Mg–Mg Bonds

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$MgCl$ and Mg_2Cl_2: From Theoretical and Thermodynamic Considerations to Spectroscopy and Chemistry of Species with Mg–Mg Bonds**

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Recently, compounds containing metal–metal bonds between main-group elements have attracted interest to a surprising extent.[1–5] In spite of the latest structural results for two crystalline Mg_2R_2 compounds ($R1 = [ArNC(NiPr_2)NAr]^-$; $R2 = [\{ArNCMe\}_2CH]^-$; Ar = 2,6-diisopropylphenyl, *i*Pr = isopropyl)[2] and in spite of a number of theoretical contributions on molecules with Mg–Mg bonds,[10–12] several important questions still remain to be answered, for example, concerning the unexpected disproportionation stability of the abovementioned Mg^I compounds. Herein, we present the following results: 1) On the basis of quantum-chemical-assisted thermodynamic calculations, a feasible synthesis of radical monomeric Mg^I halides at temperatures near 900 °C is presented. 2) The nature of the Mg–Mg bond is investigated by spectroscopic examination of MgCl and its linear dimer Mg_2Cl_2 in solid inert-gas matrixes; the Mg–Mg dissociation energy is obtained. 3) By comparing the thermodynamics of Mg_2Cl_2 (**1**), Mg_2Cp_2 (**2**, Cp = cyclopentadienyl), and a model compound $Mg_2R^*_2$ (**3**, $R^* = C(NH_2)(NCH_3)_2)$) analogous to crystalline $Mg_2(R1)_2$, the enormous disproportionation stability of the latter compound is explained. For further investigations, for example in the field of metal-rich Mg_nR_m clusters ($n > m$), the synthesis of reactive starting materials like MgCl is absolutely necessary. Initial results on the synthesis of MgCl are reported.

After the first evidence for stable alkaline earth(I) halides were shown to be erroneous about 50 years ago,[13] about 40 years ago the first ESR spectroscopic evidence was given for MgF, among other examples, as a gaseous molecule at a temperature of 2300 °C trapped in an inert-gas matrix.[18] For this purpose, MgF_2 was vaporized at about 1250 °C; subsequently, the gaseous MgF_2 molecules were dissociated to MgF and F atoms at about 2350 °C.[19] To find a feasible synthesis technique in analogy to the synthesis of AlCl at approximately 900 °C,[6] there should be no further component (e.g. Mg(g)) in the equilibrium composition besides gaseous MgCl and $MgCl_2$, otherwise the entropically favored formation of monohalides would be put at risk. In contrast to the entropically favored endothermic formation of AlCl ($Al(l) + AlCl_3(g) \rightarrow 3\,AlCl(g)$), the Mg vapor pressure is already 1.5 mbar at 800 °C; thus, we looked for a solid magnesium-containing compound with a significantly reduced Mg activity; for example, with a low decomposition pressure. We chose MgB_2, a well-known compound with unexpected superconducting capabilities,[21–23] as its Mg partial pressure had been examined in detail and amounts to not more than 10^{-3} mbar at 800 °C.[24–27]

In principle, the following reactions to produce $MgCl_2$ and MgCl could take place when HCl is passed over heated MgB_2 [Eq. (1), (2)].[28]

$$2\,MgB_2(s) + 2\,HCl(g) = H_2(g) + 2\,MgCl(g) + 4\,B(s) \qquad (1)$$

$$MgB_2(s) + 2\,HCl(g) = H_2 + MgCl_2(g) + 2\,B(s) \qquad (2)$$

The subtraction of Equation (2) from Equation (1) yields the relevant components for the equilibrium presented in Equation (3).[29]

$$MgB_2(s) + MgCl_2(g) = 2\,MgCl(g) + 2\,B(s) \qquad (3)$$

Finally, supported by several experiments on the thermal stability of MgB_2[24–26,30] as well as by quantum-chemical calculations on MgCl and Mg_2Cl_2, the temperature-dependent partial pressure curves of $MgCl_2$, MgCl, and Mg_2Cl_2 are obtained (Figure 1). Figure 1 also contains the decomposition pressure curve for MgB_2; that is, for all hypothetical model reactions discussed herein, the applied HCl pressure must be higher than the partial pressure of magnesium. When HCl is passed over MgB_2 at approximately 700 °C and when this gas phase, together with a large surplus of inert gas (N_2, Ar), is trapped on a copper surface cooled to 10 K, the Raman spectrum shown in Figure 2 results. An IR spectrum is obtained analogously (see the Supporting Information). Besides the well-known bands in $MgCl_2$ and its oligomers,[31] this spectrum displays only two further absorptions, which are assigned to monomeric and dimeric MgCl (Table 1). In the case of linear ($D_{\infty h}$) Mg_2Cl_2, the IR spectrum shows the antisymmetric MgCl vibration (ν_3) at 485 cm^{-1}; its $^{35}Cl/^{37}Cl$ shift (although partially hidden) is in accordance with the calculated values (see Table 1 and the Supporting Information). The vibration of monomeric MgCl is, as expected, red-

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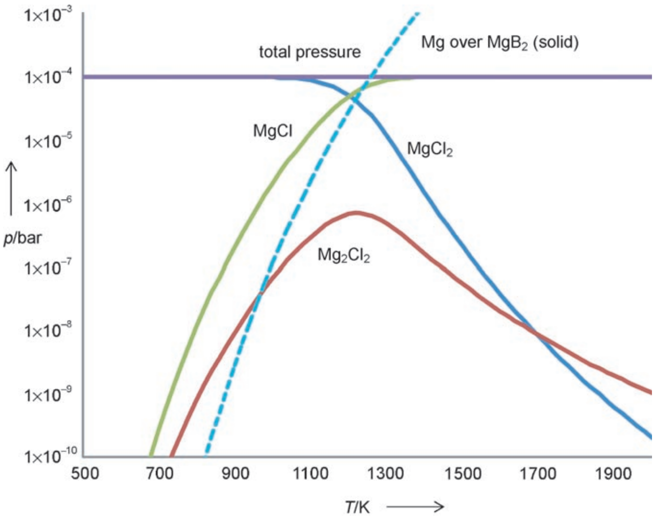

Figure 1. Partial pressures in the HCl/MgB_2(s) system ($p_{tot} = 0.1$ mbar) and the dissociation vapor pressure of MgB_2. The calculated values relate to the following reactions: $2\,MgCl(g) + 2\,B(s) = MgCl_2(g) + MgB_2(s)$ ($\Delta_R H = -264.4\ kJ\,mol^{-1}$, $\Delta_R S = -173.95\ J\,mol^{-1}\,K^{-1}$) and $2\,MgCl(g) = Mg_2Cl_2(g)$ ($\Delta_R H = -198.3\ kJ\,mol^{-1}$, $\Delta_R S = -118.1\ J\,mol^{-1}\,K^{-1}$).

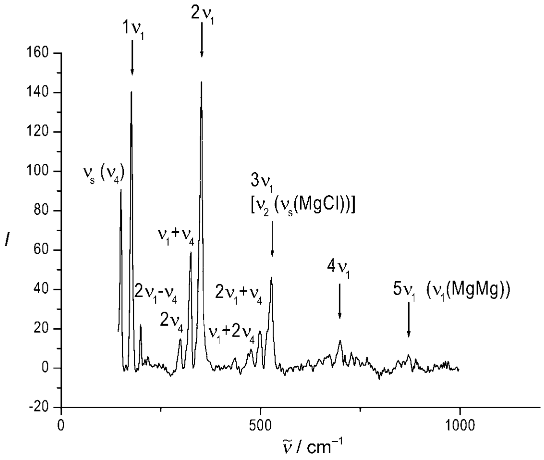

Figure 2. Raman spectrum of Mg_2Cl_2 ($D_{\infty h}$) in solid N_2 (excitation wavelength 488 nm). The Mg–Mg vibrations (ν_1, $2\,\nu_1$, $3\,\nu_1$, $4\,\nu_1$, $5\,\nu_1$) are marked by arrows (see Table 1).

shifted to $456.1\ cm^{-1}$ from the well-known value of $457.9\ cm^{-1}$[32] in the gas phase. In these IR spectra, the ratio of the absorption intensities of the MgCl vibrations of $MgCl_2$, MgCl, and Mg_2Cl_2 is 34:2:1. Taking into account the calculated IR intensities, a ratio $MgCl_2$/MgCl/Mg_2Cl_2 of 7:1:0.14 is estimated in this spectrum, which is in good accordance with the ratio of the partial pressures for these species at 830 °C, considering the rough estimation for the thermodynamic approach discussed above.[33]

Although the IR spectrum confirms the calculated gas-phase composition, the Raman spectrum is vital for the characterization of ClMgMgCl, as it displays surprisingly high band intensities owing to a resonance Raman effect (Figure 2). The Mg–Mg vibration ($\nu_1[\Sigma_g]$) is observed at $176\ cm^{-1}$, the symmetric Mg–Cl vibration ($\nu_2[\Sigma_g]$) at $527\ cm^{-1}$, and the symmetric ClMg–MgCl deformation vibration ($\nu_4[\Pi_g]$) at $150\ cm^{-1}$. Several overtones and combination modes are also observed (Table 1). This assignment is

Table 1: Vibrational frequencies (cm^{-1}) of MgCl, $MgCl_2$, and Mg_2Cl_2 determined experimentally (see text and reference [31]) and theoretically.[a]

	IR/Ar matrix	Raman/N_2 matrix/488 nm (Ar matrix/488 nm)	Theory		
			MgCl	$MgCl_2$	Mg_2Cl_2
ν_3 ($\nu_{as}(MgCl_2)[MgCl_2]$), sites[b]	596.9/581.4/567.0			628.7 (129/0)	
$(MgCl_2)_2$[b]	503.3				
ν_3 ($\nu_{as}(MgCl)[Mg_2Cl_2]$)[c]	485.0				470.5 (162/0)
$\nu(MgCl)[MgCl]$	456.1 (gas:457.92)		452.0 (53/16)		
$(MgCl_2)_2$[b]	371.2				
ν_1 ($\nu_s(MgCl_2)[MgCl_2]$)[b]	327.8			322.6 (0/10)	
$(MgCl_2)_2$[b]	265.2/254.6				
$5\,\nu_4[Mg_2Cl_2]$		872.0			
$4\,\nu_4[Mg_2Cl_2]$		699.3			
ν_2 ($\nu_s(MgCl)[Mg_2Cl_2]$) and/or $3\,\nu_4[Mg_2Cl_2]$		526.7 (531)			537.3 (0/14)
$2\,\nu_1 + \nu_4[Mg_2Cl_2]$		496			
$\nu_1 + 2\,\nu_4[Mg_2Cl_2]$		478			
$2\,\nu_1[Mg_2Cl_2]$		352.0 (355)			
$\nu_1 + \nu_4[Mg_2Cl_2]$		325.5			
$2\,\nu_4[Mg_2Cl_2]$		297			
$2\,\nu_1 - \nu_4[Mg_2Cl_2]$		199.6			
ν_1 ($\nu(MgMg)[Mg_2Cl_2]$)[d]		176.2 (178.0)			170.4 (0/39)
ν_4 $\delta_s(Mg_2Cl)[Mg_2Cl_2]$)[e]		150.3 (146.9)			113.0 (0/10)
ν_3 ($\delta(MgCl_2)[MgCl_2]$)				115.2 (54/0)	
ν_5 ($\delta_{as}(Mg_2Cl)[Mg_2Cl_2]$)					50.4 (44/0)

[a] The calculated IR and Raman intensities are given in parentheses ($km\,mol^{-1}$ and $Å\,amu^{-1}$). The normal vibrations are graphically depicted in the Supporting Information.[58] In accordance with the measured frequencies, the following internal valence force constants ($mdyn\,Å^{-1}$) were calculated: f(MgCl): 2.12 ($MgCl_2$), 1.91 (Mg_2Cl_2), 1.74 (MgCl); f(MgMg): 0.65 (Mg_2Cl_2). [b] Reference [31]. [c] Isotope splitting $Mg_2{}^{35}Cl_2/Mg_2{}^{35}Cl^{37}Cl$ (ν_3): 2.5 (exptl), $2.6\ cm^{-1}$ (theor). [d] Isotopic splitting $Mg_2{}^{35}Cl_2/Mg_2{}^{35}Cl^{37}Cl$ (ν_1): 2.2 (exptl), $1.8\ cm^{-1}$ (theor). [e] Isotopic splitting $Mg_2{}^{35}Cl_2/Mg_2{}^{35}Cl^{37}Cl$ (ν_4): 0 (exptl), $0.1\ cm^{-1}$ (theor)

Table 2: Structural parameters (pm) determined by quantum-chemical calculations (B3-LYP, DZP), total energies (a.u.), dimerization, and disproportionation energies ($2\,MgR(g) = Mg_2R_2(g)$ or $Mg_2R_2(g) = Mg(g) + MgR_2(g)$, given in $kJ\,mol^{-1}$), partial charges and shared electron numbers (SEN).[a]

	$MgCl_2$	Mg_2Cl_2 (**1**)	MCl	$MgCp_2$	Mg_2Cp_2 (**2**)	MCp	$MgR*_2$	Mg_2R*_2 (**3**)	MR*
Symmetry	$D_{\infty h}$	$D_{\infty h}$	$C_{\infty v}$	D_{5d}	D_{5d}	C_{5v}	D_{2d}	D_{2d}	C_{2v}
E_{tot}	−1120.632440	−1320.746554	−660.335524	−587.178654	−787.291531	−393.607558	−766.959937	−967.054762	−483.491164
r(MgR)	218.5	221.0	223.2	202.5	205.5	206.5	207.2	208.5	207.7
r(MgMg)		276.6			276.3			284.7	
$E_{dim.}$		−198.2			−200.6			−190.2	
$E_{disprop.}$		55.2			52.0			4.6	
SEN(MgCl)	0.59	1.06	1.10						
SEN(MgMg)	–	1.34	–						
q(Mg)	0.86	0.27	0.27						
q(Cl)	−0.43	−0.27	−0.27						

[a] In donor-stabilized **1**, $Mg_2Cl_2{\cdot}2\,NH_3$, the Mg–Mg separation is 283.1 pm, the Mg–Cl separations are 228.6 pm; $E_{disprop.}$ is calculated to be 5.3 $kJ\,mol^{-1}$.

supported by comparison of the calculated and measured $^{35}Cl/^{37}Cl$ isotope shifts (Table 1). These observations allow the Mg–Mg dissociation energy to be estimated at 197 $kJ\,mol^{-1}$ (see the Supporting Information) using the anharmonicity constant determined by the overtones of ν_1. Moreover, force constants based on experiments can be calculated (see Table 1 and the Supporting Information). All experimentally determined parameters, that is, force constants, Mg–Mg dissociation energy, and bond energies (BE; see Table 2 and the Supporting Information) correspond to the results obtained by quantum-chemical calculations (e.g. SEN, bond-length variations; Table 2). For instance, the calculated and measured bond energies and force constants of the MgCl bond decreases going from $MgCl_2$ to Mg_2Cl_2 to MgCl.

These experimentally determined structural parameters of an Mg–Mg bond, that is, force constant, vibration frequency, and dissociation energy, fit pleasingly into the element–element bonds in this row of the periodic table. The strong σ bond in the Cl_2 molecule gets significantly weaker in moving to the Na_2 molecule (Table 3).[36]

Table 3: Force constants f ($mdyn\,Å^{-1}$) and vibrational frequencies $\tilde{\nu}$ (cm^{-1}) of molecules containing element–element single bonds within the third row of the periodic table.[32]

	Na–Na [Na_2]	Mg–Mg [Mg_2Cl_2 **1**]	Al–Al	Si–Si	P–P	S–S	Cl–Cl [Cl_2]
f	0.17	0.65	1.1	1.6	2.0	2.6	3.2
$\tilde{\nu}$	159	176	373	440	460	520	557

In the experiments described above, the heating and vaporization of the inert-gas matrix results in disproportionation of the previously isolated $(MgCl)_n$ species and simultaneous formation of elemental magnesium. To understand this lability towards spontaneous disproportionation, which is in contrast to the stability of $Mg_2(R1)_2$ and $Mg_2(R2)_2$,[2] we investigated model reactions of Mg_2Cl_2, (**1**) Mg_2Cp_2 (**2**), and a model compound Mg_2R*_2 (**3**) theoretically. The calculated structural data for **1**, **2**, and **3**, which are in accordance with the published data,[10] are shown in Table 2 together with data for other compounds that are relevant for the bonding discussion. For the endothermic dissociation of **1**, **2**, and **3** into monomeric units, we obtained values of 198, 200, and 190 $kJ\,mol^{-1}$, which are in complete accordance with the spectroscopically determined value for **1** of 197 $kJ\,mol^{-1}$. The small differences between the calculated energy values are surprising, as the Mg–Mg separations within these compounds vary significantly (Table 1).

The relative stabilities of **1**, **2**, and **3** can be emphasized by the following calculated isodesmic reaction energies; model compound **3**, in line with the results for $Mg_2(R1)_2$ and $Mg_2(R2)_2$, is particularly stable:

$$Mg_2Cl_2\ (\mathbf{1}) + 2\,R^{*-} = Mg_2R^*_2\ (\mathbf{3}) + 2\,Cl^- \quad \Delta_R H = -268\ kJ\,mol^{-1} \quad (4)$$

$$Mg_2Cl_2\ (\mathbf{1}) + 2\,Cp^- = Mg_2Cp_2\ (\mathbf{2}) + 2\,Cl^- \quad \Delta_R H = -56\ kJ\,mol^{-1} \quad (5)$$

Disproportionation of **1**, **2**, and **3** to gaseous magnesium and $MgCl_2$, $MgCp_2$, or $MgR*_2$, results in endothermic energies of +55, +52, and +4.6 $kJ\,mol^{-1}$, respectively. However, as a vaporization enthalpy of 148 $kJ\,mol^{-1}$ is measured for solid magnesium,[20] all Mg–Mg compounds disproportionate exothermically into solid Mg and the corresponding Mg^{II} compounds. This effect confirms our first experiments to synthesize Mg_2Br_2 and Mg_2Cp*_2 ($Cp* = C_5Me_5$) as well as Mg_nBr_m and Mg_nCp*_m species: Solutions containing these compounds disproportionate even at −60°C by precipitation of Mg. In contrast, for Mg_2R*_2 (**3**; in analogy to the results for e.g. $Mg_2(R1)_2$) a kinetic barrier against disproportionation is expected owing to the chelate effect. Obviously, this kinetic stabilization is significantly higher than the thermodynamically favored disproportionation, and it is higher than expected considering the long Mg–Mg separation for Mg_2R_2* (**3**, compared to Mg_2Cl_2 (**1**) and Mg_2Cp_2 (**2**)). As the calculated stabilization of Mg_2Cl_2 with donors like ammonia (e.g. $Mg_2Cl_2{\cdot}2NH_3$; Table 2) is very similar to that calculated for Mg_2R_2 (R = R1, R2, and R*), even a donor-stabilized Mg_2X_2 solution should be inert with respect to disproportionation. However, these expectations remained unfulfilled during preliminary experiments; that is, the pronounced inertness of $Mg_2(R1)_2$ and $Mg_2(R2)_2$ with respect to disproportionation can be attributed mainly to the strong chelate effect; only at extremely high temperatures will the magnesium–ligand bond break. This hypothesis concerning the extreme stability of, for example, $Mg_2(R1)_2$ or Mg_2R*_2

(which could be synthesized even from solid magnesium and dissolved $MgCl_2$ in an exothermal reaction (−170 kJ) in the presence of chelating R^{*-}) is also confirmed by the stability of chelate-stabilized Al^I and similar Ga^I compounds,[37–42] from which an approach to metal-rich compounds, that is, metalloid Ga_nR_m ($n > m$) cluster compounds, has not been observed to date. Therefore, to advance the field of metalloid magnesium clusters and thus create new potential for magnesium-rich compounds, the synthesis of non-chelate-stabilized reactive species (e.g. $Mg_2Cp^*_2$) is an absolute prerequisite. In preliminary synthesis experiments using the cocondensation technique,[6] we were able to demonstrate that, for example, donor-stabilized MgBr solutions precipitate solid Mg even at a temperature of −60 °C, and that they possess the expected radical character[43] (as demonstrated by ESR spectroscopy) as monomers or as Mg_nX_n species containing an odd number of metal atoms; this radical character can still be observed even after the substitution of bromide by $N(SiMe_3)_2$ moieties, for example. Investigations on the crystallization of Mg-rich species (e.g. $Mg_nCp^*_m$ ($n > m$)), which have proved to be extremely unstable during these first experiments, are the focus of our current research.

Experimental Section

Matrix isolation, IR, and Raman spectroscopy: By passing HCl over MgB_2(s) at a temperature of 700 °C, gaseous $MgCl_2$ and MgCl are formed. The high-temperature species are condensed on a helium-cooled copper surface (ca. 12 K) together with argon (IR, Raman spectroscopy) or N_2 (Raman spectroscopy) as matrix gas. During this process, dimeric MgCl is also generated. The cryostat and the experimental conditions have been described elsewhere.[34,35] The IR spectra were obtained using a Bruker IFS 113v FTIR spectrometer (DTGS detector, resolution 1 cm^{-1}). The Raman spectra were detected with the help of a Dilor XY800 spectrometer (CCD camera, Wright instruments, resolution 1.5 cm^{-1}). The 488 and 514.5 nm lines of an Ar^+ ion laser (Coherent, Innova 90–5) were used for excitation.

Quantum-chemical calculations: The theoretically investigated molecules were calculated by means of DFT (B3-LYP functional) using the TURBOMOLE suite of programs.[45,46–52] The basis sets were of double-ζ-plus-polarization (DZP) quality, as obtained from the TURBOMOLE basis-set library.[53] The DZP basis set of magnesium, however, was taken from the work of Schaefer and coworkers.[10] It contains a McLean–Chandler contraction (12s9p/6s5p) as well as a d-type polarization function ($\eta_d(Mg) = 0.175$). Only using this atomic basis set, which was obtained taking the Mg ^3P state into account, was a proper description of molecular Mg-containing molecules possible.[54]

The force-constant matrix and the vibrational frequencies were calculated using the module NumForce.[45] The IR and Raman intensities were determined using the program SNF.[55] Population analyses of the molecules MgCl, $MgCl_2$, and Mg_2Cl_2 were performed using the method of Ahlrichs and Heinzmann (number of modified atomic orbitals: Mg 7, Cl 9). This method delivers atomic partial charges as well as shared electron numbers (SEN), which provide a measure for the covalent bond strength.[56,57]

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(the formation of some MgB_4 crystals was confirmed by our experiments), the crossing point of the vaporization pressures of $p(MgCl_2)$ and $p(MgCl)$ is shifted to a small extent. A more precise calculation was not made so far owing to the controversial thermodynamic values obtained for MgB_n phases that might be relevant for the equilibrium.[23–25,28]

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