (28)
(iii) Angles within One Formula Unit			
O(1)-Mg-O(5)	89.03 (0.40)	O(4)-Mg-O(5)	90.95 (0.40)
O(3)-Mg-O(5)	90.97 (0.40)	O(1)-Mg-O(2)	89.62 (0.42)
O(2)-Mg-O(5)	89.05 (0.40)	O(1)-Mg-O(4)	90.38 (0.42)
Br(1)-Mg-O(5)	35.58 (0.20)	Br(1)-Mg-O(2)	100.87 (0.23)
Br(1)-Mg-O(1)	56.09 (0.23)	Br(1)-Mg-O(4)	79.13 (0.23)
Mg-O(1)-C(11)	124.12 (0.80)	Mg-O(2)-C(21)	125.13 (0.80)
Mg-O(1)-C(14)	123.59 (0.80)	Mg-O(2)-C(24)	119.42 (0.70)
C(11)-O(1)-C(14)	112.28 (1.13)	C(21)-O(2)-C(24)	115.44 (1.14)
O(1)-C(11)-C(12)	105.40 (1.14)	O(2)-C(21)-C(22)	104.35 (1.12)
C(11)-C(12)-C(13)	107.58 (1.15)	C(21)-C(22)-C(23)	105.36 (1.12)
C(12)-C(13)-C(14)	113.55 (1.13)	C(22)-C(23)-C(24)	107.36 (1.12)
C(13)-C(14)-O(1)	101.06 (1.11)	C(23)-C(24)-O(2)	100.34 (1.11)

[a] The sd in the distances refer to the least significant digits. [b] In this and in subsequent entries the second identical distance between corresponding pairs of atoms related by the center of inversion (Table III) is omitted.

bromine atoms of an adjacent formula unit provide the ligands to the metal. The skeletal geometry about the magnesium is that of a fairly distorted octahedron. The crystal is polymeric, i.e., an infinite array of bromine-bridged formula units. This is a situation in which two of the four bromine ligands (inner-sphere atoms) are joined to the metal by intraformula unit bonds, and two by interformula unit bonds.

For comparison, the data given by Perucaud and LeBihan[16] for their tetragonal complex 1 have been illustrated in Figures 5 and 6. The magnesium atom is six-coordinate, with oxygens from four THF rings and two bromine atoms providing the ligands. The skeletal geometry about the metal is that of a nearly perfect octahedron. There are distinct molecules in this crystal, with the two bromine ligands being joined to the metal by intramolecular bonds. The similarities, and also the significant differences, between the structures of the tetragonal

Table VI. Some Interatomic Distances (Å) and Angles (deg), and Their Standard Deviations (×10^3 in Parentheses), for Orthorhombic $MgBr_2(C_4H_8O)_2$.

(i) Distances within One Formula Unit			
Mg-O(1)	2.126 (13)	Mg-Br(1)	2.633 (13)
Mg-O(2)		Mg-Br(3)	
Mg-C(11)[a]	3.147 (20)	Mg-C(12)	4.368 (20)
Mg-C(14)	3.169 (19)	Mg-C(13)	4.425 (19)
Br(1)-O(1)	3.531 (24)	Br(1)-O(2)	3.532 (24)
Br(1)-Br(3)	3.662 (2)		
Br(1)-C(21)	3.484 (35)	Br(1)-C(24)	4.755 (34)
Br(1)-C(14)	3.704 (41)	Br(1)-C(22)	4.795 (25)
Br(1)-C(23)	3.898 (32)	Br(1)-C(13)	4.898 (31)
Br(1)-C(11)	4.556 (29)		
O(1)-C(11)	1.476 (27)	C(11)-C(12)	1.470 (27)
O(1)-C(14)	1.448 (27)	C(12)-C(13)	1.571 (32)
		C(13)-C(14)	1.454 (23)
(ii) Distances between Bridging Bromines and Atoms in Adjacent Formula Unit			
Br(2)···Mg	2.799 (14)		
Br(4)···Mg			
Br(2)···O(2)[a]	3.348 (22)	Br(2)···O(1)	3.350 (22)
Br(2)···Br(3)	4.01 (2)	Br(2)···C(14)	4.582 (31)
Br(2)···C(24)	3.479 (37)	Br(2)···C(21)	4.741 (33)
Br(2)···C(11)	3.723 (38)	Br(2)···C(12)	4.943 (26)
Br(2)···C(13)	3.993 (26)	Br(2)···C(23)	4.974 (32)
(iii) Distances between Atoms in Adjacent Formula Units			
C(14)···C(14)	3.697 (34)	O(1)···O(1)	4.218 (42)
O(1)···C(11)	3.909 (37)	Mg···O(1)	4.294 (42)
Br(2)···C(12)	4.129 (41)	O(1)···C(14)	4.223 (43)
		C(12)···C(12)	4.481 (43)
(iv) Angles Involving Atoms in the Same and in Adjacent Formula Units			
Br(1)-Mg-O(1)	95.20 (0.72)	Br(2)-Mg-O(1)	84.53 (0.71)
Br(1)-Mg-O(2)	95.24 (0.72)	Br(2)-Mg-O(2)	84.49 (0.71)
Br(1)-Mg-Br(3)	88.09 (0.50)	Br(2)-Mg-Br(4)	81.70 (0.50)
O(1)-Mg-O(2)	165.46 (0.95)	Br(1)-Mg-Br(4)	95.10 (0.50)
		Br(1)-Mg-Br(2)	176.80 (0.50)
Mg-O(1)-C(11)	120.70 (1.55)	Mg-O(1)-C(14)	123.43 (1.60)
C(11)-O(1)-C(14)	111.84 (2.07)	C(11)-C(12)-C(13)	109.50 (2.33)
O(1)-C(11)-C(12)	106.60 (2.22)	C(12)-C(13)-C(14)	106.82 (2.61)
		C(13)-C(14)-O(1)	103.75 (2.50)

[a] In this and in subsequent entries the second identical distance between corresponding pairs of atoms related by a diad axis (Table IV) is omitted.

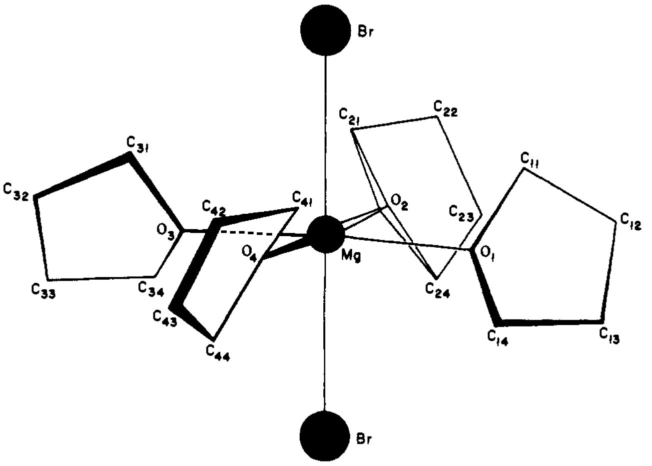


Figure 5. Computer generated drawing of the formula unit of tetragonal $MgBr_2(C_4H_8O)_4$ (**1**) from data in ref 16.

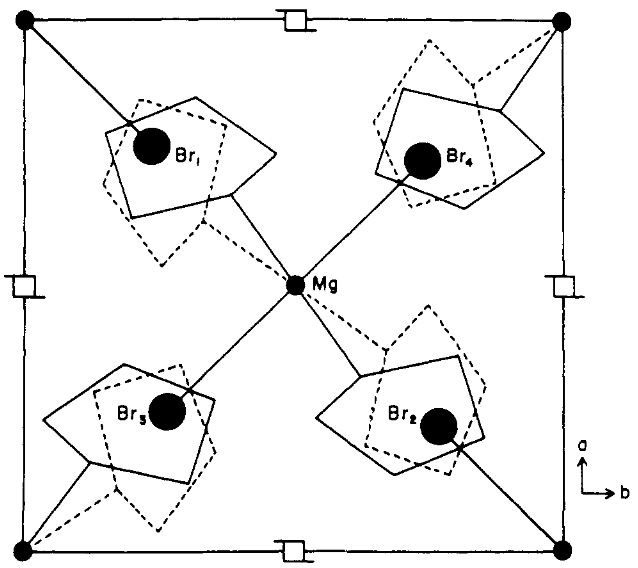


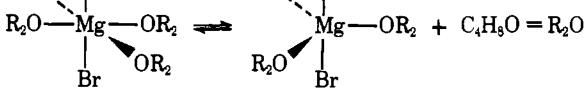
Figure 6. Projection of the unit cell contents of the tetragonal crystals **1** viewed along the perpendicular to the *ab* plane (data from ref 16).

(**1**) and the triclinic (**3**) complexes will be discussed below. Note also the "falling domino" effect of the four THF rings in **1** (Figure 5); this effect is carried to an extreme in the case of **3** (Figure 1), possibly to accommodate the bromine atoms and the water.

Comparisons between the three complexes **1**, **3**, and **4** are summarized in Table VII. Note, in particular, the differences between inner and outer sphere Mg-Br interatomic distances, the latter being 4.651 (3) Å in the triclinic complex **3**.

Discussion

The data presented in this paper show that the Mg^{2+} in a crystalline compound is capable of binding different numbers of the same uncharged, aprotic, donor molecule, e.g., THF, in the presence of the same counterion, Br^-, depending on the nature of the *aprotic medium* from which the compound crystallizes. The Mg^{2+} can retain its six coordination, and yet give rise to molecular or to polymeric crystals, as in the 4THF complex **1** vs. the 2THF complex **4**. Or the Mg^{2+} may change to five coordination, as is probably the case in the 3THF complex **2**. Although this latter structure is still speculative, the elegant work of Vallino[4] on $CH_3MgBr(C_4H_8O)_3$ justifies the analogy. There is little doubt that in anhydrous THF solution the following equilibrium exists, since one can obtain either the microcrystalline powder **2** or the tetragonal crystals **1** by allowing crystallization to occur above ca. 30 °C or below 5 °C, respectively.[14]



1 **2**

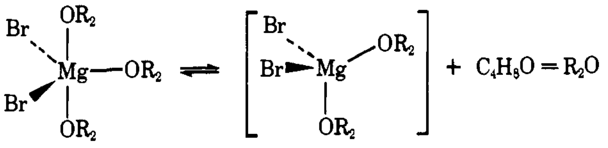
When the 3THF complex **2** is placed in dichloromethane solution, a THF molecule is lost; addition of hexane, benzene,

Table VII. Geometry About the Metal in Magnesium Bromide-Tetrahydrofuran Complexes

Complex	Coordination No. and ligands	Main bond distances, Å, and angles, deg,
Tetragonal $MgBr_2(C_4H_8O)_4$	Six	Mg-O = 2.165[a]
	4 oxygens from THF	Mg-Br = 2.625[b]
	2 bromines	O-Mg-O = 90
		Br-Mg-O = 90
Triclinic $MgBr_2(C_4H_8O)_4(H_2O)_2$	Six	Mg-O = 2.117[c]
	4 oxygens from THF	Mg-O = 2.164[c]
	2 oxygens from Water	Mg-O = 2.042[d]
		O-Mg-O = ~90
Orthorhombic $MgBr_2(C_4H_8O)_2$	Six	Mg-O = 2.126[b]
	2 oxygens from THF	Mg-Br = 2.633[e]
	4 bromines	Mg···Br = 2.799
		Br-Mg-O = ~85, 95
		Br-Mg-Br = ~82, 88, 95

[a] Three others related by two diad axes. [b] Another related by a diad axis. [c] Two others related by center of inversion. [d] Another related by center of inversion. [e] Two others related by diad axis.

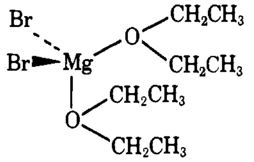
or diethyl ether to the solution induces crystallization of the polymeric 2THF complex **4**. This observation can be accommodated by the hypothesis that a permutational isomer of **2**, namely **2′**, ejects THF from its apical position.



2′

polymerizes to **4**

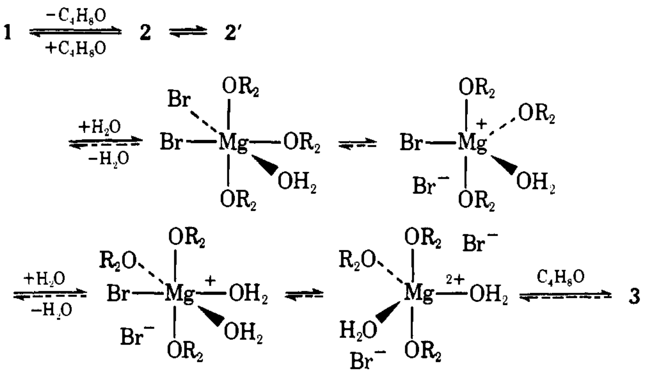
Schibilla and LeBihan[20] have described a complex, $MgBr_2[O(C_2H_5)_2]_2$, which consists of independent molecules



with distorted tetrahedral four-coordinate magnesium bonded to two bromine atoms and two ether oxygens. The Mg-O distances are normal,[18,19] 2.16 and 2.13 Å, but the Mg-Br distances are rather long, 3.18 and 3.32 Å, almost intermediate between the distances found for the inner-sphere bromines in complexes **1** and **4** and the outer-sphere bromine in complex **3**. The $MgBr_2[O(C_2H_5)_2]_2$ structure is unstable at 23 °C, and apparently it is incapable of achieving stabilization by bromine bridging as in complex **4**. This difference in behavior may simply reflect steric differences, i.e., the magnesium atom is more crowded when it is coordinated to the noncyclic ether than to the cyclic analogue.

The present study also discloses the tendency of Mg^{2+} to bind an uncharged protic ligand, such as water, while retaining its six coordination and the molecular character of its crystal, as in the $4THF \cdot 2H_2O$ complex **3**. This compound is obtained when limited amounts of water are introduced into the THF solution of the 3THF complex **2** or the 4THF complex **1**. This process represents a double nucleophilic substitution of the bromine ligands in **1** by water to yield **3**; the following speculative dissociative mechanism accommodates the results (Scheme I). In this mechanism, which conforms to microscopic reversibility, the entering ligand (H_2O) approaches the five-coordinate metal complex in the equatorial plane of the trigonal bipyramid, with a collinear ("in line") entry-departure stereochemistry, to yield the two new sets of six- and five-coordinate complexes required to produce the observed complex **3**, after addition of the final THF molecule.

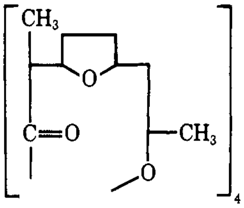
Scheme I



In the dissociations **1** ⇌ **2** + C_4H_8O and **2**, **2′** ⇌ **4** + C_4H_8O, the leaving group is a THF molecule. These processes occur in anhydrous low dielectric media, THF or dichloromethane (plus hexane, benzene, or diethyl ether). In the substitution **1** + $2H_2O$ → **3**, the first step is also a loss of THF, but subsequent steps involve the separation of Br^- from the corresponding six-coordinate magnesium. The rationale for this change in the nature of the leaving group is that the presence of water as one of the ligands significantly alters the character of the magnesium atom and facilitates the charge separation that develops in **3** (note the Mg-Br interatomic distance of 4.651 Å).

The triclinic complex **3** cannot be transformed into any of the other complexes, **1**, **2**, or **4**. On the other hand, when a THF solution of the orthorhombic complex **4** is treated with limited amounts of water, the triclinic complex **3** is produced. All the complexes, **1**-**4**, are rapidly converted into $MgBr_2(H_2O)_6$ in aqueous solution.

In summary, the ability of Mg^{2+}, in combination with a given anion, Br^-, to associate with a variable number of aprotic and protic ligands, THF and H_2O, gives rise to a series of complexes, **1**-**4** and $MgBr_2(H_2O)_6$, which have quite different crystal and molecular structures. These differences are reflected in differences in properties,[14] not only those which depend on the structure of the molecule itself, but also those which are related to intermolecular forces. Although the structure of a complex in the crystalline state and in solution may be quite different, this is not necessarily the case,[21,22] in particular for solutions of molecular crystals in aprotic solvents of relatively low polarity. These are basic considerations pertinent to the general problem of ionophoresis,[23] i.e., the transport of metal ions across hydrophobic barriers in general and biomembranes in particular. Keeping in mind the differences between simple aprotic organic solvents and the phospholipids of biomembranes, it is reasonable to expect that ionophoretic phenomena are intimately connected with crystal and molecular properties of the metal salt complex. The well known ionophore nonactin[24] is a simple tetracarboxylic ester containing four THF units per molecule. Lasalocid (X537A)[25] also contains THF units in its molecule, in addition to salicylic acid functions, which can provide the anion as well as the aprotic and protic donors to a suitable metal ion in complex formation. Aprotic functions, such as ethers (R_2O), thio ethers (R_2S), and tertiary amines (R_3N), and protic functions, such as alcohols, phenols, primary and secondary amines, as well as salt-forming groups, like carboxylic acids and phosphodiesters, are present in many ionophores, as well as in the



nonactin

biomembranes themselves. The ability of the Mg^{2+} ion to form anhydrous as well as partly hydrated salt complexes with some of these functions, including the phosphate of phospholipids, especially cardiolipins,[26,27] is an important datum in considerations of biological Mg ionophoresis.

Supplementary Material Available: structure factors for the triclinic and orthorhombic crystals (18 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Alkyl and Aryl Elimination from η^5-Cyclopentadienylalkyl(and -aryl)dicarbonyliron(II) Complexes Initiated by Mercury(II) Halides

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Abstract: The reactions of η^5-$C_5H_5Fe(CO)_2R$ (R = alkyl and aryl) with HgX_2 (X = Cl, Br, or I) in organic solvents (usually THF or isopropyl alcohol) were found to proceed by three distinct pathways, affording the following products: (1) η^5-$C_5H_5Fe(CO)_2X$ and RHgX, (2) η^5-$C_5H_5Fe(CO)_2HgX$ and RX, and (3) Hg_2X_2 and various substances derived from decomposition of the oxidized η^5-$C_5H_5Fe(CO)_2R$. The observed pathway(s) for the cleavage of the Fe–R bond depends principally on the ligand R. Accordingly, primary alkyl and aryl groups cleave mainly via reaction 1; secondary and tertiary alkyl, benzyl, and allyl groups react either exclusively or substantially by path 2; and the good electron releasing groups $CH(CH_3)_2$ and $CH_2C(CH_3)_3$ display the redox behavior of path 3. The rates of these cleavage reactions were monitored by infrared and ^1H NMR spectroscopy, mostly at 25 °C. Third-order kinetics, first order in η^5-$C_5H_5Fe(CO)_2R$ and second order in HgX_2, were found for reactions 1 and 2 in THF or isopropyl alcohol, whereas second-order kinetics, first order in each of η^5-$C_5H_5Fe(CO)_2R$ and HgX_2, were found for reaction 3. Generally, the rate constants increase with the more negative values of the Taft σ^* of the alkyl group or σ^+ of the aryl group, indicative of the electrophilic nature of these cleavages. A positive salt effect and a large solvent effect, THF (1) $\ll$ isopropyl alcohol or acetone ($\sim 10^3$) $\ll$ nitrobenzene ($\sim 10^5$), were found in all cases. A mechanism is proposed which involves reversible addition of HgX_2 to the metal in η^5-$C_5H_5Fe(CO)_2R$, followed either by decomposition of the adduct to products (path 3) or by reaction with another molecule of HgX_2 to give $[\eta^5\text{-}C_5H_5Fe(CO)_2(HgX)R]^+HgX_3^-$. This second intermediate then undergoes reductive elimination of RHgX (path 1) or dissociation of R^+ (path 2) to afford the observed products. Consistent with the proposed mechanism, the reaction by path 2 between the optically active η^5-$C_5H_5Fe(CO)_2{}^*CH(CH_3)C_6H_5$ and $HgCl_2$ yields racemic $C_6H_5(CH_3)CHCl$.

Cleavage reactions of transition metal–carbon σ bonds (M–R), both eliminative,

$$M\text{-}R + ex \rightarrow M\text{-}X + ER$$

and insertion-like,

$$M\text{-}R + EX \rightarrow M\text{-}X\text{-}E\text{-}R$$

are processes of great importance in catalysis and stoichiometric synthesis.[2-4] Although the literature abounds in examples of such reactions, there is relatively little known about their mechanisms.

We have recently been engaged in a systematic investigation of mechanisms of cleavage reactions of η^5-$C_5H_5Fe(CO)LR$ (L = CO or P donor ligand) and related complexes with vari-