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Preparation of HMgX Compounds and Their Reactions with Alane and Borane in Tetrahydrofuran

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The preparation of hydridomagnesium halides (HMgX, where X = Cl or Br) by the reaction of magnesium halides with an active form of magnesium hydride in THF has been achieved. These products have been found to be soluble and stable in THF and ebullioscopic molecular weight studies show them to be dimeric in THF. The infrared spectra of HMgCl and HMgBr in THF solution showed a broad absorption at 1280 ± 20 cm^{-1} which is probably due to one of the MgH_2Mg stretching modes. The Mg–H stretching bands were determined by comparison of the HMgX spectra with the corresponding DMgX compounds. X-ray powder-pattern studies on the HMgX compounds indicate that dissociation into MgH_2 and MgX_2 occurs when the solvent is removed. Reaction of HMgX compounds with alane and borane in THF resulted in the formation of $XMgAlH_4$ and $XMgBH_4$, respectively. Their infrared spectra in solution and x-ray powder-pattern data of the solids are reported.

Introduction

Hydridomagnesium halides (HMgX, where X = halogen) represent a novel new class of compounds which have been highly sought after for sometime. Since MgH_2 is very insoluble in all solvents with which it does not react, it is not surprising that it reacts very poorly as a heterogeneous mixture with organic substrates that are normally easily reduced. The HMgX compounds, particularly if soluble in some solvent, could function as selective reducing agents toward organic substrates[2] and also as intermediates in the preparation of novel complex magnesium hydrides. Even more importantly these compounds might serve as substitute hydroboration reagents of greater selectivity toward olefins and alkynes.

Wiberg and Strebel[3] in 1957 reported the preparation of THF-soluble HMgCl and HMgBr by the reaction of ethyl Grignard reagents with diborane (eq 1). However, numerous

$$6RMgX + B_2H_6 \xrightarrow{THF} 6HMgX + 2BR_3 \quad (1)$$

attempts[4] to repeat the preparation of HMgX compounds according to the exact procedure of Wiberg and Strebel only resulted in the isolation of chloromagnesium borohydride (eq 2). Sometime later Dymova and Eliseeva[5] reported that

$$3C_2H_5MgCl + 2B_2H_6 \xrightarrow[25\ ^\circ C]{THF} 3ClMgBH_4 + B(C_2H_5)_3 \quad (2)$$

HMgX compounds could be prepared in diethyl ether as insoluble solids by the hydrogenolysis of ethylmagnesium halides. It is interesting that they reported these compounds disproportionate to MgH_2 and MgX_2 when THF is added since Wiberg and co-workers had reported their preparation in THF. We have also repeated this work in detail and have shown that the solid products obtained in these reactions involving diethyl ether as a solvent are actually physical mixtures of MgH_2 and MgX_2 as determined by x-ray powder-diffraction analysis.[6] A third route reported by Rice and co-workers[7] for the preparation of nonsolvated HMgBr involved the pyrolysis of ethylmagnesium bromide at elevated temperature. This report was supported by x-ray powder-pattern data. However, when we desolvated $MgBr_2{\cdot}Et_2O$ to correspond to the exact amount of ether present in $HMgBr{\cdot}0.27Et_2O$ (exact analysis of reaction product), the powder-diffraction pattern was the same showing that the $HMgBr{\cdot}0.27Et_2O$ was actually a physical mixture of MgH_2 and $MgBr_2{\cdot}0.54Et_2O$.[8]

Since our last report concerning the existence of HMgX compounds published in 1970, the existence of HMgX compounds has been in doubt. In this paper, we would now like to report that hydridomagnesium halides do exist, that they can be prepared readily, and that they react as would be predicted.

Experimental Section

Instrumentation. Manipulation of air-sensitive materials was accomplished by use of standard bench-top techniques and by the use of a dry box equipped with an atmosphere purification system for removal of oxygen and moisture.[9] X-ray powder-diffraction data were obtained using a Phillips Norelco x-ray unit, using an 11.46-cm diameter camera with Ni-filtered Cu Kα radiation. Exposure times were 6.0 h for all samples. *d* spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA–TGA studies were carried out under vacuum using a modified Mettler Thermoanalyzer II. Infrared spectra in THF solution were recorded on a Perkin-Elmer 621 high-resolution spectrophotometer using KBr cells.

Reagents. Tetrahydrofuran (Fisher Certified reagent) was distilled over sodium aluminum hydride immediately prior to use. Triply sublimed magnesium was obtained from the Dow Chemical Co. Lithium aluminum hydride and $LiAlD_4$ (Ventron Metal Hydrides Division) solutions in diethyl ether were prepared as described previously.[10] Aluminum hydride in THF was prepared by the reaction of 100% sulfuric acid on lithium aluminum hydride in tetrahydrofuran at −10 °C.[11] Borane in THF was obtained from Ventron Alfa Products. Diethylmagnesium and diphenylmagnesium were prepared by the reaction of diethyl- and diphenylmercury at 60 and 150 °C, respectively, in excess magnesium.[12] Magnesium chloride and magnesium bromide in THF and magnesium iodide in diethyl ether were prepared by the reaction of magnesium metal with the corresponding mercuric halides as described earlier.[8] X-ray powder patterns of magnesium halides were obtained by removing solvent under vacuum followed by vacuum drying at 25 °C (0.1 mm) for $^1/_2$ h.

Elemental Analyses. Hydridic hydrogen analysis was performed by hydrolyzing the solid or solution samples on a vacuum line and measuring the liberated hydrogen. Magnesium determinations were carried out by EDTA titration at pH 10 using Eriochrome Black T as an indicator. Aluminum was masked by complexation with triethanolamine when present together with magnesium. Aluminum analyses were carried out by addition of excess EDTA following by back-titrating at pH 4 in 50% ethanol with a solution of zinc acetate using dithizone as an indicator. Boron was analyzed as boric acid by the mannitol method. Halide was determined by Volhard titration.

Preparation of HMgCl by the Reaction of MgH_2 with $MgCl_2$ in 1:1 Ratio in THF. To a slurry of active MgH_2 (4.0 mmol) in THF was added 11.4 mL of a 0.35 M THF solution of $MgCl_2$ (4.0 mmol) dropwise with continuous stirring at room temperature. The reaction was exothermic and resulted in a clear solution within 15 min of stirring. This solution was analyzed and its infrared spectrum was recorded. Anal. Calcd for HMgCl: 1.00:1.00:1.00. Found: 0.98:1.00:1.04. The solvent was removed under vacuum and the white crystalline product was dried for 30 min at 25 °C (0.3 mm) and analyzed. Anal. Calcd for HMgCl·1.0THF: 1.00:1.00:1.00:1.00. Found: 0.98:1.00:1.02:1.00. The x-ray powder-diffraction pattern of the solid was recorded and the DTA–TGA was recorded.

Preparation of HMgBr by the Reaction of MgH_2 with $MgBr_2$ in 1:1 Ratio in THF. To a slurry of active MgH_2 (4.0 mmol) in THF was added 40.1 mL of a 0.10 M THF solution of $MgBr_2$ (4.0 mmol)

Table I. Infrared Data (THF Solution, cm^{-1})

HMgCl	DMgCl	HMgBr	DMgBr
1380 m	1390 m	1410 m	1405 m
1320 m		1380 m	1360 sh
1290 mb	1120 m	1345 m	950 mb
1120 m	940 s	1260 mb	800 sh
990 s	800 sh	1118 m	700 s
800 sh	700 s	1010 s	660 m
710 s	600 m	800 s	550 sb
600 m	550 sb	700 s	390 w
580-50 m	390 m	670 s	
396 m		570 mb	
		390 m	

Table II. Infrared Data (Solution Spectra, cm^{-1})

$ClMgAlH_4\cdot$ 4THF	$BrMgAlH_4\cdot$ 4THF	$ClMgBH_4\cdot$ 2THF	$BrMgBH_4\cdot$ 2THF
1715 s	1725 s	2375 s	2380 s
1410 w	1410 w	2230 m	2230 w
1120 w	1121 w	2158 s	2155 s
970 m	972 m	2060 w	2055 w
790 m	795 m	1420 w	1415 m
760 s	760 m	1365 m	1350 w
680 w		1115 w	1120 w
		1015 w	990 m
		830 w	810 w
		665 m	665 m
		395 s	385 s

dropwise with constant stirring at room temperature. The reaction was exothermic and gave a clear solution after 15 min of stirring. The solution was analyzed and its infrared spectrum was recorded. Anal. Calcd for HMgBr: 1.00:1.00:1.00. Found: 0.97:1.00:1.02. The THF solvent was removed under vacuum and the white crystalline product was dried under reduced pressure at 25 °C (0.1 mm) for $^1/_2$ h. The solid product was analyzed and its x-ray powder-diffraction pattern and DTA–TGA were recorded. Anal. Calcd for HMgBr·1.5THF: 1.00:1.00:1.00:1.50. Found: 0.95:1.00:1.02:1.42.

Attempted Preparation of HMgI. To a slurry of active MgH_2 (4.0 mmol) in ether was added 16 mL of a 0.25 M ether solution of MgI_2 (4.0 mmol) dropwise with stirring. The reaction mixture was stirred for 4 h and the insoluble solid as well as supernatant solution were analyzed. Solid Anal. Calcd for MgH_2: 1.00:2.00. Found: 1.00:1.95. Solution Anal. Calcd. for MgI_2: 1.00:2.00. Found: MgI = 1.00:2.01.

The above reaction was repeated using THF as solvent with stirring for 10 h. The insoluble solid was analyzed. Anal. Calcd for [(15% MgH_2) + (15% MgI_2) + (70% $MgI(OBu^n)$)]: 0.30:1.00:1.00:0.70. Found: $H:Mg:I:HOBu^n$ = 0.30:1.00:1.08:0.71. It seems that if at any stage HMgI was formed, it cleaved THF to give *n*-butoxy groups. The supernatant solution contained no magnesium, hydrogen or iodine.

Reaction of HMgX (X = Cl or Br) with Alane and Borane in 1:1 Ratio in THF. When alane or borane in THF was added dropwise to a well-stirred HMgX solution in THF at room temperature in 1:1 ratio, a clear solution resulted. Infrared spectra of these solutions were recorded (Table I). When the solvent was removed under vacuum, crystalline white solids were formed in each case. The products were analyzed (Table II) and x-ray powder patterns were recorded (Table IV).

In order to verify that the products were really $XMgAlH_4$ and $XMgBH_4$ and not a mixture of MgX_2 and $Mg(AlH_4)_2$ and $Mg(BH_4)_2$, respectively, fractional crystallization studies were carried out with the results shown in Table IV.

Results and Discussion

Previous workers attempting to prepare HMgX compounds employed elemental analysis, but particularly powder diffraction and solubility characteristics of the compounds, in order to determine whether the product was a single compound (HMgX) or a physical mixture (MgH_2 and MgX_2). In our earlier reports, we have shown that the reactions proposed by other workers as possible routes to HMgX compounds resulted in a physical mixture of MgH_2 and MgX_2 by establishing that the x-ray powder patterns of the so-called HMgX compounds are simply due to MgX_2 with the same amount of ether. However, in the present paper we report that HMgX compounds do exist in THF solution but disproportionate when removed from solution. It is interesting that the report by Russian workers[5] that HMgX compounds can be prepared in ether, but disproportinate in THF, was found to be just the opposite as we have been able to prepare and characterize HMgX compounds as stable THF-soluble compounds.

Table III. Analysis of the Products Formed by Reaction of HMgX with Alane or Diborane in THF

Reactants	Anal. (ratio) (Cl or Br):Mg:(Al or B):H:THF	Product
$HMgCl + AlH_3$	1.02:1.01:1.00:4.10:4.02	$ClMgAlH_4\cdot 4THF$
$HMgBr + AlH_3$	1.02:1.00:1.02:4.08:4.05	$BrMgAlH_4\cdot 4THF$
$2HMgCl + B_2H_6$	1.04:1.02:1.00:3.98:2.04	$ClMgBH_4\cdot 2THF$
$2HMgBr + B_2H_6$	1.03:1.01:1.00:4.01:2.10	$BrMgBH_4\cdot 2THF$

Table IV. X-Ray Powder-Pattern *d*-Spacing Data of Products of the Reactions of HMgX with AlH_3 or B_2H_6 in THF

$ClMgAlH_4\cdot$ 4THF	$BrMgAlH_4\cdot$ 4THF	$ClMgBH_4\cdot$ 2THF	$BrMgBH_4\cdot$ 2THF
11.5 m	11.7 s	9.6 w	9.0 m
9.4 m	9.71 m	8.2 w	8.3 w
8.7 w	8.05 s	7.0 w	8.0 m
8.0 m	7.12 s	5.6 w	5.95 w
7.3 w	6.19 m	5.5 w	5.60 m
7.0 m	4.39 vs	4.90 w	4.15 m
6.15 w	3.86 m	4.30 vw	3.90 m
5.80 w			3.82 m
5.24 w			3.45 w
4.70 w			3.05 w
4.10 s			2.52 w
3.80 w			2.37 w
2.93 m			2.32 vs
2.55 m			2.12 vw
1.80 w			

We would like to report that hydridomagnesium halides (HMgX, where X = Cl or Br) have been prepared by the reaction of magnesum halides with an active form of magnesium hydride slurried in THF. The active form of magnesium hydride was prepared by the reaction of Ph_2Mg or Et_2Mg with equimolar amounts of $LiAlH_4$ in diethyl ether (eq 3). The MgH_2 is very insoluble in ether whereas the

$$R_2Mg + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2R_2 \tag{3}$$

$$MgH_2 + MgX_2 \xrightarrow[RT]{THF} 2HMgX \tag{4}$$

$LiAlH_2R_2$ compound is quite soluble. The MgH_2 is filtered, washed with ether, and then slurried in freshly distilled THF. Addition of a THF solution of MgX_2 (where X = Cl or Br) to the slurry of MgH_2 in THF at room temperature results in an exothermic reaction and a clear solution within a few minutes. Since MgH_2 is very insoluble in THF, it is clear that reaction of the MgH_2 has taken place. This clear solution is stable at room temperature for 24 h without any evidence of THF cleavage. However, it has been observed that HMgBr does cleave THF at room temperature after 5 days (20% cleavage). Both HMgCl and HMgBr can be stored for longer times (30 days) without cleavage by storing in a refrigerator (−20 °C).

All attempts to prepare HMgCl and HMgBr from active MgH_2 and $MgCl_2$ or $MgBr_2$ in diethyl ether failed. No reaction was observed to take place. Because of the insoluble nature of MgI_2 in THF, an attempt was made to prepare HMgI by addition of a solution of MgI_2 in diethyl ether to MgH_2 slurry in diethyl ether. After stirring in ether with no evidence of reaction, THF was added producing an exothermic reaction. The reaction mixture was stirred for $^1/_2$ h after which time it was determined that some THF cleavage took place,

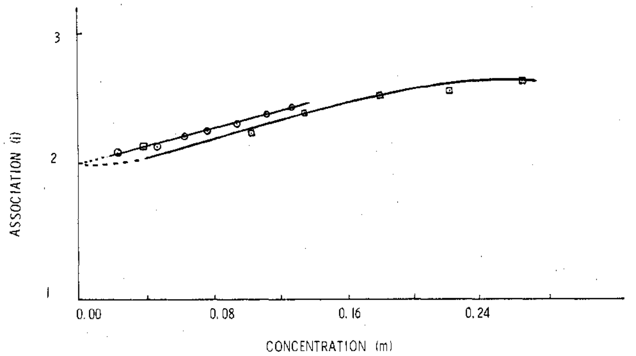

Figure 1. Molecular association studies of HMgCl (A) and HMgBr (B) in tetrahydrofuran.

but there was no evidence for a THF-soluble HMgI compound. After 10 h of reaction, about 70% cleavage was observed. An x-ray powder pattern of the reaction product showed strong lines due to $MgI_2 \cdot 6THF$ rather than the expected $HMgI \cdot 3THF$. The nonreactivity of MgH_2 toward MgI_2 in THF in $^1/_2$ h is probably due to the insoluble nature of MgI_2 in THF. The DTA–TGA data of this reaction product gave no hydrogen evolution at 300 °C, as expected for MgH_2 decomposition, but instead showed extensive decomposition expected of THF cleavage products (e.g., $Mg(OBu)_2$).

Contrary to earlier reports, HMgCl and HMgBr are quite soluble in THF. A 1.5 M solution of HMgCl in THF was prepared whereas HMgBr could only be prepared up to 0.50 M concentration. Ebullioscopic molecular weight studies on HMgCl and HMgBr in THF showed both compounds to be dimeric in dilute solution and gave some indication of associating further in more concentrated solution (Figure 1). Infrared spectra of HMgCl and HMgBr have been recorded in THF solution and the absorption bands are given in Table I. The spectra of HMgCl and HMgBr both contain a medium to strong absorption band in the region 1280 ± 20 cm^{-1}, which is not present in the spectrum of $MgCl_2$ or $MgBr_2$ in THF. This same band was absent in the spectrum of the deuterio-analogue compounds (DMgBr and DMgCl) in THF. However, a new band appeared at 930 cm^{-1} thus establishing the 1280-cm^{-1} band as the Mg–H absorption. The presence of the Mg–H stretching band in the region 1260–1300 cm^{-1} suggests the presence of bridging hydrogen atoms in the MgH_2Mg group by analogy with the vibrational modes of the BeH_2Be group in $RBeH$[13] and $HBeCl$[14] compounds. A strong band present at 700 cm^{-1} in the spectra of HMgCl and HMgBr is probably due to the deformation mode of Mg–H which is shifted to 550 cm^{-1} as a broad band in the spectra of the DMgX compounds. Infrared data for the HMgX and DMgX compounds are given in Table V.

The deuteriomagnesium halides DMgX (where X = Cl and Br) were prepared by the reaction of magnesium deuteride slurried in THF with an appropriate magnesium halide (eq 5). The MgD_2 was prepared by the reaction of lithium

$$MgD_2 + MgX_2 \xrightarrow{THF} 2DMgX \quad (5)$$

aluminum deuteride with diethylmagnesium in diethyl ether (eq 6). The NMR spectra of HMgCl and HMgBr in THF

$$LiAlD_4 + Et_2Mg \xrightarrow[RT]{Et_2O} MgD_2 + LiAlD_2Et_2 \quad (6)$$

did not give any fruitful information regarding the Mg–H proton. On the basis of molecular weight and spectroscopic studies, the molecular structure of HMgX in THF is suggested to be that represented below

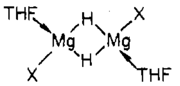

Table V. Fractional Crystallization of the Products of the Reactions of HMgX with AlH_3 or B_2H_6 in THF

Reaction	Fraction	Anal. (ratio) X:Mg:(Al or B):H
1. HMgCl + AlH_3	I	1.02:1.02:1.00:3.92
	II	1.03:1.02:1.00:3.96
	III	1.00:1.00:1.01:3.95
2. HMgBr + AlH_3	I	1.03:1.01:1.02:4.02
	II	1.02:1.00:1.02:3.98
	III	1.00:1.02:1.03:4.00
3. 2HMgCl + B_2H_6	I	1.10:1.05:1.00:3.90
	II	1.06:1.03:1.00:3.95
	III	0.97:1.00:1.04:4.04
4. 2HMgBr + B_2H_6	I	1.12:1.07:1.00:3.88
	II	1.05:1.02:1.00:3.95
	III	0.95:1.00:1.07:4.13

When the THF solvent was removed from HMgCl and HMgBr, solids with empirical formula $HMgCl \cdot 1THF$ and $HMgBr \cdot 1.5THF$ were formed. The x-ray powder-diffraction patterns of these solids were identical with those of $MgCl_2 \cdot 2THF$ and $MgBr_2 \cdot 3THF$ indicating disproportionation of $HMgCl \cdot THF$ to MgH_2 and $MgCl_2 \cdot 2THF$ and $HMgBr \cdot 1.5THF$ to MgH_2 and $MgBr_2 \cdot 3THF$. However, these solids redissolved immediately when THF was added. DTA–TGA studies of the solid formed when THF was removed from a solution of HMgCl showed decomposition at 300 °C with hydrogen evolution. On the other hand, HMgBr decomposed with no hydrogen evolution but rather decomposition of THF cleavage products was indicated.

When AlH_3 in THF was added to an equimolar amount of HMgX (where X = Cl or Br) in THF solution, an exothermic reaction resulted to give a clear solution.

$$HMgX + AlH_3 \xrightarrow[RT]{THF} XMgAlH_4 \quad (7)$$

Infrared spectra of $ClMgAlH_4$ and $BrMgAlH_4$ showed Al–H stretching bands at 1715 and 1725 cm^{-1}, respectively. The spectra were similar to that reported earlier by us.[10] X-ray powder-pattern data of the solids $XMgAlH_4 \cdot 4THF$ formed after the removal of solvent were found to be similar to that reported earlier.[10]

We reported earlier[4] the preparation of $ClMgBH_4$ by the reaction of diborane with a Grignard reagent (eq 2). $ClMgBH_4$ has also been prepared according to eq 8 and 9.

$$MgCl_2 + Mg(BH_4)_2 \xrightarrow{THF} 2ClMgBH_4 \quad (8)$$

$$MgCl_2 + NaBH_4 \xrightarrow[65\,°C]{THF} ClMgBH_4 + NaCl \quad (9)$$

Reaction 8 produces a quantitative yield of $ClMgBH_4$ although the reaction is quite slow whereas reaction 9 does not give good yields.

We have been able to prepare $ClMgBH_4$ as well as $BrMgBH_4$ in THF solution quantitatively under very mild conditions by the reaction of HMgX (where X = Cl or Br) with diborane in THF. When diborane in THF is added slowly to a THF solution of HMgX, an exothermic reaction results and a clear solution analyzing for $XMgBH_4$ is formed (eq 10).

$$2HMgX + B_2H_6 \xrightarrow[RT]{THF} XMgBH_4 \quad (10)$$

The infrared spectrum of $ClMgBH_4$ in THF showed B–H absorption bands at 2375 and 2158 cm^{-1} and in the case of $BrMgBH_4$, B–H stretching bands were observed at 2380 and 2155 cm^{-1}. Other infrared bands are given in Table II.

Fraction crystallization studies showed that $XMgBH_4$ compounds in THF solution are stable toward disproportionation. When THF was removed from a solution of $ClMgBH_4$ and $BrMgBH_4$, solids of empirical formula $ClMgBH_4 \cdot 2THF$ and $BrMgBH_4 \cdot 2THF$ formed. Both of these compounds were found to be soluble in benzene which is a further indication of their stability toward disproportionation since $MgCl \cdot 2THF$ and $Mg(BH_4)_2 \cdot 4THF$ are not soluble in benzene. X-ray powder-pattern data (Table IV) also indicate the absence of a physical mixture of MgX_2 and $Mg(BH_4)_2$ since no lines characteristic of $MgX_2 \cdot nTHF$ were found. Ebullioscopic molecular weight studies in refluxing tetrahydrofuran showed both $ClMgBH_4$ and $BrMgBH_4$ to be monomeric.

Reactions of HMgX compounds in THF with olefins, alkynes, ketones, etc., are in progress.

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Registry No. HMgCl, 63866-76-2; HMgBr, 63866-75-1; $MgCl_2$, 7786-30-3; $MgBr_2$, 7789-48-2; MgH_2, 7693-27-8; AlH_3, 7784-21-6; B_2H_6, 19287-45-7; $ClMgAlH_4$, 63937-04-2; $BrMgAlH_4$, 63937-03-1; $ClMgBH_4$, 12227-98-4; $BrMgBH_4$, 63866-77-3; DMgCl, 63866-78-4; DMgBr, 63866-79-5.

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Theoretical Studies of Valence Orbital Binding Energies in Solid ZnS, ZnO, and ZnF_2

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SCF-Xα scattered wave MO cluster calculations are presented for the ZnS_4^{6-}, ZnS_6^{10-}, ZnO_4^{6-}, ZnO_6^{10-}, ZnF_4^{2-}, and ZnF_6^{4-} molecular clusters and for diatomic ZnS. In solid ZnS the Zn 3d levels are essentially core orbitals lying about 7.5 eV below the S 3p nonbonding orbitals. In solid ZnO this energy difference is reduced to about 6 eV and the orbitals at the top of the valence region have significant Zn 3d–O 2p antibonding character. In solid ZnF_2, bonding and antibonding Zn 3d–F 2p orbital sets are clearly evident at the top of the valence region and have an energy separation of about 4 eV. SCF-Xα photoionization transition state calculations for the ZnF_6^{4-} cluster accurately predict both the energy and relative intensity of the peaks in the XPS spectrum of $ZnF_2(s)$. The observed and calculated ligand p–Zn 3d energy differences in these solids are smaller than those calculated and observed for gas-phase molecules of the same stoichiometry by 2–4 eV. This difference can be understood qualitatively in terms of the ionic model.

I. Introduction

Zn^{2+} is four-coordinate in the binary compounds ZnS(s) and ZnO(s) but six-coordinate in $ZnF_2(s)$. Zn^{2+} also exists in six-coordination with oxygen in $ZnCO_3(s)$ and a number of other oxidic compounds, while it is six-coordinate with S only in the high-pressure compound $ZnS_2(s)$.[1]

Based on considerations of ionic radius ratio[2] and the similarity in ionic radius of Zn^{2+} and Mg^{2+},[3] zinc would be expected to prefer six-coordination with oxygen as does Mg^{2+}. The preference of Zn^{2+} for four-coordination has often been explained in terms of its high electronegativity and consequent strong capacity for covalent bonding.[4] A scheme for predicting fractional ionicity from dielectric constant data[5-7] has correctly predicted the four-coordination of Zn^{2+} in ZnO. A similar method based on orbital binding energy differences in x-ray photoelectron spectra (XPS) has found ZnO to be in the ionicity range expected for four-coordination.[8]

However, our recent theoretical study of the electronic structure of ZnO[9] resulted in a new assignment of the ZnO valence region x-ray photoelectron spectrum (XPS) which yielded a spectral ionicity higher than that expected for a four-coordinate material. In addition, valence region XPS studies of ZnF_2[10] showed two widely separated peaks which were attributed to crystal field splitting within the Zn 3d orbitals, a feature not present in the spectrum of ZnO or ZnS.[11] SCF-Xα molecular orbital calculations on Zn^{2+} in tetrahedral and octahedral coordination with oxygen[12] also showed substantial differences in the degree of mixing of Zn 3d and O 2p orbitals as a function of coordination number, as well as in the crystal field splitting within the Zn 3d–O 2p antibonding or crystal field orbitals. These considerations have led to a more complete study of the series of zinc–ligand clusters ZnO_4^{6-}, ZnO_6^{10-}, ZnS_4^{6-}, ZnS_6^{10-}, ZnF_6^{4-}, and ZnF_4^{2-} using the SCF-Xα scattered wave cluster MO method.[12] The calculational methods and results are described in sections II and III and compared with available experimental data in section IV. In section V we compare the electronic structures of Zn-containing gas-phase molecules and solids of the same stoichiometry and of four- and six-coordinate solid polymorphs. Section VI considers methods for the prediction of Zn coordination number.

II. Calculational Method

The SCF-Xα method has been thoroughly reviewed.[13] It is a computationally efficient, first principles, molecular orbital cluster technique which employs Slater's statistical exchange approximation and a multiple scattering technique similar to that of the KKR method of band theory. The MO energies obtained by this technique correspond well to the density of states maxima observed in the XPS of many metal oxides (e.g., MgO, Al_2O_3, TiO_2).[14] Band widths, on the other hand, are observed experimentally to be larger than the spread of cluster MO energies, as might be expected. The SCF-Xα method also gives accurate energies and intensities for optical transitions[15] if the cluster involved is isolated from its surroundings, as is $FeCl_4^-$ in salts with, e.g., tetramethylammonium as counterion. In homodesic crystals, the SCF-Xα cluster approach sometimes yields accurate optical transition energies[16] and sometimes does not.[17] The accuracy of the result