first example of a binuclear organometallic in which a paramagnetic state is within thermal range. It has been estimated that in diamagnetic polynuclear carbonyls wherein the strong metal–metal exchange interaction is formalized by metal–metal bonds (*e.g.*, $Fe_2(CO)_9$), the singlet–triplet separation is of the order of $\sim$700 cm.$^{-1}$. The strong exchange interaction in I presumably is effected by the tetra-bridged structure in which the V–S–V angle probably is near the tetrahedral value. Finally, it appears likely that the magnetic behavior described above can occur only in bridged vanadium (or titanium) complexes of this type since with other transition metals the inert gas configuration can be attained with (or without) the formation of metal–metal bonds. Other paramagnetic V(0) complexes are $[(C_6H_5)_3P]_2V(CO)_4$[13] and the mononuclear $V(CO)_6$,[14] which have the expected moments of 1.8 B.M. for one unpaired electron.

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Reactions of the Borohydride Group with the Proton Donors Hydroxylammonium, Methoxyammonium, and Hydrazinium-magnesium Ions[1]

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Ammonia and amines, coördinated either to a proton as ammonium ion or to metal cations, have sufficient acidity to react with the borohydride group yielding amine boranes or borohydrides of low stability that degrade to amine boranes.[3] This reaction has now been applied to the ions $Mg(N_2H_4)_x^{++}$, $CH_3ONH_3^+$, and $HONH_3^+$.

If solutions are chilled and concentrations kept low, $MgCl_2 \cdot 6H_2O$ may be dissolved in hydrazine without $Mg(OH)_2$ forming. The addition of $NaBH_4$ to such solutions results in the precipitation of NaCl, but no gas is evolved. While this indicates that an intermediate magnesium borohydride is stable in the solution, it is not isolated, since removing the solvent yields a solid that evolves hydrogen, and $N_2H_4 \cdot BH_3$[4] appears as a product.

The original $MgCl_2 \cdot 6H_2O$ solution may be evaporated carefully and vacuum dried to yield a solid magnesium chloride hydrazinate. Hydrogen evolves when this hydrazinate is allowed to react with $NaBH_4$ in tetrahydrofuran suspension, and $N_2H_4 \cdot BH_3$ is again a product.

Methoxyammonium chloride and $NaBH_4$ as a tetrahydrofuran suspension also give the corresponding $CH_3ONH_2 \cdot BH_3$.[5]

Hydroxylammonium salts do not give $HONH_2 \cdot BH_3$ under similar conditions. While the evolved hydrogen:borohydride mole ratio in the first two cases approaches 1:1, it is 1:3 with the $HONH_3^+$ salts, unless the reaction is conducted well below room temperature. The product is a solid formulated as $(HONBH)_x$, although secondary reactions with the solvent have prevented a truly definitive characterization.

$(HONBH)_x$ may be the borazine ($x = 3$), but this has not been definitely established in the present work. Molecular weight values have been erratic, and the infrared spectrum shows broad and ill-defined absorptions beyond 6.5 μ.

In reactions conducted at $-80°$, H_2 evolution does slow near 1:1 H_2:BH_4^- when ethers of high base strength are the reaction media. However, products isolated in the cold evolve additional hydrogen when warmed to room temperature, paralleling the direct reaction of B_2H_6 and $HONH_2$.[6] Once, using trimethylene oxide, the final solid had a hydrolyzable hydrogen content greater than theory for $(HONBH)_x$ but still well below that expected for the hydroxylamino- or hydroxylamine borane. In all other cases, only $(HONBH)_x$ remained after gas evolution ceased.

It should be noted that $(HONBH)_x$ is *extremely hazardous*. It explodes with high brisance under conditions of mild friction or impact. One sample, isolated by evaporating a tetrahydrofuran solution, exploded when simply pierced with a spatula.

Experimental

All reactions were carried out under nitrogen atmospheres and at room temperature except where specified. Ethers were dried over CaH_2. Hydrazine was a 96+% commercial product.

Hydrogen was measured in a closed system with a mercury filled gas buret, on a scale calculated not to exceed the capacity of the buret. Reactions were initiated by injection of a measured volume of solvent through a serum cap, and the pressure adjusted during measurements to compensate for the vapor pressure of the solvent.

Larger preparative reactions, described below, were conducted in magnetically stirred erlenmeyer flasks.

(1) **$N_2H_4 \cdot BH_3$—Method 1.**—$MgCl_2 \cdot 6H_2O$ (0.41 g., 2 mmoles) and $NaBH_4$ (0.15 g., 4 mmoles) were mixed in 20 ml. of iced hydrazine. A small amount of NaCl (X-ray identification) precipitated and was filtered off; no gas evolved. The hydrazine was evaporated under a N_2 stream and the resulting solid vacuum-dried. NaCl was present in this material, and hydrogen evolution could now be detected. The solid was allowed to stand under hexane for 1 week, and then extracted with tetra-

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[1] This work was carried out under Contract DA-30-069-ORD-2487 for the Advanced Research Projects Agency.

[2] Rocketdyne, A Division of North American Aviation, Canoga Park, California.

[3] R. W. Parry, D. R. Schultz, and P. R. Giradot, *J. Am. Chem. Soc.*, **80**, 1 (1958).

[4] J. Goubeau and E. Ricker, *Z. anorg. allgem. Chem.*, **310**, 123 (1961).

[5] T. C. Bissot, D. H. Campbell, and R. W. Parry, *ibid.*, **80**, 1868 (1958).

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hydrofuran to yield $N_2H_4 \cdot BH_3$ upon removal of solvent. The yield was 79% based on starting borohydride.

The infrared spectrum, melting point, and elemental analyses were identical with that of a known sample.

(2) **$N_2H_4 \cdot BH_3$—Method 2.**—$MgCl_2 \cdot xN_2H_4$ was prepared by adding 4.1 g. of $MgCl_2 \cdot 6H_2O$ to 20 ml. of iced N_2H_4, evaporating under N_2 to a thick clear sirup, and vacuum drying by prolonged pumping at room temperature. The yield (4.5 g.) and nitrogen analysis (50.73 found; 50.03 theory) correspond to $MgCl_2 \cdot 4N_2H_4$, but the material was not characterized further. This solid (1.8 g., 8 mmoles, assuming the tetrahydrazinate) and 0.6 g. (16 mmoles) of $NaBH_4$ were allowed to react in tetrahydrofuran suspension. Hydrogen began to evolve immediately, and, after 8 days, an 83% yield of $N_2H_4 \cdot BH_3$ was isolated from solution. In the hydrogen evolution apparatus, the $H_2:BH_4^-$ ratio was shown to be 1:1.

In neither of the above methods was the actual fate of the magnesium ion determined, although the stoichiometry and material balances lead to the equation

$$MgCl_2 \cdot 4N_2H_4 + 2NaBH_4 \longrightarrow 2(N_2H_4 \cdot BH_3) + 2H_2 + Mg(N_2H_3)_2$$

(3) **$CH_3OHN_2 \cdot BH_3$.**—CH_3ONH_3Cl (0.84 g., 10 mmoles) and $NaBH_4$ (0.38 g., 10 mmoles) yielded 0.26 g. (43%) of soluble product after overnight reaction in tetrahydrofuran suspension. Without any purification other than vacuum drying, the solid melted at 53–58° (dec.) (lit.[5] 55°) and analyzed for $CH_3ONH_2 \cdot BH_3$. (*Anal.* Calcd.: B, 17.6; hydrolyzable H, 4.7. Found: B, 19, hydrolyzable H, 4.9). This material also was sensitive to friction and impact. In the hydrogen evolution apparatus, the $H_2:BH_4^-$ ratio approached 1:1 after several days.

(4) **$(HONBH)_x$.**—Two products always appeared when $HONH_3^+$ salts reacted with borohydrides. The first, soluble in ethers, has been formulated as $(HONBH)_x$; the second, arising from reaction of the first with the solvent, did not give consistent analyses. It is believed to be polymeric, since it was relatively insoluble and small quantities of it formed stable gels with solvents such as tetrahydrofuran. The relative amounts of each product that formed were not completely predictable, although the second was favored if $HONH_3Cl$ was used, or if solutions of $(HONBH)_x$ stood for prolonged periods or were warmed slightly. The following procedure was the most successful for obtaining $(HONBH)_x$. $NaBH_4$ (0.38 g., 10 mmoles) and $(HONH_3)_2SO_4$ (0.82 g.; 5 mmoles) were stirred in 50 cc. of tetrahydrofuran for 3 to 4 days. The solution was filtered, concentrated (N_2 stream) to 5 ml., refiltered, and the product precipitated with 50 ml. of *n*-pentane. Filtration and vacuum drying yielded 0.37–0.45 g. (70–96%) of product. *Anal.* Calcd. for $(HONBH)_x$: B, 25.3 ; N, 32.7; hydrolyzable H, 2.35. Found: B, 24.3, 23.2; N, 30.4, 28.3; hydrolyzable H, 2.33, 2.22, 1.99. Small amounts of carbon always were found, presumably from contamination by the polymer.

The white hygroscopic solid did not melt up to 100° (detonations beyond this temperature). Its density (liquid displacement) was 1.35 ± 0.15 g./cc. Molecular weight determinations (cryoscopic in *p*-dioxane) did not give consistent results. Some values were near 150, but values much higher also were obtained, possibly due to the presence of polymer. The infrared spectrum (mull) showed broad OH, NH, and BH absorptions, but was otherwise ill-defined.

Gas evolution measurements in a wide variety of ethers always gave an $H_2:BH_4^-$ ratio approaching 3:1 at room temperature. At −80°, the evolution rate slowed near 1:1 when tetrahydrofuran, *p*-dioxane, or trimethylene oxide were the solvents. Filtering and removing cold solvent *in vacuo* left a white solid that foamed and gassed when warmed to room temperature, and, except in one case, only $(HONBH)_x$ was isolated. The solid from the trimethylene oxide run had an infrared spectrum slightly different from the usual material and analyzed 3.2% hydrolyzable hydrogen.

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Complexes of the Rare Earths. IV. Electrophoretic Examination of the Hydrolysis of N-Hydroxyethylethylenediaminetriacetic Acid Chelates

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In a recent note Gupta and Powell[1] have reported on the interaction between the rare earth–N-hydroxyethylethylenediaminetriacetic acid (HEDTA) chelates and an equivalent amount of base and have concluded that species of the form $RChOH^-$ exist in such solutions. We have confirmed their results with a titration technique[2] and have found formation constants in good agreement with theirs.

We also have performed electrophoresis experiments on solutions containing the hydrolysis products of lanthanum, neodymium, dysprosium, and ytterbium chelates. We believe that the results are worth presenting since they are consistent with the behavior expected of solutions containing principally a neutral complex and a single negatively charged species, as inferred from the titration experiments, and provide good supporting evidence by an independent method for the correctness of conclusions drawn from the titration data.

Experimental

Electrophoresis experiments were performed at 1.00° with a Spinco Model H electrophoresis apparatus. An 11-ml. quartz Tiselius cell with reference paths was used, and schlieren and interference fringe photographs were taken simultaneously. Fringe displacements and mobilities were calculated as described previously.[3] Conductances were measured at 0°, using a Jones bridge and a conductance cell of the Jones and Bollinger type.

In all experiments the rare earths, at a total molar concentration of about 0.0018, adjusted to the desired pH with 0.1 *M* potassium hydroxide, were studied in 0.1 *M* potassium nitrate as supporting electrolyte. The details of solution preparation have been described elsewhere.[4] The experimental situation is analogous to the commonly encountered electrophoresis of proteins in a buffer, the complex species and the potassium nitrate corresponding to the protein and buffer components, respectively Fig. 1). Above pH 10, the concentration of free hydroxide ion becomes appreciable and should be indicated as KOH in the appropriate phases.

Results and Discussion

In all experiments at pH values where significant hydrolysis would be expected (as shown by the acid dissociation constant of the chelates) a single moving boundary, proceeding toward the anode, was observed

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[1] A. K. Gupta and J. E. Powell, *Inorg. Chem.*, **1**, 955 (1962).

[2] The entire run of our titration was less than 1 hr., whereas Gupta and Powell equilibrated their samples at each point for 100 hr.

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