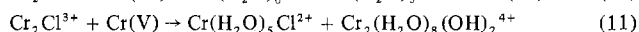
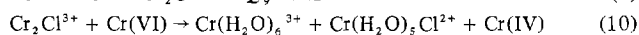
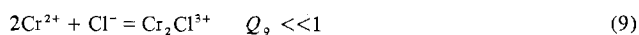


### Discussion

Reductions of Cr(VI) have been the subjects of many mechanistic studies, and extensive evidence exists for series of one-electron transfers analogous to those shown by eq 2-4. Because of this evidence we think these steps probably do occur during net reaction 1, and in the following discussion we assume they do occur. However, our data, as those of earlier workers,<sup>4,5</sup> imply that additional steps occur.

Our data show that the elementary reaction(s) yielding  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  and the elementary reaction(s) yielding  $\text{Cr}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$  compete more effectively (with elementary steps yielding  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ) at high  $[\text{Cr}(\text{II})]$  and at high  $[\text{Cl}^-]$ . These observations cannot be rationalized solely by any combination of reactions 2-8.

Reactions 2-4 and various combinations of reactions 6-11



are consistent with the observations listed just above. Each of reactions 10 and 11 competes more effectively than the other reactions discussed here at high  $[\text{Cr}(\text{II})]$  and at high  $[\text{Cl}^-]$  and yields  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  along with  $\text{Cr}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$  or a presumed precursor of  $\text{Cr}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ . Other reactions involving higher polymers of Cr(II) would also be in accord with our data. Our failure to find spectral evidence for a Cr(II) dimer indicates that (if it is indeed formed) the extent of formation is small, or the visible spectrum is similar to that of monomer.

The small amounts of  $^{51}\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  and  $^{51}\text{Cr}(\text{H}_2\text{O})_6^{3+}$  produced in the labeling experiment indicate the pathways taking Cr(VI) to monomer are not major pathways under the conditions of that experiment. Yet, in the experiments at lowest  $[\text{Cr}(\text{II})]_0$  and  $[\text{Cl}^-]$ , greater than 75% of the product was monomer, indicating that a significant amount of Cr(VI) had to be converted to monomer. These observations are in accord with eq 10 (to produce the  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ ) followed by eq 6a, or 7, or 8 (to produce  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  from Cr(VI), in greater amounts at lower  $\text{Cr}^{2+}$ ) but are not in accord with eq 11. A sequence involving eq 10 as the sole process leading to  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  predicts that even at very low  $[\text{Cr}(\text{II})]_0$ , a labeling experiment would yield no  $^{51}\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ , but a significant amount of  $^{51}\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . We did not test this prediction by experiment, but it appears that it would have to be approximately true regardless of the mechanism, owing to the very small *total* amount of  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  and the large amount of total monomer that is produced at low  $[\text{Cr}(\text{II})]_0$ .

The failures to detect a large quantity of  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  product when Fe(II) or Cu(I) was the reductant appear to be further evidence that Cr(VI) is not the principal source of  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ . This evidence and the result of the labeling experiment seem to require that  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  must come primarily from the Cr(II). If Cr(II) is the source of  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ , then it is reasonable to expect that other oxidants could also yield  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ . Further, if Cr(II) *dimer* (or other polymer) is responsible for  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ , as we have argued, then other oxidants might also produce  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  with a yield increasing with  $[\text{Cr}(\text{II})]_0$  and  $[\text{Cl}^-]$ . These expectations were met with molecular oxygen. In addition, oxygenation of Cr(II) has been found by other workers to be second order in Cr(II), in aqueous perchlorate media<sup>11</sup> and in aqueous ammonia-bromide media.<sup>12</sup> In both

of these studies, a peroxy-bridged Cr(II) dimer was proposed. Other Cr(II) dimers that are known to exist are chromium(II) alkanatoates, of which the chromium(II) acetate hydrate is the best characterized.<sup>13</sup>

Our attempts to gain information about the behavior of unstable Cr(IV) and Cr(V) species showed that these species do not ultimately become chlorochromium(III) species upon reduction by Cr(II) (or by Fe(II) or Cu(I)) under the conditions of our study. This result could occur because the intermediates do not form thermodynamically stable chloro complexes. If Cr(V) is an oxy anion as has been suggested,<sup>14</sup> then it would not be expected to form stable chloro complexes; if Cr(IV) is an aquo cation as has also been suggested,<sup>14</sup> then we expect it to form complexes of finite stability. The failure to convert Cr(IV) and Cr(V) to chlorochromium(III) could also arise from unfavorable rates. It is not surprising that chlorochromium(IV) complexes could form slowly relative to the lifetime of Cr(IV) or even that uncomplexed Cr(IV) could be reduced much faster than complexed Cr(IV). A more definite conclusion is that Fe(II) or Cu(I) reduction of Cr(IV) did not occur primarily by a chloride-bridged mechanism in our experiments; such reductions would have led to chlorochromium(III). It seems particularly noteworthy that even Cu(I) converted less than 10% of the Cr(VI) to  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ , even though Cu(I) was extensively complexed by chloride,<sup>15</sup> in our experiment.

The most interesting implication of this study is the unexpected one that chloride-bridged dimeric chromium(II) species exist. Our evidence indicates that this is a mechanistically significant species. We suggest that the possible existence of Cr(II) dimers should be considered in connection with other mechanistic studies, especially if complexing anions are present.

**Registry No.**  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , 14873-01-9;  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ , 17712-88-8;  $\text{Cr}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ , 37380-89-5;  $\text{H}_2\text{CrO}_4$ , 7738-94-5; chromium(II) perchlorate, 13931-95-8.

(13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 821.

(14) C. Altman and E. L. King, *J. Amer. Chem. Soc.*, **83**, 2825 (1961).

(15) L. G. Sillen, Ed., *Chem. Soc., Spec. Publ.*, No. 17, 285 (1964).

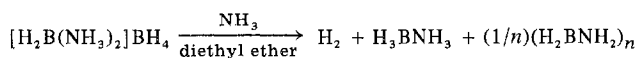
Contribution from the Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innsbruck, Austria

### Conversion of Dihydridodiammineboron(III) Borohydride to Ammonia-Borane without Hydrogen Evolution

Erwin Mayer

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It has been known for some 15 years that ammonia-borane can be formed from dihydridodiammineboron(III) borohydride.<sup>1</sup> In all such previous reports  $\text{H}_2$  was observed as a product along with another product usually assumed to be  $(\text{H}_2\text{BNH}_2)_n$ . The equation previously written is

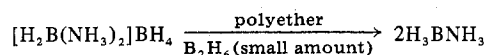


(1) S. G. Shore and R. W. Parry, *J. Amer. Chem. Soc.*, **80**, 8 (1958).

(11) R. W. Kolaczowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

(12) T. B. Joyner and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 516 (1961).

Recently I have found that  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  will convert to  $\text{H}_3\text{BNH}_3$  without  $\text{H}_2$  evolution in a polyether solution containing  $\text{B}_2\text{H}_6$ . The data support the new equation



With diglyme as solvent 91% of the original  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  was converted in one run to  $\text{H}_3\text{BNH}_3$  after 40 hr at  $25^\circ$ . In a second run 80% of the original salt was converted after an equivalent time. When monoglyme was used as solvent, the reaction was much slower, and in two runs only 22% and 37% of  $\text{H}_3\text{BNH}_3$  were formed after 60 hr.

It appears that  $\text{NH}_3$  in diethyl ether catalyzes decomposition with  $\text{H}_2$  generation while diborane in polyether yields  $\text{H}_3\text{BNH}_3$  as the sole product of decomposition.

Contrary to earlier literature reports<sup>1,2</sup> I found that solid  $\text{H}_3\text{BNH}_3$  of high purity did not undergo conversion to  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  even when the  $\text{H}_3\text{BNH}_3$  was held at  $50^\circ$  for 13 days.

### Experimental Section

**General Information.** Ether solvents were vacuum distilled from  $\text{LiAlH}_4$  suspensions into the reaction flask.  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  was prepared in liquid ammonia<sup>3</sup> and extracted with diethyl ether before use to remove any  $\text{H}_3\text{BNH}_3$  impurities.  $\text{H}_3\text{BNH}_3$  was prepared from  $\text{B}_2\text{H}_6$  and  $\text{NH}_3$  in diethyl ether.<sup>4</sup>

**$[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  in Diglyme with  $\text{B}_2\text{H}_6$ .** Diglyme (20 ml) was condensed onto 2.45 mmol of  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  (0.12 M) and 0.26 mmol of  $\text{B}_2\text{H}_6$  was added. The evacuated system was stirred at  $-23^\circ$  until  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  had dissolved completely. Afterward, the clear solution was warmed to room temperature and stirred with a magnetic bar for 40 hr. A 0.090-mmol amount of  $\text{H}_2$  was formed after this period and only a trace of precipitate was formed. Diglyme was pumped off quantitatively and fractionated. A 0.21-mmol amount of  $\text{B}_2\text{H}_6$  was recovered. From the solid nonvolatile residue 4.45 mmol of  $\text{H}_3\text{BNH}_3$  (1.82  $\text{H}_3\text{BNH}_3/[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ ) was extracted with diethyl ether. After pumping off the ether solvent  $\text{H}_3\text{BNH}_3$  was washed with *n*-hexane to remove any grease impurities and characterized by its X-ray powder pattern and infrared spectrum. The ether-insoluble residue consisted of 0.22 mmol of unreacted  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  as was shown by its X-ray powder pattern. No evidence was found for the formation of any other reaction products.

In another experiment 1.36 mmol of  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  was dissolved in 15 ml of diglyme (0.091 M) and 0.15 mmol of  $\text{B}_2\text{H}_6$  added. After 40 hr of reaction time at room temperature 0.045 mmol of  $\text{H}_2$  was formed. A 0.13-mmol amount of  $\text{B}_2\text{H}_6$  was recovered and 2.16 mmol of  $\text{H}_3\text{BNH}_3$  (1.59  $\text{H}_3\text{BNH}_3/[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ ) could be isolated.

**$[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  in Monoglyme with  $\text{B}_2\text{H}_6$ .** The reaction was carried out as described above with diglyme as solvent.  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  (0.99 mmol) was dissolved in 15 ml of monoglyme (0.067 M) and 0.14 mmol of  $\text{B}_2\text{H}_6$  was added. After 60 hr of reaction time at  $25^\circ$  0.01 mmol of  $\text{H}_2$  was formed. A 0.12-mmol amount of  $\text{B}_2\text{H}_6$  was recovered and 0.44 mmol of  $\text{H}_3\text{BNH}_3$  was isolated (0.44  $\text{H}_3\text{BNH}_3/[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ ). The diethyl ether insoluble residue consisted again of unreacted  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ .

In a second experiment a more concentrated solution was used (1.15 mmol of  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$  in 5 ml of monoglyme, 0.23 M) and 0.15 mmol of  $\text{B}_2\text{H}_6$  was added. After an equivalent reaction time, 0.094 mmol of  $\text{H}_2$  and 0.13 mmol of  $\text{B}_2\text{H}_6$  were isolated. A 0.84-mmol amount of  $\text{H}_3\text{BNH}_3$  was formed (0.73  $\text{H}_3\text{BNH}_3/[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ ).

**Attempted Conversion of  $\text{H}_3\text{BNH}_3$  into  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ .** A sample of 1.27 mmol of pure  $\text{H}_3\text{BNH}_3$  was stored at room temperature over 4 months in an evacuated glass ampoule. No trace of  $\text{H}_2$  was formed over this period and  $\text{H}_3\text{BNH}_3$  was completely soluble in diethyl ether.

Another sample of 1.91 mmol of  $\text{H}_3\text{BNH}_3$  was heated for 13 days at  $50^\circ$ . Higher temperatures could not be used because  $\text{H}_2$  formation became considerable. A 0.16-mmol amount of  $\text{H}_2$  (0.084  $\text{H}_2/\text{H}_3\text{BNH}_3$ ) was formed. The solid residue was extracted with

(2) E. Wiberg and E. Amberger, "Hydrides of the Elements of Main Groups I-IV," Elsevier, Amsterdam, 1971, p 151; K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, Berlin, 1965.

(3) S. G. Shore, K. W. Boedekker, and J. A. Pratton, *Inorg. Syn.*, **9**, 4 (1967).

(4) E. Mayer, *Inorg. Chem.*, **11**, 866 (1972).

diethyl ether and 1.74 mmol of  $\text{H}_3\text{BNH}_3$  recovered (91% of originally used material). The decomposition of 9%  $\text{H}_3\text{BNH}_3$  corresponds well with the formation of 8.4%  $\text{H}_2$  indicating decomposition of  $\text{H}_3\text{BNH}_3$  into polymeric borazane. The X-ray patterns of the sample stored at room temperature and of the sample heated at  $50^\circ$  contained no reflections of  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ .

**Registry No.**  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ , 17125-97-2;  $\text{H}_3\text{BNH}_3$ , 17596-45-1;  $\text{B}_2\text{H}_6$ , 19287-45-7; hydrogen, 1333-74-0.

Contribution from the Department of Chemistry, Revelle College, University of California, San Diego, La Jolla, California 92037

### Synthetic Procedure for Some Acidotetraamminechromium(III) Complexes

Gerald Wirth, Claudio Bifano, R. Tom Walters, and R. G. Linck\*

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In 1970, Vaughn, DeJovine, and Seiler published a paper in this journal describing the synthesis of *trans*- $[\text{Cr}(\text{en})_2\text{FCl}]\text{ClO}_4$ .<sup>1</sup> This molecule was of great interest to us so we have repeated the above-referenced synthesis. In the course of our investigation we have modified the conditions of the original technique somewhat and have found our modification to be of great utility for the synthesis of a variety of Cr(III) complexes. We have not established the limits of the applicability of the synthesis but have satisfied ourselves that the method is powerful and should be described. In this report we describe in detail the syntheses of *trans*- $[\text{Cr}(\text{en})_2\text{FCl}]\text{ClO}_4$ , *trans*- $[\text{Cr}(\text{en})_2\text{FBr}]\text{ClO}_4$ , *trans*- $[\text{Cr}(\text{NH}_3)_4\text{F}_2]\text{ClO}_4$ , and *trans*- $[\text{Cr}(\text{NH}_3)_4\text{FCl}]\text{ClO}_4$  and indicate how the method of synthesis can be applied in other cases.

### Experimental Section

**Synthesis of *trans*- $[\text{Cr}(\text{en})_2\text{FCl}]\text{ClO}_4$ .** A 10-g sample of *trans*- $[\text{Cr}(\text{en})_2\text{FH}_2\text{O}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ , prepared as described by Vaughn, Stvan, and Magnuson,<sup>2</sup> was slurried with 5 g of  $\text{NH}_4\text{Cl}$  in 150 ml of methanol and stirred in the dark at  $40^\circ$  for 18-24 hr. The crude product was removed by filtration and recrystallized from warm water by addition of  $\text{NaClO}_4$  followed by cooling. Spectral data are given in Table I. *Anal.* Calcd for *trans*- $[\text{Cr}(\text{en})_2\text{FCl}]\text{ClO}_4$ : Cr, 15.95. Found: Cr, 15.96.

**Synthesis of *trans*- $[\text{Cr}(\text{en})_2\text{FBr}]\text{ClO}_4$ .** A 3.5-g sample of *trans*- $[\text{Cr}(\text{en})_2\text{FH}_2\text{O}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  was treated with 3.5 g of  $\text{NH}_4\text{Br}$  in 25 ml of methanol. The mixture was stirred vigorously at  $40^\circ$  for 24 hr after which it was filtered and the precipitate dried. The crude complex was dissolved in 15% water in order to decrease the amount of complex that aquates during the recrystallization.<sup>3</sup> After addition of  $\text{NaClO}_4$  to the filtered solution it was cooled to  $0^\circ$ ; this yielded a precipitate that was washed with ethanol and dried *in vacuo*. The yield was 1.4 g, 45%. Spectral data are given in Table I. *Anal.* Calcd for *trans*- $[\text{Cr}(\text{en})_2\text{FBr}]\text{ClO}_4$ : Cr, 14.03; F, 5.13. Found: Cr, 14.11; F, 5.13.

**Synthesis of *trans*- $[\text{Cr}(\text{NH}_3)_4\text{F}_2]\text{ClO}_4$ .** The starting material for this synthesis was *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{O}]\text{Cl}_2$ , prepared as described.<sup>4</sup> A sample of 6 g of this complex was treated with 6 g of finely ground  $\text{NH}_4\text{F}$  in 120 ml of methanol and the slurry was stirred at  $40^\circ$  in the dark for 17 hr. The solid was removed by filtration and washed with ethanol; it was then dissolved in warm, dilute HCl. The solution was filtered into solid  $\text{NaClO}_4$  and cooled. The solid that resulted from this procedure was still a mixture of compounds, but a final recrystal-

(1) J. W. Vaughn, J. M. DeJovine, and G. J. Seiler, *Inorg. Chem.*, **9**, 684 (1970).

(2) J. W. Vaughn, O. J. Stvan, and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).

(3) A detailed report of the aquation kinetics of this complex as well as several related complexes will appear elsewhere.

(4) D. W. Hoppenjans and J. B. Hunt, *Inorg. Chem.*, **8**, 505 (1969).