high-volatility metal halides can be rationalized by a rather simple thermodynamic model which correlates dimerization enthalpies of individual metal halides to the stabilities of their gaseous complexes assuming a constant entropy contribution (third law). Postulated relative stabilities of gaseous complexes containing MX_2 and $AlCl_3$, $AlBr_3$, $GaCl_3$, or $FeCl_3$ have been verified by experiments of our own as well as by stability constants reported in the literature. Furthermore the model can be used to interpret the instability of gaseous complexes containing a group 4 tetrahalide or a group 5 trihalide as the volatile partner. It is therefore felt that the model could be useful in predicting stabilities of gaseous complexes in not yet investigated systems.

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Registry No. $MgFe_2Cl_8$, 60840-49-5; $CaFe_2Cl_8$, 44006-14-6; $SrFe_2Cl_8$, 60840-50-8; $BaFe_2Cl_8$, 44006-13-5; $CoAl_2Br_8$, 60873-91-8; $CuAl_2Cl_8$, 58915-60-9; $CoGa_2Cl_8$, 59217-71-9; $MgCl_2$, 7786-30-3; $CaCl_2$, 10043-52-4; $SrCl_2$, 10476-85-4; $BaCl_2$, 10361-37-2; $CoBr_2$, 7789-43-7; $CuCl_2$, 7447-39-4; $CoCl_2$, 7646-79-9; $FeCl_3$, 7705-08-0; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3.

Supplementary Material Available: Tables II–V, VII–IX, XI, XIV, and XV containing experimental data such as extinctions, volumes, results of chemical analysis, etc., which allow the reader to reevaluate the themodynamic data contained in the tables appearing in full in this paper (9 pages). Ordering information is given on any current masthead page.

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Preparation of Magnesium Zinc Hydrides. $MgZnH_4$ and $Mg(ZnH_3)_2$

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Magnesium bis(trihydridozincate) $[Mg(ZnH_3)_2]$ and magnesium tetrahydridozincate ($MgZnH_4$) have been synthesized by two different preparative routes. One method involves the reaction of dimethylmagnesium with dimethylzinc in 1:2 and 1:1 molar ratios in ether followed by addition of $LiAlH_4$ to the so-called soluble "ate" complexes resulting in the precipitation of the insoluble hydrides $Mg(ZnH_3)_2$ and $MgZnH_4$. The other method involves the metathetical reaction of $MgBr_2$ with $LiZn(CH_3)_3$ in a 1:2 molar ratio and with $Li_2Zn(CH_3)_4$ in a 1:1 molar ratio to form the "ate" complexes followed by addition of $LiAlH_4$ resulting in the precipitation of $Mg(ZnH_3)_2$ and $MgZnH_4$, respectively. The new hydrides were characterized by DTA–TGA, x-ray powder diffraction and elemental analysis. Detailed infrared and NMR investigations of the so-called "ate" complexes ($MgZn(CH_3)_4$ and $Mg[Zn(CH_3)_3]_2$) revealed that these compounds are better described by more complex equilibria. Proton NMR spectra of the "ate" complexes were obtained over a wide temperature range giving some information as to their composition in solution.

Introduction

During the last few years we have been engaged in a general study of the preparation and characterization of complex metal hydrides of zinc,[1] magnesium,[2] copper,[3] and beryllium.[4] The preparation of these compounds involves the reduction of an ether-soluble "ate" complex ($M_nM'_mR_{2m+n}$) with either $LiAlH_4$ or AlH_3. This reaction results in the precipitation of the insoluble hydride ($M_nM'_mH_{2m+n}$), leaving in solution the ether-soluble $LiAlR_nH_{4-n}$. The preparation of Li_2ZnH_4 demonstrates the method (eq 1).

$$2CH_3Li + (CH_3)_2Zn \xrightarrow{Et_2O} Li_2Zn(CH_3)_4 \xrightarrow{2LiAlH_4} Li_2ZnH_4\downarrow + 2LiAl(CH_3)_2H_2 \quad (1)$$

From our studies of complex metal hydrides of the type $M_nM'_mH_{2m+n}$ (n = 1–3; m = 1,2), we have found that the stability of the hydrides to disproportionation (eq 2) is related

$$M_nM'_mH_{2m+n} \rightarrow nMH + mM'H_2 \quad (2)$$

to the electropositivity of M and M′. Evidence thus far indicates that if M is more electropositive than M′, the resulting complex metal hydride is stable. Since magnesium has an electronegativity of 1.2 and zinc 1.6,[5] we thought that it should be possible to prepare $Mg(ZnH_3)_2$ and $MgZnH_4$ as stable complex metal hydrides. In this paper, we report the preparation and characterization of these two new complex metal hydrides as well as an attempt to characterize the nature of the "ate" complex precursors by variable-temperature NMR and infrared studies.

Experimental Section

All operations were performed under nitrogen at the bench using typical Schlenk-tube techniques[6] or in a drybox equipped with a recirculating system using manganous oxide columns to remove oxygen and moisture.[7] All compounds were dried to a constant weight on a high-vacuum line.

Instrumentation. Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Spectra of solids were obtained as Nujol (dried over sodium and stored in the drybox) mulls between CsI plates and solutions were run in matched 0.10-mm path length KBr cells. X-ray powder diffraction data were obtained on a Philips-Norelco x-ray unit using a 114.5-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed (in the drybox) in 0.5-mm capillaries and exposed to x rays for 10 h. *d* spacings were read on a precalibrated scale equipped with viewing apparatus and the intensities of the lines were visually estimated. DTA–TGA were obtained under vacuum using a Mettler Thermoanalyzer II with a high-vacuum attachment.[8]

Proton spectra were obtained using an A-60 spectrometer and the low-temperature spectra were obtained using the standard low-temperature accessories supplied by Varian Associates.

Materials. Dimethylzinc was prepared from methyl iodide and the Zn(Cu) couple by a modification of the procedure of Noller.[9] Dimethylmagnesium was prepared from dimethylmercury and magnesium metal.[10] Ether solutions of magnesium bromide were prepared from $HgBr_2$ and magnesium metal in ether solvent[11] and ether solutions of $LiAlH_4$ (Ventron) were prepared by a previously described procedure.[12] Methyllithium in ether solution was obtained from Foote Mineral Co. and stored at −20 °C until ready to use. The reactants were standardized prior to use and transferred volumetrically. Diethyl ether was distilled fresh from $LiAlH_4$.

Analytical Work. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump. Metals were determined by complexometric titration with EDTA. Zinc and magnesium in the presence of aluminum were determined by masking the aluminum with triethanolamine and titrating the remaining metal with EDTA. Zinc in the presence of magnesium and aluminum was determined by masking magnesium with ammonium fluoride. Aluminum and zinc in the presence of magnesium were determined by standard EDTA titration (pH 4.0) using dithizone indicator. Analysis for halides was carried out using the Volhard procedure.

Proton NMR Study of the "Ate" Complexes in Diethyl Ether. Ether solutions of CH_3Li, $(CH_3)_2Mg$, and $(CH_3)_2Zn$ were mixed in the appropriate molar ratios to form the "ate" complexes $LiZn(CH_3)_3$, $Li_2Zn(CH_3)_4$, and presumably $Mg[Zn(CH_3)_3]_2$ and $MgZn(CH_3)_4$. A small amount of each solution was transferred to a 5-mm thin-wall NMR tube under nitrogen; the tube was sealed and stored in Dry Ice or in a freezer at −20 °C. Low-temperature spectra were recorded after the system was allowed to come to equilibrium at each temperature.

Preparation of Magnesium Bis(trihydridozincate), $Mg(ZnH_3)_2$. (a) Reaction of $LiAlH_4$ with the Product of the Reaction of $MgBr_2$ and $LiZn(CH_3)_3$ in a 1:2 Ratio. In a 200-ml three-neck round-bottom flask containing 10 ml of 0.892 M (8.92 mmol) dimethylzinc in diethyl ether was added under nitrogen with stirring 5.30 ml of 1.682 M (8.92 mmol) methyllithium in ether. After the solution had been stirred at room temperature for 1 h, 36 ml of a 0.124 M (4.46 mmol) solution of $LiAlH_4$ in ether was added slowly to the reaction mixture during stirring. A white precipitate rapidly formed and the mixture was stirred for an additional hour at room temperature. The white solid was filtered under vacuum using a medium-frit filter funnel and washed with about 300 ml of freshly distilled diethyl ether in small portions. The resulting solid was vacuum-dried (0.05 mm) overnight at room temperature and weighed 0.880 g (92% yield). Anal. Calcd for $Mg(ZnH_3)_2{\cdot}0.76(C_2H_5)_2O$:[13] Mg, 11.16; Zn, 60.01; H, 2.77; $(C_2H_5)_2O$, 25.90. Found: Mg, 11.13; Zn, 60.00; H, 2.86; $(C_2H_5)_2O$, 26.06. The Mg:Zn:H molar ratio is 1.00:2.00:6.20.

(b) Reaction of $LiAlH_4$ with the Product Obtained by Reaction of $Mg(CH_3)_2$ and $Zn(CH_3)_2$ in a 1:2 Ratio. An ether solution of dimethylmagnesium (3.44 mmol) was added dropwise to dimethylzinc (7.01 mmol) in ether. After 4 h of stirring at room temperature, the reaction mixture was diluted with 60 ml of ether, treated with 5.32 mmol of $LiAlH_4$ in ether, and stirred for 1 h. The resulting white precipitate was filtered and washed with about 300 ml of ether. The white solid product was vacuum-dried for 17 h and weighed 0.535 g. The product exhibited a Mg:Zn:H ratio of 1.00:1.97:5.79. Anal. Calcd for $Mg(ZnH_3)_2{\cdot}0.47Et_2O$:[13] Mg, 12.40; Zn, 66.72; H, 3.08; $(C_2H_5)_2O$, 17.78. Found: Mg, 12.95; Zn, 68.53; H, 3.10; $(C_2H_5)_2O$, 17.37.

Preparation of Magnesium Tetrahydridozincate, $MgZnH_4$. (a) Reaction of $LiAlH_4$ with the Product of the Reaction of $MgBr_2$ and $Li_2Zn(CH_3)_4$ in a 1:1 Ratio. The procedure for this experiment is similar to the previous one. Dimethylzinc (7.93 mmol) in diethyl ether was added to 15.86 mmol of methyllithium in ether and stirred for about 1 h at room temperature, followed by addition of 7.93 mmol of magnesium bromide–ether solution. The resulting solution was stirred for 3 h and then 7.93 mmol of lithium aluminum hydride in ether was added. A white solid was immediately formed which was stirred for an additional hour and then washed with 300 ml of dry ether and filtered. The compound after vacuum-drying (10^{-5} mm) for 17 h weighed 0.670 g (85% yield). Anal. Calcd for $MgZnH_4{\cdot}0.34(C_2H_5)_2O$:[13] Mg, 20.46; Zn, 55.04; H, 3.39; $(C_2H_5)_2O$, 21.09. Found: Mg, 20.34; Zn, 55.18; H, 3.34; $(C_2H_5)_2O$, 21.10. The Mg:Zn:H molar ratio was 1.00:1.00:3.98.

(b) Reaction of $LiAlH_4$ with the Product of the Reaction of $Mg(CH_3)_2$ and $Zn(CH_3)_2$ in a 1:1 Ratio. Dimethylzinc (7.10 mmol) in diethyl ether was added dropwise to a stirred ether solution of dimethylmagnesium (7.10 mmol). After the mixture was stirred for 4 h at room temperature, about 55 ml of ether was added to dilute the reaction mixture before the dropwise addition (14.20 mmol) of $LiAlH_4$ in ether. The white precipitate which rapidly formed during the $LiAlH_4$ addition was stirred for an additional hour, filtered, washed with about 300 ml of ether, and vacuum-dried (10^{-5} mm for 17 h) to constant weight at room temperature. The resulting solid was analyzed and the Mg:Zn:H molar ratio was found to be 1.00:1.07:4.09. Anal. Calcd for $MgZnH_4{\cdot}0.28(C_2H_5)_2O$:[13] Mg, 21.23; Zn, 57.10; H, 3.52; $(C_2H_5)_2O$, 18.13. Found: Mg, 20.10; Zn, 58.12; H, 3.41; $(C_2H_5)_2O$, 18.30.

Synthesis of MgH_2 and ZnH_2. Magnesium hydride was prepared by the reaction of $LiAlH_4$ with $Mg(C_2H_5)_2$ in a 1:2 molar ratio in diethyl ether according to a previously reported procedure[14] and zinc hydride was prepared by the reaction of $LiAlH_4$ and $Zn(CH_3)_2$ in a 1:1 molar ratio in ether solution also following a previously reported procedure.[15] Both compounds were dried under vacuum for several hours prior to analysis. Elemental analysis of the dried products showed a Mg:H ratio of 1.00:2.08 for $MgH_2{\cdot}0.09(C_2H_5)_2O$ and a Zn:H ratio of 1.00:2.10 for $ZnH_2{\cdot}0.19(C_2H_5)_2O$. Zinc hydride slowly began to turn gray after 4 h of drying at room temperature but was stable indefinitely at Dry Ice temperature. For this reason the ZnH_2 was dried at room temperature for 4 h followed by storage at Dry Ice temperature. Magnesium hydride was stable indefinitely at room temperature.

Results and Discussion

Preparation of Magnesium Bis(trihydridozincate), $Mg(ZnH_3)_2$. (a) Reaction of $LiAlH_4$ with the Product of the Reaction of $MgBr_2$ and $LiZn(CH_3)_3$ in a 1:2 Molar Ratio. The reaction of $(CH_3)_2Zn$ and CH_3Li in 1:1 molar ratio in diethyl

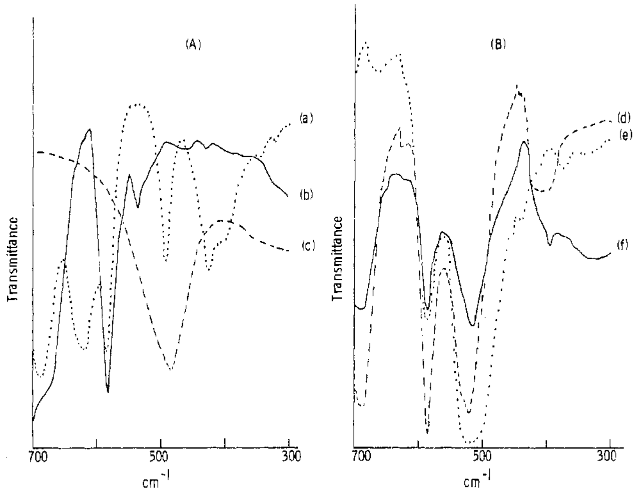
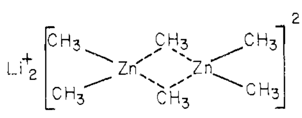


Figure 1. Infrared spectra of ether solutions of (a) ···· CH_3Li + $(CH_3)_2Zn$ in 1:1 mole ratio, (b) — $(CH_3)_2Zn$, (c) --- CH_3Li, (d) --- $(CH_3)_2Mg$ + $(CH_3)_2Zn$ in 1:2 mole ratio, (e) ···· $(CH_3)_2Mg$ and (f) — $MgBr_2$ + 2(solution produced on mixing CH_3Li and $(CH_3)_2Zn$ in 1:1 mole ratio).

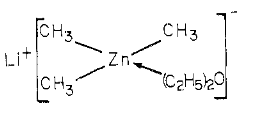
ether yields a clear solution. The infrared spectrum of the resultant solution showed absorption bands at 685 (s), 620 (s), 583 (s), 482 (ms) and 425 cm^{-1} (ms). Since the bands at 620 and 425 cm^{-1} are not present in either CH_3Li or $(CH_3)_2Zn$, complex formation is indicated. The band at 482 cm^{-1} can be assigned to the $\nu(Li-CH_3)$ vibration in CH_3Li and the band at 583 cm^{-1} can be assigned to the $\nu_{as}(Zn-CH_3)$ vibration in $(CH_3)_2Zn$ on the basis of assignments already reported in the literature.[16,17] It is therefore, probable that an equilibrium like (3) exists in solution.

$$CH_3Li + (CH_3)_2Zn \rightleftharpoons LiZn(CH_3)_3 \qquad (3)$$

The proton chemical shifts of methyllithium and dimethylzinc consist of a single sharp resonance at room temperature as well as at low temperature (−86 °C). The results imply either formation of a complex with only one kind of methyl group or a very rapid methyl group exchange involving different species in solution. Although the NMR data obtained at the lowest temperature possible in ether (∼−90 °C) are not definitive, they are consistent with the infrared results indicating an equilibrium (eq 3). Possible structures for $LiZn(CH_3)_3$ are represented by A and B. Structure A is



A



B

similar to the structure suggested earlier for $NaZn(C_2H_5)_3$[18] and structure B is similar to the structure reported earlier for similar compounds.[19]

When an ether solution of $MgBr_2$ is added in a 1:2 ratio to the solution containing CH_3Li and $(CH_3)_2Zn$ in a 1:2 molar ratio, a metathetical reaction takes place according to eq 4.

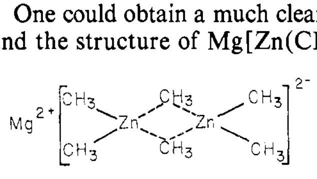
$$MgBr_2 + 2LiZn(CH_3)_3 \rightarrow [(CH_3)_2Mg + 2(CH_3)_2Zn] + 2LiBr \qquad (4)$$

The infrared spectrum of the resultant solution (Figure 1) showed bands at 405 (w), 520 (s), 595 (s), and 685 cm^{-1} (s). The bands at 520 and 595 cm^{-1} can be assigned to $\nu(Mg-CH_3)$ absorption in $(CH_3)_2Mg$ and $\nu_{as}(Zn-CH_3)$ absorption in $(CH_3)_2Zn$, respectively. The proton NMR spectrum of the above solution showed only one singlet at all temperatures indicating either formation of a compound with only one type of methyl group or a rapid exchange involving different species in solution. However, since the infrared spectrum does show two bands corresponding to $\nu(Mg-CH_3)$ and $\nu_{as}(Zn-CH_3)$ vibration as found in $(CH_3)_2Mg$ and $(CH_3)_2Zn$, it is probable that an equilibrium of the type shown in eq 5 exists in solution

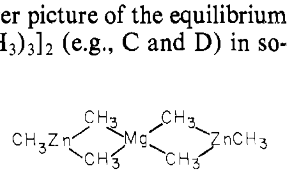
$$Mg[Zn(CH_3)_3]_2 \rightleftharpoons (CH_3)_2Mg + 2(CH_3)_2Zn \qquad (5)$$

although no conclusive evidence was obtained for the existence of $Mg[Zn(CH_3)_2]_2$ in solution.

One could obtain a much clearer picture of the equilibrium and the structure of $Mg[Zn(CH_3)_3]_2$ (e.g., C and D) in so-



C



D

lution if methyl exchange on the NMR time scale at −86 °C was sufficiently slow to observe all of the different types of methyl groups present. Unfortunately this was not the case.

The reaction of $LiAlH_4$ with the product of the reaction of $MgBr_2$ and $LiZn(CH_3)_3$ in a 1:2 molar ratio gave a white solid which exhibited the empirical formula $Mg(ZnH_3)_2$. The infrared spectrum of the solid showed two broad bands, one at 400–650 cm^{-1} and the other at 1200–1900 cm^{-1}. The x-ray powder diffraction pattern showed it to be a new compound and not a physical mixture of MgH_2 and ZnH_2 (Table II). Noncondensable gas evolution (H_2) during vacuum DTA–TGA was observed at 112 and 212 °C. On the other hand, DTA exhibited an endotherm at 88 °C (loss of ether) followed by an exotherm at 112 °C (15.26% loss in weight) and an endotherm at 212 °C (1.19% loss of weight). The endothermic weight loss at 112 °C is due to loss of ether and evolution of hydrogen gas whereas the second weight loss is due to evolution of hydrogen gas only and corresponds to 1 mol of hydrogen present in $Mg(ZnH_3)_2$. It is suggested that the decomposition takes place according to eq 6–8 with $Mg(ZnH_3)_2$ dissociating

$$\text{step I} \quad Mg(ZnH_3)_2 \rightarrow 2ZnH_2 + MgH_2 \ (\text{exotherm, } 112\ ^\circ C) \qquad (6)$$

$$2ZnH_2 \rightarrow 2Zn + 2H_2 \qquad (7)$$

$$\text{step II} \quad MgH_2 \rightarrow Mg + H_2 \ \ (\text{endotherm, } 212\ ^\circ C) \qquad (8)$$

to ZnH_2 and MgH_2 at 112 °C which immediately decomposes to zinc and hydrogen. The decomposition of MgH_2 then takes place at 212 °C to magnesium and hydrogen. It is important to note that pure ZnH_2 decomposes at 105 °C under the same conditions and is considerably less stable at room temperature than $Mg(ZnH_3)_2$. (Pure ZnH_2 prepared by the reaction of $LiAlH_4$ and $(CH_3)_2Zn$ begins to turn black 2–3 h after isolation at room temperature whereas $Mg(ZnH_3)_2$ does not begin to turn black under the same conditions until after 48 h. Furthermore, ZnH_2 begins to decompose at −20 °C after 4 days whereas $Mg(ZnH_3)_2$ is stable indefinitely.)

(b) Reaction of $LiAlH_4$ with the Product of the Reaction of $(CH_3)_2Mg$ and $(CH_3)_2Zn$ in a 1:2 Molar Ratio. The reaction of dimethylmagnesium with dimethylzinc in a 1:2 molar ratio produces a clear solution. The infrared spectrum of the resultant solution was identical with the spectrum of the solution prepared by the reaction of $MgBr_2$ with $LiZn(CH_3)_3$ described previously. Similarly, the proton NMR spectrum of the above solution showed only one sharp single resonance at all temperatures (Table I). Therefore, the identity of the resultant solution can be best described by equilibrium 9. Reaction

$$2(CH_3)_2Zn + (CH_3)_2Mg \rightleftharpoons Mg[Zn(CH_3)_3]_2 \qquad (9)$$

of $LiAlH_4$ with the resultant mixture produced a white solid. The infrared spectrum and x-ray powder diffraction showed it to be $Mg(ZnH_3)_2$. The vacuum DTA–TGA of this compound was identical with that obtained for the product of the

Table I. Proton NMR of "Ate" Complexes[a]

Reactants	Expected "ate" complexes	Chem shifts, ppm: Room temp	Chem shifts, ppm: −86 °C
	$Zn(CH_3)_2$	1.78	1.85
	$LiCH_3$	3.08	3.27
	$Mg(CH_3)_2$	2.60	2.82
$LiCH_3 + Zn(CH_3)_2$	$LiZn(CH_3)_2$	2.07	2.08
$MgBr_2 + 2LiZn(CH_3)_2$	$2LiBr + Mg[Zn(CH_3)_3]_2$	2.00	2.08
$2LiCH_3 + Zn(CH_3)_2$	$Li_2Zn(CH_3)_4$	2.33	2.56
$MgBr_2 + Li_2Zn(CH_3)_4$	$2LiBr + MgZn(CH_3)_4$	2.22	2.28
$Zn(CH_3)_2 + Mg(CH_3)_2$	$MgZn(CH_3)_4$	2.23	2.33
$2Zn(CH_3)_2 + Mg(CH_3)_2$	$Mg[Zn(CH_3)_3]_2$	2.08	2.19

[a] Chemical shifts of methyl protons were measured upfield from the center of the ether triplets. All methyl resonances were observed as singlets.

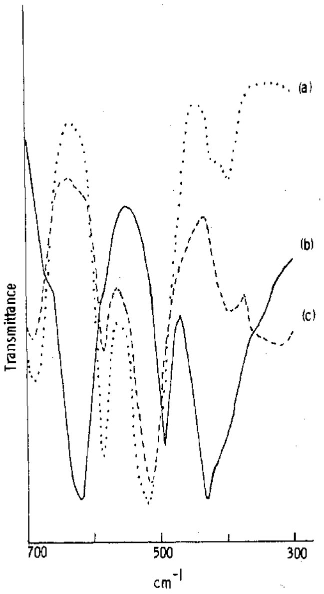


Figure 2. Infrared spectra of ether solutions of (a) ···· $(CH_3)_2Mg$ + $(CH_3)_2Zn$ in 1:1 mole ratio, (b) — CH_3Li + $(CH_3)_2Zn$ in 2:1 mole ratio, and (c) --- $MgBr_2$ + solution produced on mixing CH_3Li and $(CH_3)_2Zn$ in 2:1 mole ratio.

reaction described earlier when the $Mg[Zn(CH_3)_3]_2$ was obtained from $LiZn(CH_3)_3$ and $MgBr_2$ in a 2:1 ratio.

Preparation of Magnesium Tetrahydridozincate ($MgZnH_4$). (a) Reaction of $LiAlH_4$ with the Product of the Reaction of $MgBr_2$ and $Li_2Zn(CH_3)_4$ in a 1:1 Molar Ratio. The infrared spectrum of the solution obtained by stirring a solution of CH_3Li with $(CH_3)_2Zn$ in diethyl ether in a 2:1 molar ratio is recorded in Figure 2. The spectrum shows three strong bands at 430, 480, and 620 cm⁻¹. The band at 480 cm⁻¹ can be assigned to the Li–C stretching vibration in CH_3Li whereas the bands at 430 and 620 cm⁻¹ are at the same frequency as the two bands attributed to $LiZn(CH_3)_3$. Therefore, it is probable that the solution consists predominantly of CH_3Li and $LiZn(CH_3)_3$ with possibly a small amount of $Li_2Zn(CH_3)_4$ (eq 10). The proton NMR spectrum of the resultant solution showed only one sharp single resonance peak at all temperatures. This again implies either formation of a complex with only one kind of methyl group or rapid exchange of methyl groups.

$$2CH_3Li + (CH_3)_2Zn \rightarrow LiZn(CH_3)_3 + CH_3Li \rightleftharpoons Li_2Zn(CH_3)_4 \quad (10)$$

The reaction of $MgBr_2$ with the reaction product of CH_3Li and $(CH_3)_2Zn$ in a 2:1 ratio in ether (eq 10) was carried out in an attempt to effect reaction 11. In spite of the fact that the reaction of CH_3Li with $(CH_3)_2Zn$ in a 2:1 ratio does not produce exclusively $Li_2Zn(CH_3)_4$ (according to infrared spectra) it is still possible that $MgZn(CH_3)_4$ can be produced in this reaction via a more involved series of steps. The infrared spectrum of the resultant solution showed bands at 400 (m), 516 (s), 585 (ms), and 680 cm⁻¹ (m). The bands at 516 and 585 cm⁻¹ can both be assigned to $\nu(Mg–CH_3)$ absorption in $(CH_3)_2Mg$ or the 516-cm⁻¹ band could be assigned to $\nu(Mg–CH_3)$ absorption in $(CH_3)_2Mg$ and the 585-cm⁻¹ band to $\nu_{as}(Zn–CH_3)$ absorption in $(CH_3)_2Zn$. The choice in assignment is due to the fact that the 585-cm⁻¹ band is exhibited by both $(CH_3)_2Mg$ and $(CH_3)_2Zn$ and secondly the 585-cm⁻¹ band is weak in $(CH_3)_2Mg$ compared to the 515-cm⁻¹ band whereas it is nearly as strong in the solution formed from the reaction of $MgBr_2$ with the reaction product of CH_3Li with $(CH_3)_2Zn$ in a 2:1 ratio. Therefore there are two reasonable interpretations of the reaction product in question and they are represented by eq 12 and 13.

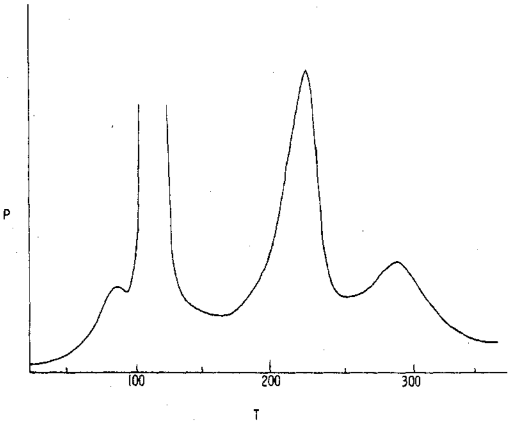
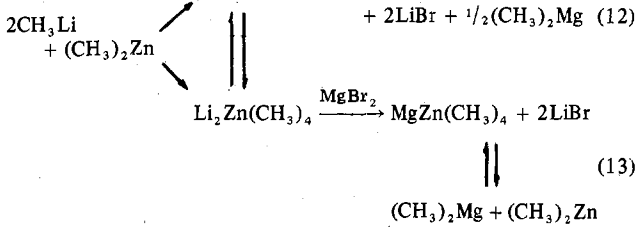


Figure 3. Vacuum DTA–TGA of $MgZnH_4$.

$$Li_2Zn(CH_3)_4 + MgBr_2 \rightarrow MgZn(CH_3)_4 + 2LiBr \quad (11)$$



$$\begin{array}{l} 2CH_3Li + (CH_3)_2Zn \nearrow LiZn(CH_3)_3 + CH_3Li \xrightarrow{MgBr_2} {}^1/_2Mg[Zn(CH_3)_3]_2 + 2LiBr + {}^1/_2(CH_3)_2Mg \quad (12) \\ \qquad\qquad \searrow Li_2Zn(CH_3)_4 \xrightarrow{MgBr_2} MgZn(CH_3)_4 + 2LiBr \\ \qquad\qquad\qquad\qquad\qquad\qquad MgZn(CH_3)_4 \rightleftharpoons (CH_3)_2Mg + (CH_3)_2Zn \quad (13) \end{array}$$

The proton NMR spectrum of the above solution showed only one single sharp resonance peak at all temperatures (Table I) indicating either formation of a complex with only one type of methyl group or a rapid exchange involving different species in solution.

Reaction of $LiAlH_4$ with the reaction product of the above reaction yields an insoluble white compound which exhibited the empirical formula $MgZnH_4$. The infrared spectrum of the solid showed two broad bands at 400–650 and 1200–1900 cm⁻¹. The x-ray powder diffraction pattern showed it to be different from a mixture of MgH_2 and ZnH_2 (Table II). The vacuum DTA–TGA of this compound is shown in Figure 3. The first weight loss corresponding to an endothermic change at 80 °C is due to loss of ether. The second exothermic change at 92 °C is due to loss of hydrogen gas which is also accompanied by the loss of ether. The third and fourth weight losses at 210 and 277 °C correspond to the decomposition of MgH_2 to magnesium and hydrogen according to eq 14–18. The question of course is whether the product is $MgZnH_4$ as one would expect from eq 19 or physical mixture of

Table II. X-Ray Powder Pattern *d*-Spacing Data

$MgH_2\cdot 0.09Et_2O$		$ZnH_2\cdot 0.19Et_2O$		$MgH_2 + ZnH_2$		$MgZnH_4\cdot 0.34Et_2O$[a]		$MgZnH_4\cdot 0.28Et_2O$[b]		$Mg(ZnH_3)_2\cdot 0.76Et_2O$[c]		$Mg(ZnH_3)_2\cdot 0.47Et_2O$[d]	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
3.75	w	4.45	s	4.45	s	4.32	m	1.92	s, br	3.80	s	3.80	s
3.20	s	3.26	m	3.75	w	3.80	m	1.68	s, br	1.98	s	1.99	s
2.50	s	3.12	m	3.26	m	2.95	s						
2.02	vw	2.90	w	3.10	m	2.74	m						
1.67	m	2.78	m	2.82	w	2.67	s						
		2.50	m	2.50	ms	2.42	w						
		2.23	vw	2.18	w	1.74	vw						
		2.17	vw	2.0	w								

[a] $Li_2Zn(CH_3)_4 + MgBr_2 + LiAlH_4$ in diethyl ether. [b] $(CH_3)_2Zn + (CH_3)_2Mg + LiAlH_4$ in diethyl ether. [c] $LiZn(CH_3)_3 + MgBr_2 + LiAlH_4$ in diethyl ether. [d] $2(CH_3)Zn + (CH_3)_2Mg + LiAlH_4$ in diethyl ether.

Table III. Thermal Decomposition of Complex Metal Hydrides of Zinc and Magnesium

Compd (sample wt, mg)	Thermicity	Range of transn (peak max), °C	% wt loss
MgH_2 (49.5)	Endo	60–180 (120)	5.8 (loss of ether)
	Endo	300–390 (345)	6.0
ZnH_2 (40.2)	Exo	105	18.4 (loss of ether and hydrogen gas)
$MgZnH_4$[a] (52.5)	Endo	80	(loss of ether)
	Exo	80–112 (92)	10.85 (loss of ether and hydrogen gas)
	Endo	170–235 (210)	1.14
	Endo	240–305 (277)	0.57
$MgZnH_4$[b] (54.7)	Endo	90	(loss of ether)
	Exo	90–120 (105)	13.71 (loss of ether and hydrogen gas)
	Endo	180–230 (210)	1.09
	Endo	250–300 (280)	0.73
$Mg(ZnH_3)_2$[c] (58.3)	Endo	88	(loss of ether)
	Exo	80–130 (112)	15.26
	Endo	170–240 (212)	1.19
[d]$Mg(ZnH_3)_2$[d] (56.4)	Endo	90	(loss of ether)
	Exo	80–130 (112)	20.4 (loss of ether and hydrogen gas)
	Endo	165–210 (196)	1.06
$MgH_2 + ZnH_2$ (46.8) (1:1 molar ratio)	Endo	80	(loss of ether)
	Exo	75–120 (95)	18.8 (loss of ether and hydrogen gas)
	Endo	260–365 (315)	1.92

[a] $Li_2Zn(CH_3)_4 + MgBr_2$. [b] $(CH_3)_2Zn + (CH_3)_2Mg + 2LiAlH_4$. [c] $2LiZn(CH_3)_2 + MgBr_2 + {}^3/_2LiAlH_4$. [d] $2(CH_3)_2Zn + (CH_3)_2Mg + {}^3/_2 LiAlH_4$.

$$\text{step I}\quad 2MgZnH_4 \rightarrow Mg(ZnH_3)_2 + MgH_2{}^* \tag{14}$$

$$Mg(ZnH_3)_2 \rightarrow MgH_2 + 2ZnH_2 \tag{15}$$

$$ZnH_2 \rightarrow Zn + H_2 \quad \text{(exotherm, 92 °C)} \tag{16}$$

$$\text{step II}\quad MgH_2 \rightarrow Mg + H_2 \quad \text{(endotherm, 210 °C)} \tag{17}$$

$$\text{step III}\quad MgH_2{}^* \rightarrow Mg + H_2 \quad \text{(endotherm, 277 °C)} \tag{18}$$

$$\begin{array}{l} MgZn(CH_3)_4 \xrightarrow{2LiAlH_4} MgZnH_4 + LiAl(CH_3)_2H_2 \\ \quad\ \ \downarrow\uparrow \\ (CH_3)_2Mg + (CH_3)_2Zn \end{array} \tag{19}$$

$Mg(ZnH_3)_2$ and MgH_2 as would be expected from eq 20.

$$Mg[Zn(CH_3)_3]_2 + Mg(CH_3)_2 \xrightarrow{4LiAlH_4} Mg(ZnH_3)_2 + MgH_2 + 4LiAl(CH_3)_2H_2 \tag{20}$$

Since one cannot predict the predominant reaction product from a mixture of reactants in equilibrium, it is difficult on the basis of infrared analysis of the reactant mixture to specify either pathway 19 or 20 as the reaction course. The DTA–TGA is consistent with either the formation of $MgZnH_4$ followed by disproportionation at 92 °C to $Mg(ZnH_3)_2$ and MgH_2 or simply the direct formation of the latter. This distinction by DTA–TGA is impossible due to the fact that such a proposed disproportionation would be masked by the other proposed transformations taking place at 92 °C, namely, disproportionation of $Mg(ZnH_3)_2$ to MgH_2 and ZnH_2 and also decomposition of the ZnH_2. Thus it is clear that the first part of step I, i.e., $MgZnH_4$ disproportionating to $Mg(ZnH_3)_2$ and MgH_2, may or may not take place.

Thus on the basis of infrared and DTA–TGA studies, it is impossible to say whether the reaction product of $LiAlH_4$ with the solution formed from $MgBr_2$ and the solution of CH_3Li and $(CH_3)_2Zn$ in 2:1 ratio is $MgZnH_4$ or a physical mixture of $Mg(ZnH_3)_2$ and MgH_2. However, the x-ray powder diffraction comparison appears to be definitive in allowing a selection between the two possibilities. The powder diffraction of the product in question is different from that of a mixture of MgH_2 and ZnH_2 and is also quite different from a mixture of $Mg(ZnH_3)_2$ and MgH_2 (Table II). Since this product has the empirical formula $MgZnH_4$ and contains none of the strong x-ray lines due to MgH_2, ZnH_2, or $Mg(ZnH_3)_2$, then it must be a single compound of molecular formula $MgZnH_4$.

(b) Reaction of $LiAlH_4$ with the Products of the Reaction of $(CH_3)_2Mg$ with $(CH_3)_2Zn$ in a 1:1 Molar Ratio. When an ether solution of dimethylmagnesium is added to an ether solution of dimethylzinc in a 1:1 molar ratio, a clear solution results. The desired series of reactions is represented by eq 21. The infrared spectrum of the solution produced on mixing

$$(CH_3)_2Mg + (CH_3)_2Zn \rightarrow MgZn(CH_3)_4 \xrightarrow{2LiAlH_4} MgZnH_4 + 2LiAl(CH_3)_3H_2 \tag{21}$$

$(CH_3)_2Mg$ and $(CH_3)_2Zn$ in a 1:1 molar ratio was identical with the spectrum described earlier obtained for the solution produced on mixing $MgBr_2$ with the solution produced on mixing CH_3Li and $(CH_3)_2Zn$ in a 2:1 ratio. As described earlier for the latter reaction, definitive interpretation of the infrared spectrum is not possible and hence the composition can be represented by either eq 12 or 13. The proton NMR spectrum of the clear solution formed on mixing $(CH_3)_2Mg$ with $(CH_3)_2Zn$ in ether in a 1:1 ratio showed only one sharp single resonance peak at all temperatures.

Reaction of $LiAlH_4$ with the above solutions produced a white solid. The infrared spectrum of the solid was identical with $MgZnH_4$ formed in section (a). The x-ray powder diffraction pattern is listed in Table II. It is surprising to note that the lines do not correspond exactly with the lines observed for $MgZnH_4$ prepared in (a). However, the lines are quite different from the patterns obtained either for a physical mixture of MgH_2 and ZnH_2 or for $Mg(ZnH_3)_2$. It is of course possible that $MgZnH_4$ prepared by this method may have a different crystal structure than the product formed in (a). The vacuum DTA–TGA of this compound was identical with that of $MgZnH_4$ formed in (a) and the data are listed in Table III.

In conclusion, $MgZnH_4$ and $Mg(ZnH_3)_2$ were prepared by two different routes. The integrity of these complexes as a single compound rather than a physical mixture of MgH_2 and ZnH_2 has been established by their characteristic x-ray powder diffraction patterns.

Registry No. $Mg(ZnH_3)_2$, 60949-89-5; $MgZnH_4$, 60949-90-8; MgH_2, 7693-27-8; ZnH_2, 14018-82-7; $Zn(CH_3)_2$, 544-97-8; $LiCH_3$, 917-54-4; $LiAlH_4$, 16853-85-3; $Mg(CH_3)_2$, 2999-74-8; $MgBr_2$, 7789-48-2.

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Synthesis and Characterization of $(NF_4)_2TiF_6$ and of Higher NF_4^+ and Cs^+ Poly(perfluorotitanate(IV)) Salts

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Metathesis between Cs_2TiF_6 and NF_4SbF_6 in HF solution was used to prepare the novel perfluoroammonium salt $(NF_4)_2TiF_6$. The compound is a white crystalline solid, stable to about 200 °C. It was characterized by elemental analysis and infrared, Raman, and ^{19}F NMR spectroscopy. X-ray powder data show that the compound (tetragonal, $a = 10.715$ Å, $c = 11.114$ Å) is isotypic with $(NF_4)_2GeF_6$ and $(NF_4)_2SnF_6$. Thermal or HF solution displacement reactions between NF_4BF_4 and TiF_4 produced the polyperfluorotitanate(IV) salts $NF_4Ti_2F_9$ and $NF_4Ti_3F_{13}$. Heating of NF_3, F_2, and TiF_4 to 190 °C at an autogenous pressure of 160 atm produced a salt of the approximate composition $NF_4Ti_6F_{25}$. For comparison, TiF_4 and the salts Cs_2TiF_6, $Cs_2Ti_2F_{10}$, and $CsTi_2F_9$ were synthesized and characterized by vibrational spectroscopy.

Introduction

Although the nonexistence of an NF_5 parent molecule and the high ionization potentials of NF_3 and fluorine made the original synthesis of NF_4^+ salts difficult,[1] their surprisingly high thermal stability permits the syntheses of salts of relatively weak Lewis acids. Thus, the preparation of stable NF_4^+ salts[2,3] containing GeF_5^-, GeF_6^{2-}, SnF_5^-, and SnF_6^{2-} anions has been recently reported. Since NF_4^+ salts are of significant interest for solid propellant NF_3–F_2 gas generators[4] for chemical HF–DF lasers, the synthesis of novel higher performing NF_4^+ salts is desirable. In this paper, we report on the syntheses and properties of NF_4^+ salts derived from TiF_4.

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those previously described.[2-4] The CsF was fused in a platinum crucible and powdered in the drybox. The NF_3 and F_2 were prepared at Rocketdyne, the HF (Matheson) was dried as previously described,[5] and the BrF_5 (Matheson) was purified by fractional condensation prior to use. Pure NF_4BF_4 was prepared from NF_3, F_2, and BF_3 by uv photolysis[2] at −196 °C and the NF_4SbF_6 was synthesized as previously described.[4] A 10 year old sample of commercial TiF_4 (Allied) had undergone partial hydrolysis but was converted back to pure TiF_4 by fluorinating it in a Monel cylinder for 2 days at 250 °C with F_2 at 70 atm. Both, treated and untreated, samples of TiF_4 were used in the displacement reactions with NF_4BF_4. In some cases the course of the reactions was influenced by the choice of the TiF_4.

Synthesis of Cs_2TiF_6. Dry CsF (40.3 mmol) and TiF_4 (20.15 mmol) were combined in a passivated Teflon FEP ampule. Anhydrous HF (3 ml of liquid) was added at −78 °C. The mixture was warmed to 24 °C and stirred for 1 h until all solid material had dissolved. The volatile materials were pumped off at 70 °C for 2 h. The white solid residue (8.621 g; weight calcd for 20.15 mmol of Cs_2TiF_6 8.619 g) was shown by infrared and Raman spectroscopy to be Cs_2TiF_6 of excellent purity. The products obtained from both untreated and prefluorinated TiF_4 were undistinguishable. The solubility of Cs_2TiF_6 in anhydrous HF at 24 °C was found to be about 4 g/g of HF.

Synthesis of $Cs_2Ti_2F_{10}$. This salt was synthesized from equimolar amounts of Cs_2TiF_6 and prefluorinated TiF_4 either by heating in a Monel cylinder to 180 °C for 7 days or by stirring the mixture in liquid anhydrous HF for 4 days at 25 °C and pumping off the volatile material at 50 °C for 3 h. The observed weights closely corresponded to those expected for $Cs_2Ti_2F_{10}$. Vibrational spectroscopy showed only small amounts of TiF_6^{2-} and $Ti_2F_9^-$ for the product of the thermal reaction and of TiF_4, $Ti_2F_9^-$, TiF_6^{2-}, and a higher polyanion (Raman band at 778 cm^{-1}) for the HF reaction.

Synthesis of $CsTi_2F_9$. This salt was prepared as described above for $Cs_2Ti_2F_{10}$, except for using Cs_2TiF_6 and TiF_4 in a 1:3 mole ratio. Vibrational spectroscopy showed that the product from the HF reaction contained mainly $Ti_2F_9^-$ with traces of TiF_4 and $Ti_2F_{10}^{2-}$ being present. The product from the thermal reaction was a mixture of approximately $4TiF_4$, $4CsTi_2F_9$, and $2Cs_2Ti_2F_{10}$.