[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

The Reaction between the Copper(II)–Ethylenediamine Complexes and D-Mannosan

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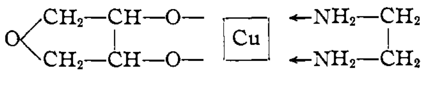
Spectrophotometric, conductometric and optical rotation studies indicate that monoethylenediamine–copper(II) and bis ethylenediamine–copper(II) react with D-mannosan to form the monoethylenediamine–D-mannosan-copper(II) complex in basic solution.

A study of the reaction between the copper(II)–ethylenediamine complexes and *cis*-glycol, *cis*-3,4-dihydroxytetrahydrofuran (erythritol anhydride), was reported in a previous paper.[2] Conductometric titrations and spectrophotometric studies showed that the product of the reaction of the anhydride with each of the copper(II)–ethylenediamine complexes was the complex



$$O\left\langle\begin{matrix}CH_2-CH-O-\\ \quad\ \ | \\ CH_2-CH-O-\end{matrix}\right.\ \boxed{Cu}\ \begin{matrix}\leftarrow NH_2-CH_2\\ \qquad\quad | \\ \leftarrow NH_2-CH_2\end{matrix}$$

This resulted from a simple bimolecular reaction between the glycol and $[(Cu(en)]^{2+}$. However, with the $[Cu(en)_2]^{2+}$ complex, one molecule of ethylenediamine had to be replaced by a molecule of the glycol.

Since it was desirable to verify the above conclusion by the application of additional experimental methods and the use of another suitable polyhydric alcohol, D-mannosan (D-mannose<1,5>β <1,6> anhydride), was selected. This optically active compound would also permit optical rotation studies. Reeves[3] states that D-mannosan is the most active complex-forming substance encountered in a survey of many sugar derivatives and that the glycol grouping involved in reaction with cuprammonium hydroxide is the pair of hydroxyl groups on carbon atoms 2 and 3. It was concluded from spectrophotometric, optical rotation and conductivity studies that a simple bimolecular reaction occurred between D-mannosan and cuprammonium hydroxide. The present paper presents the results of studies made with D-mannosan and the copper(II)–ethylenediamine complexes.

Experimental

Spectrophotometric studies and conductometric titrations were made as in the previous study.[2] In optical rotation experiments a Gaertner Lippich triple field polarimeter was used. A one dm. tube similar to one described by Reeves[4] was modified by sealing a glass-stoppered bulb on the side-arm. The mercury blue line (436 mμ) was isolated by means of Corning Filters 5113 and 038. All optical rotations were measured at 25 ± 2°. The constant ionic strength was maintained by addition of potassium nitrate.

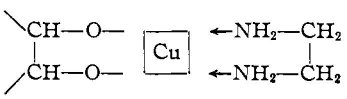
The D-mannosan was that used by Reeves in earlier studies[3,5] and when the reaction between the copper(II)–ethylenediamine complexes and D-mannosan was followed by optical rotation measurements two solutions were prepared which were identical in concentrations of copper(II), ethylenediamine and glycol, but one contained in addition 0.1 M sodium hydroxide. Optical rotation was followed in two series of experiments; in one series the base-free solution was placed in the tube and the solution containing the base was added from a micro-buret, in the second series the opposite operation was performed.

The technique of saturation studies developed by Ruff[6] and widely used in spectrophotometric studies was employed with polarimetric instead of spectrophotometric data. The solutions were handled in the same way as described above for the addition of sodium hydroxide. Polarimetric saturation and continuous variation studies have also been employed by Reeves and Blouin[7] in studies involving titanium complexes.

Results and Discussion

If the *cis*-hydroxyl groups of erythritol anhydride and D-mannosan react similarly with the copper(II)–ethylenediamine complexes, it would be expected that the absorption and conductometric data should reflect this fact. The absorption curves of the products formed in the reaction between D-mannosan and the copper(II)–ethylenediamine complexes, shown in Fig. 1, are almost identical with those obtained previously[2] for the complexes with erythritol anhydride. Examination of the conductometric titration curves of $[Cu(en)]^{2+}$ and D-mannosan (Fig. 2), and of $[Cu(en)_2]^{2+}$ and the glycol (Fig. 3) obtained with sodium hydroxide show that they, too, give similar data as those for the complexes and the anhydride, that is, breaks occur in the curves at the same OH/Cu ratio of 2.

Since the results of spectrophotometric and conductometric experiments with D-mannosan are so similar to those obtained with erythritol anhydride, it can be concluded that the complex formed from bis-ethylenediamine–copper(II) and D-mannosan is similar in structure to that formed with the anhydride, and that both have the structure



$$\begin{matrix}\diagdown CH-O-\\ \ \ | \\ \diagup CH-O-\end{matrix}\ \boxed{Cu}\ \begin{matrix}\leftarrow NH_2-CH_2\\ \qquad\quad | \\ \leftarrow NH_2-CH_2\end{matrix}$$

Further evidence to support this conclusion was found in studies of optical rotation.

Uncomplexed D-mannosan in the concentration employed had an observed rotation of −0.77° (1 dm.). This rotation was observed with all combinations of constituents of the system in the absence of sodium hydroxide. The change in rotation as a function of sodium hydroxide concentration is shown in Fig. 4. Curve A represents studies with the $[Cu(en)]^{2+}$ ion. This curve indicates that a complex is readily formed with D-mannosan and that the reaction is complete even at low concentrations of base.

The region of turbidity occurring from less than 0.1 to 0.02 M base and the nearly equal optical ro-

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[1] Abstracted in part from a dissertation submitted by Leon Segal to Tulane University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] H. B. Jonassen, R. E. Reeves and L. Sigal, THIS JOURNAL, **77**, 2667 (1955).

[3] R. E. Reeves, *ibid.*, **73**, 957 (1951).

[4] R. E. Reeves, *Advances in Carbohydrate Chem.*, **6**, 133 (1951).

[5] R. E. Reeves, THIS JOURNAL, **71**, 2116 (1949).

[6] O. Ruff, *Z. physik. Chem.*, **76**, 21 (1911).

[7] R. E. Reeves and F. A. Blouin, THIS JOURNAL, **76**, 5233 (1954).

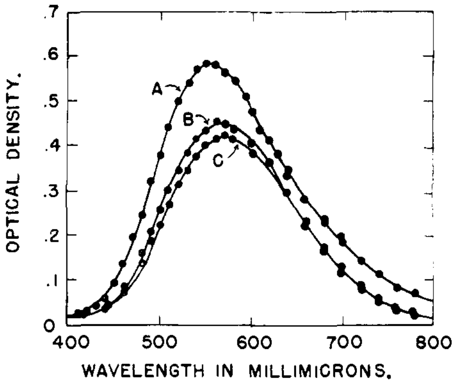

Fig. 1.—Absorption curves for the complexes of D-mannosan and copper(II)-ethylenediamine in 0.1 *M* sodium hydroxide: A, 0.01 *M* $[Cu(en)_2]^{2+}$; B, 0.01 *M* $[Cu(en)_2]^{2+}$ + 0.02 *M* mannosan; C, 0.01 *M* $[Cu(en)]^{2+}$ + 0.02 *M* mannosan.

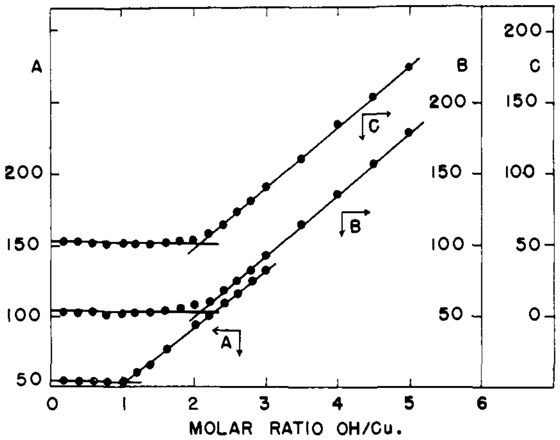

Fig. 2.—Conductometric titration of 0.0025 *M* $[Cu(en)]^{2+}$ and D-mannosan with 0.25 *M* NaOH: A, $[Cu(en)]^{2+}$ alone; B, complex plus 0.005 *M* mannosan; C, complex plus 0.0125 *M* mannosan.

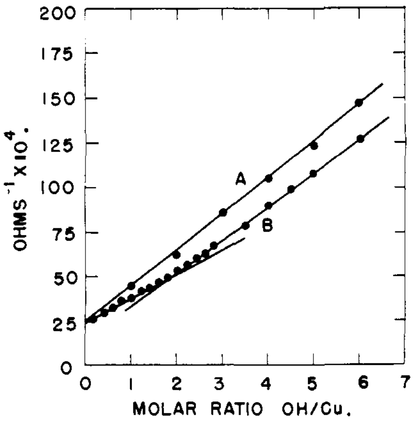

Fig. 3.—Conductometric titration of 0.001 *M* $[Cu(en)_2]^{2+}$ and D-mannosan with 0.1 *M* NaOH: A, $[Cu(en)_2]^{2+}$ alone; B, complex plus 0.002 *M* mannosan.

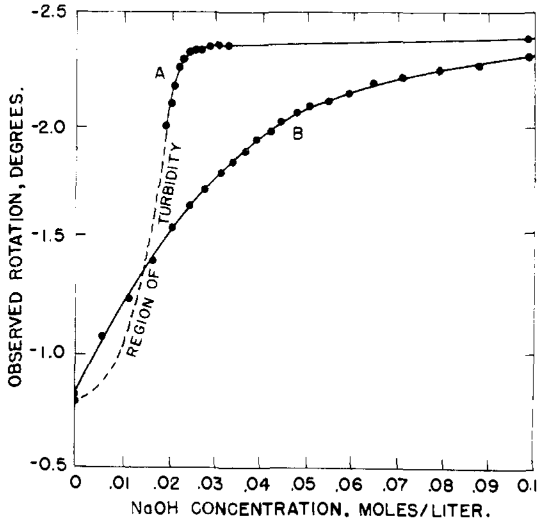

Fig. 4.—The change in optical rotation as NaOH is added to solutions of D-mannosan and (A) $[Cu(en)]^{2+}$ and (B) $[Cu(en)_2]^{2+}$. The concentration of (A) $[Cu(en)]^{2+}$ and (B) $[Cu(en)_2]^{2+}$ = 0.01 *M*. The concentration of D-mannosan = 0.02 *M*.

tations at base concentrations of 0.05 and 0.1 *M* sodium hydroxide both confirm certain effects observed in the spectrophotometric experiments. In those spectrophotometric studies precipitates were obtained in the $[Cu(en)]^{2+}$-glycol system with 0.01 and 0.02 *M* sodium hydroxide solutions. Furthermore, the clear solution obtained with 0.05 *M* base showed the same absorption characteristics as that with 0.1 *M* base.

Curve B represents results with $[Cu(en)_2]^{2+}$. The shape of this curve indicates that high base concentrations are required to force the $[Cu(en)_2]^{2+}$ ion to react completely with the mannosan. This was also observed in the spectrophotometric absorption curves obtained with $[Cu(en)_2]^{2+}$ and erythritol anhydride.[2] This is understandable since one ethylenediamine molecule must be removed from the complex in order to allow the glycol to react.

The close approach of curve B to curve A at 0.1 *M* base suggests that the same product is formed in the two systems. This conclusion was also drawn from the spectrophotometric and the conductometric studies.

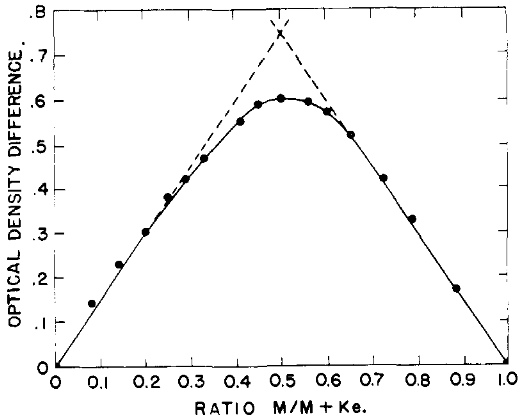

Fig. 5.—Saturation study of the $[Cu(en)_2]^{2+}$-mannosan system using optical rotation: M = solution 0.01 *M* in copper(II) ion, 0.02 *M* in ethylenediamine (therefore 0.01 *M* in $[Cu(en)_2]^{2+}$) and 0.1 *M* in NaOH; Ke solution 0.01 *M* in D-mannosan and 0.1 *M* in NaOH.

Further evidence is furnished by the saturation study (Fig. 5) when $[Cu(en)_2]^{2+}$ and D-mannosan interact. Regardless of whether the mannosan was added to the $[Cu(en)_2]^{2+}$ or *vice versa*, the peak of the curve was located at a mole fraction 0.5. This indicates that the reaction takes place in a molecular ratio of 1:1, which is identical with the results of the spectrophotometric continuous variation studies with erythritol anhydride.[2] A saturation study could not be made with the $[Cu(en)_2]^{2+}$ ion because it is unstable in the presence of sodium hydroxide.

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The Heat Capacities of Potassium Ferricyanide and Potassium Cobalticyanide from 15 to 300°K. A Magnetic Transition in Potassium Ferricyanide

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The heat capacities of potassium ferricyanide and potassium cobalticyanide have been measured from 15 to 300°K. The standard entropies of the salts at 298.16°K. are 100.4 and 96.0 ± 0.2 cal. deg.$^{-1}$ mole^{-1}, respectively. The thermodynamic properties of ferricyanide and ferrocyanide ions have been calculated. A gradual transition, magnetic in nature, occurs at about 131°K. in the paramagnetic potassium ferricyanide. Ordering of the spin moments may not be complete at 15°K. in this salt.

The calorimetric determination of the entropy of paramagnetic substances by means of heat capacity measurements and by use of the third law of thermodynamics frequently requires measurements to temperatures below 15°K. A paramagnetic substance, which is in a disordered state, must become ordered at some low temperature, and if the substance is magnetically dilute, as in paramagnetic alums and hydrates, this ordering may occur at temperatures well below 15°K. In the relatively few cases where complete heat capacity measurements have been made at these low temperatures, the entropy change associated with the ordering process has agreed with that calculated from theory. The addition of the magnetic entropy contribution to the usual Debye extrapolation is justified in such cases. However, considerable discretion is required, because the anomalous heat capacities caused by a changing population of the electronic energy levels in the solid may extend to higher temperatures where a differentiation from the lattice heat capacities becomes difficult.

The magnetic properties of potassium ferricyanide, $K_3Fe(CN)_6$, which correspond to $S = {}^1/_2$, have been the subject of a number of experimental[2,3] and theoretical studies.[4] According to Howard, crystalline field theory gives three doubly degenerate energy levels of which only the lowest will be occupied at room temperature. Hence, the total magnetic entropy to be expected at low temperatures is not $R \ln 6$, as in a ferric alum, but $R \ln 2$. This magnetic entropy of $R \ln 2$ should be lost at temperatures below 15°K. The susceptibility measurements also indicate the potassium ferricyanide is disordered magnetically at 15°K., and there are no abnormal changes in the susceptibility at higher temperatures. Nevertheless, Dr. Richard Bersohn suggested to us that a transition might occur at higher temperatures due to interaction between ferricyanide ions in the crystal. We have measured the heat capacity of potassium ferricyanide from 15 to 300°K. for this reason, as well as to obtain the thermodynamic properties of the substance.

A gradual transition was found in potassium ferricyanide, with a maximum occurring in the heat capacity at about 131°K. In order to show that this transition is magnetic in nature, it was then necessary to measure the heat capacity of the diamagnetic potassium cobalticyanide, $K_3Co(CN)_6$, which is presumably isomorphous with the ferricyanide. The heat capacity of potassium cobalticyanide, which was measured from 15 to 300°K., is normal. The entropy change associated with the gradual transition in the ferricyanide, which is an important factor in the interpretation of the nature of such a transition, was estimated by using the normal heat capacities of the cobalticyanide as a guide. Unfortunately, a complete interpretation of these results is not yet possible.

Material.—Potassium ferricyanide for the calorimetric determination was commercial C.P. material (maximum impurities less than 0.02%) recrystallized three times from distilled water. This product was subjected to vacuum desiccation to remove most of the water. All measurements were made on a single loading of 160.8990 g. *in vacuo*, or 0.488689 mole. Correction has been made for the presence of 0.0109 weight per cent. water indicated by slight distortion of the heat capacity curve near the ice point. The molecular weight of potassium ferricyanide was taken as 329.246.

Potassium cobalticyanide (potassium hexacyanocobaltate-(III)) was prepared by the method of Benedetti-Pichler.[5] To an aqueous solution of cobaltous chloride potassium cyanide was added dropwise; the finely divided precipitate of cobaltous cyanide was filtered and washed once with cold water. The moist product was transferred to a solution of potassium cyanide sufficiently concentrated to dissolve the cobaltous cyanide completely. This solution was heated and held at the boiling point for 15 minutes, whereupon hydrogen was evolved, and the solution turned yellow. Pale yellow crystals of potassium cobalticyanide precipitated from the cold solution. The product was recrystallized from distilled water five times in order to remove all traces of potassium cyanide. Potassium cyanide undergoes a non-isothermal transition[6] near 168°K. with a total heat effect of 300 cal./mole; 0.05 weight per cent. potassium cyanide would be detected by distortion of the heat capacity curve

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(1) Allied Chemical and Dye Corporation Fellow, academic year 1948–1949.

(2) L. C. Jackson, *Proc. Roy. Soc.* (*London*), **A140**, 695 (1933).

(3) L. C. Jackson, *Proc. Phys. Soc.* (*London*), **50**, 707 (1938).

(4) J. Howard, *J. Chem. Phys.*, **3**, 813 (1935).

(5) A. A. Benedetti-Pichler, *Z. anal. Chem.*, **70**, 258 (1927).

(6) C. Messner and W. Ziegler, THIS JOURNAL, **63**, 2703 (1941).