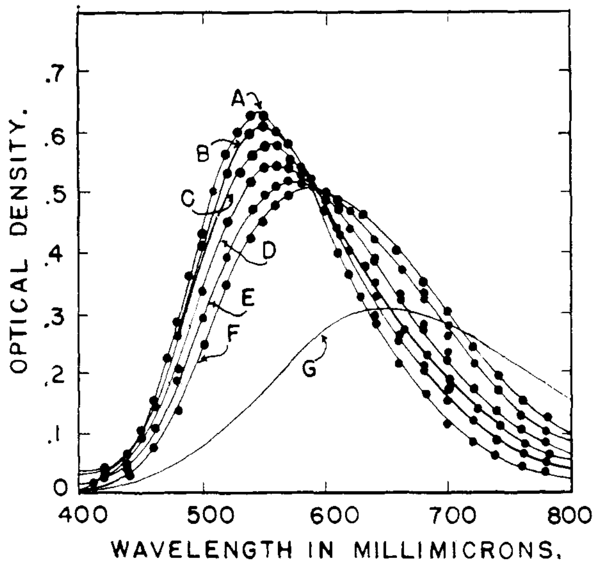
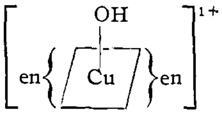


Fig. 1.—Absorption curves of $(Cu(en)_2)^{+2}$ in increasing concentrations of sodium hydroxide; copper concentration 0.01 *M:* A, no NaOH; B, 0.05 *M;* C, 0.1 *M;* D, 0.2 *M;* E, 0.4 *M;* F, 0.6 *M;* G, $(Cu\text{-}en)^{+2}$, no NaOH.

of 0.5 indicates that, as expected, two ethylenediamine molecules reacted with one copper(II) ion. The curve prior to the break, however, is nearly horizontal if only $[Cu(en)_2]^{2+}$ is formed. The negative slope obtained in the presence of excess hydroxide ions seems to indicate the withdrawal of highly conducting hydroxide ions.

The change in conductance indicated by the slope after the second break in the curve corresponds to the withdrawal of two hydroxide ions and the formation of $Cu(OH)_2$. Since this slope is twice that of the line prior to the first break, this seems to indicate that the change in the conductance of the region prior to the first break arises from the withdrawal of only one hydroxide ion from the solution.

The withdrawal of one hydroxide ion and the simultaneous reaction of two molecules of ethylenediamine with the copper(II) ion can be explained by the formation of a complex of the type



where the copper(II) ion is pentacovalent. For the average equilibrium constant for this reaction

$$[Cu(en)_2]^{2+} + OH^- \rightleftharpoons [Cu(en)_2(OH)]^{1+}$$

calculated from the absorption curves of Fig. 1, $\log K = 0.7301$. It is postulated that this complex of pentacovalent copper(II) is responsible for Jolley's observation of the increased solubility of cupric hydroxide in ethylenediamine solution when sodium hydroxide is added to the system. It can be explained by the equations

$$Cu(OH)_2 + 2en \rightleftharpoons [Cu(en)_2]^{2+}$$

$$[Cu(en)_2]^{2+} + OH^- \rightleftharpoons [Cu(en)_2(OH)]^{1+}$$

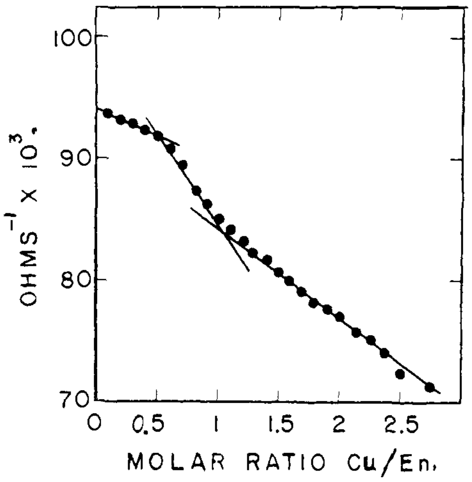


Fig. 2.—Conductometric titration of 0.004 *M* ethylenediamine in 0.05 *M* NaOH with 0.1 *M* copper nitrate.

$$[Cu(en)_2(OH)]^{1+} + Cu(OH)_2 \rightleftharpoons [Cu(en)_2]^{2+} + [Cu(OH)_3]^{1-}$$

$$[Cu(OH)_3]^{1-} + OH^- \rightleftharpoons [Cu(OH)_4]^{2-}$$

The over-all reaction would be

$$2Cu(OH)_2 + 2en \xrightarrow{\text{excess } (OH^-)} [Cu(en)_2]^{2+} + [Cu(OH)_4]^{2-}$$

Without sodium hydroxide the reaction would be

$$Cu(OH)_2 + 2en \rightleftharpoons [Cu(en)_2]^{2+}(OH)_2$$

It might be pointed out that the cuprate ion[11] $[Cu(OH)_4]^{2-}$ gives a blue solution which would not have been noticed by Jolley in the intense blue of the $[Cu(en)_2]^{2+}$ ion.

[11] R. Scholder, R. Felsenstein and A. Apel, *Z. anorg. Chem.*, **216**, 138 (1933).

RICHARDSON CHEMISTRY LABORATORY
TULANE UNIVERSITY
NEW ORLEANS, LA.

The Stability of the Silver Complex of Tris-(hydroxymethyl)-aminomethane[1]

BY RUTH E. BENESCH AND REINHOLD BENESCH

RECEIVED DECEMBER 22, 1954

In connection with a recently developed method for the determination of sulfhydryl groups in proteins,[2] in which the silver–tris complex is used as the titrant, it became of interest to determine the stability of this complex.

The association constants were determined by the method of Bjerrum.[3] The tris used was a recrystallized sample of "Sigma 121" (Sigma Chemical Co., St. Louis, Mo.) and the silver nitrate was Merck "Primary Standard." The $\bar{n}$ for the complex approached a limiting value of 2, which is analogous to other silver–amine complexes and which excludes interaction between the silver and the oxygen atoms of the tris. The association con-

---

[1] This compound will hereafter be referred to as tris.

[2] Benesch, *J. Biol. Chem.*, in press.

[3] J. Bjerrum, "Metal–Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

stants found were: $\log k_1 = 3.09$, $\log k_2 = 3.47$ and $\log K_2 = \log k_1k_2 = 6.56$ at 23°. This is in excellent agreement with the value of $\log K_2 = 6.51$, which can be calculated from the data on the solubility of silver chloride in tris given by Bates and Pinching.[4]

These data may be compared with the corresponding value for the silver–ammonia complex, determined under the same conditions, *i.e.*, $\log K_2 = 7.30$. As would be expected from these values, the half-wave potential at the rotating platinum electrode of the silver–tris complex was found to be only slightly more positive (*ca.* 30 millivolts) than that of the silver–ammonia complex under the same conditions.

In view of the rather bulky substituent groups on the α-carbon atom, it seems surprising at first sight that the reactivity of tris toward silver should be of the same order as that of ammonia. Moreover, its ratio of $\log K_{2_{\mathrm{Ag}^+}}/pK_{a_{\mathrm{H}^+}}$ is 0.81, which is almost identical with that of ammonia, *i.e.*, 0.79. Both these values are above those encountered with other primary amines.[5,6] It is suggested that the substituent groups do not interfere with the reactivity of the nitrogen atom because intramolecular hydrogen bonding between the hydroxymethyl groups leads to a highly symmetrical structure as shown in Fig. 1. This structure also is consistent with the crystalline state of this compound in contrast to other primary amines.

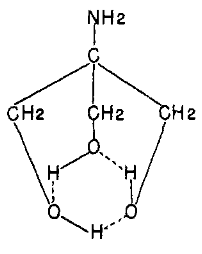


Fig. 1.

Acknowledgment.—This investigation was supported in part by a research grant H-1565 from the National Heart Institute of the National Institutes of Health, Public Health Service and by a grant from the National Science Foundation.

[4] R. G. Bates and G. D. Pinching, *J. Research Natl. Bur. Standards*, **43**, 519 (1949).

[5] R. V. Bruehlman and F. H. Verhoek, THIS JOURNAL, **70**, 1401 (1948).

[6] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall Inc., New York, N. Y., 1952.

DEPARTMENT OF BIOCHEMISTRY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

Tetrahydrofuran–Borine

BY BERNARD RICE, JEANETTE A. LIVASY[1] AND GEORGE W. SCHAEFFER

RECEIVED DECEMBER 30, 1954

The solid–liquid equilibrium for tetrahydrofuran and diborane has been investigated from zero to 0.34 mole per cent. of diborane. Within the range studied, the system (Fig. 1 and Table I) has a single eutectic with a composition of 9 mole per cent. diborane and a temperature of −117°. The compound tetrahydrofuran–borine, $C_4H_8O:BH_3$, is clearly indicated at 33 mole per cent. by the sharp maximum. Existence of the compound is further indicated by the homogeneous solid phase which appears at this composition and by the rapid increase in the saturation pressure of diborane at compositions just above 33 mole per cent. diborane. The point at mole per cent. 0.34 is not reliable, but serves to isolate the maximum. The high diborane pressures made extension of the data to higher diborane concentration difficult and suggest that the solubility of diborane in tetrahydrofuran–borine is negligible. The melting point of the compound is about −34° as determined by direct observation and by extrapolation of the melting point–composition curve to 33 mole per cent.

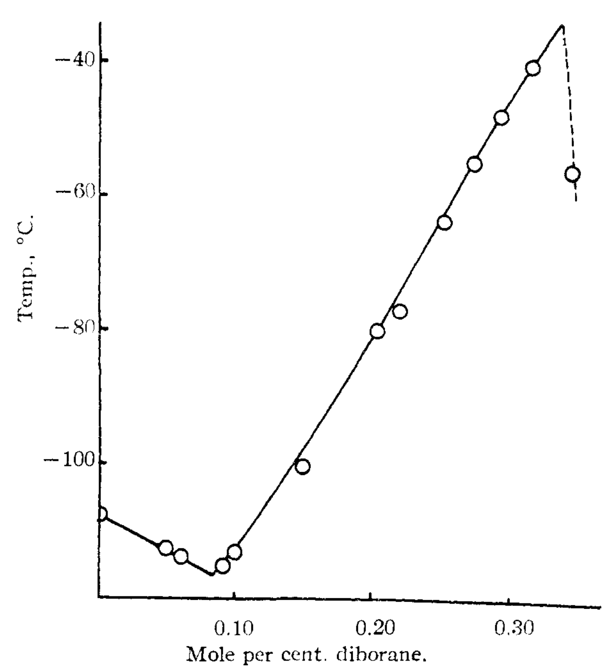


Fig. 1.—The system tetrahydrofuran–diborane.

TABLE I

Mole % B_2H_6	Temp., °C.	Mole % B_2H_6	Temp., °C.
0.00	−107.8	0.22	−76.7
.05	−112.5	.25	−63.6
.06	−114.0	.27	−54.7
.09	−114.7	.29	−48.2
.10	−113.6	.31	−40.1
.15	−100.2	.34	−56.2
.20	− 79.8		

These results are consistent with the solubility data of Elliot, *et al.*,[2] who interpreted the dependence of the solubility on the square root of the diborane pressure to imply the existence of tetrahydrofuran–borine. These investigators found no indication from solubility data of the existence of diethyl ether–borine and this compound may be presumed much less stable than tetrahydrofuran–borine. Dimethyl ether–borine[3] is the only other compound of this class for which evidence has been advanced. It has been shown to exist below −78° and is evidently much less stable than the compound reported herein. Under comparable conditions, no evidence for diethyl

---

[1] Taken from a thesis presented by Jeanette A. Livasy to the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Master of Science, June, 1955.

[2] J. R. Elliot, W. L. Roth, G. F. Roedel and E. M. Boldebuck, THIS JOURNAL, **74**, 5211 (1952).

[3] H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 296 (1938).