

TABLE III
TENDENCY FOR COMPLEX FORMATION (BJERRUM)

	Ac ⁻	Supporting electrolyte anions Cl ⁻	NO ₃ ⁻
Cu ⁺⁺	2.6	...	<0
Pb ⁺⁺	2.7	...	(1.1)
Cd ⁺⁺	2.2	2.3	...
Tl ⁺	(0)	(0.7)	...

no competition from the anions of the supporting electrolyte. Such competition does exist in the case of lead, however, and is very strong in the case of cadmium. Hence it would be expected that the strongest reaction with the carboxyl groups of serum albumin, in the presence of the particular supporting electrolytes used in this investigation, will occur with copper. Lead should be next strongest, with cadmium showing little interaction. This is precisely what is observed acid to pH 4, as can be seen from an examination of Fig. 1. No combination at all is to be expected for thallium.

Note.—After this paper was completed, it was learned that a precise study of the reaction between zinc and human serum albumin by the equilibrium dialysis method has been made by F. R. N. Gurd and D. S. Goodman, of Harvard University. Their results, too, show that binding occurs primarily at the imidazole groups. The value of $\log K_0$ at 0° in 0.15 M NaNO₃ was found to be 2.82; the value of 2.9 given in this paper (Table II) is in good agreement with that. Gurd and Goodman have also studied the reaction between zinc and imidazole itself, and have found for the logarithm of the first association constant the value 2.76. At the same time, G. Felsenfeld and J. T. Edsall determined the association constants between copper and imidazole: for the logarithm of the first constant in 0.15 M NaNO₃ at 22.5° they obtain the value 4.40. This value is higher than that reported in this paper for serum albumin, but not too much so, considering that carboxyl group binding, which is very pronounced in the case of copper, has been entirely ignored in our analysis. In any event, these values indicate that the properties of the imidazole groups of serum albumin, with respect to metal binding, are certainly not very different from the properties of imidazole itself.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Preparation and Properties of N-Monosubstituted Ethylenediamine Complexes of Cobalt and Nickel^{1,2}

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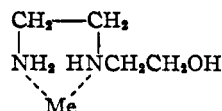
The tris-cobalt(III) complex of NH₂CH₂CH₂NHCH₂CH₂OH was prepared with the expectation that coordination through the nitrogen atoms would allow the hydroxyl group to remain free for further reaction. Not only did these hydroxyl groups appear to be unresponsive chemically but the resulting compound showed a remarkable inertness toward most common reagents. Other cobalt(III) and nickel(II) compounds of this hydroxy-diamine and other N-monosubstituted ethylenediamines were prepared but none possessed the inert character of the above complex. Of the hydroxy derivatives investigated, the greatest stability of the coordination compounds is attained when the hydroxyl group is two carbon atoms removed from the nitrogen.

Introduction

The change in properties and reactivity of the central metal ion accompanying coordination has been quite thoroughly investigated, but little attention has been given to the effect of coordination upon the chemical nature of the ligands in a complex compound. Sparsely scattered throughout the literature are references to a number of reactions which have been carried out on coordinated molecules and ions but most of these reactions are merely incidental to other lines of investigation.⁴⁻⁸

In the present work the first substance studied as a coordinating molecule was the diamine N-hydroxyethylethylenediamine, NH₂CH₂CH₂NHCH₂CH₂OH. Coordination to a metal ion would

be expected to occur through the nitrogen atoms



The hydroxyl group consequently should be left free for further reaction. If this group retains typical organic characteristics in the resulting coordination compound, esterification of the group or replacement with other groups might be anticipated. The unexpected extreme stability encountered in the tris-hydroxyethylethylenediamine cobalt(III) salts and the unreactivity of the hydroxyl group in these complexes prompted an investigation of other N-monosubstituted ethylenediamine complexes. The diamines employed and the symbolization used in this paper are indicated below.

(1) From the Ph.D. Thesis of L. J. Edwards, University of Michigan, June, 1950.

(2) Presented in part before the Division of Physical and Inorganic Chemistry, 117th Meeting of the American Chemical Society, Detroit, Michigan, April 17, 1950.

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(4) F. Feigl and H. A. Suter, *J. Chem. Soc.*, 378 (1948).

(5) I. I. Chernyaev, *Ann. inst. platine*, No. 7, 52 (1939); *C. A.*, **24**, 2684 (1930).

(6) E. G. J. Hartley, *J. Chem. Soc.*, 1066 (1910); *ibid.*, 705 (1912); *ibid.*, 1196 (1913); *ibid.*, 101 (1933); *Proc. Chem. Soc.*, **26**, 90 (1910); *ibid.*, **28**, 101 (1912); *ibid.*, **29**, 188 (1913).

(7) H. D. K. Drew, *J. Chem. Soc.*, 2328 (1932).

(8) M. A. Dahlen, *Ind. Eng. Chem.*, **31**, 839 (1939).

Diamine	Symbol
Ethylenediamine, NH ₂ CH ₂ CH ₂ NH ₂	en
N-Methylethylenediamine, NH ₂ CH ₂ CH ₂ NHCH ₃	me-en
N-Ethylethylenediamine, NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₃	et-en
N-(n-Propyl)-ethylenediamine, NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₃	pr-en
N-Hydroxyethylethylenediamine, NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ OH	etol-en

Diamine	Symbol
N-(3-Hydroxypropyl)-ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{OH}$	prol-en
N-(2-Hydroxypropyl)-ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}(\text{OH})\text{CH}_3$	iprol-en

Experimental Results

Metal Complexes Containing N-Monosubstituted Ethylenediamines.—Compounds of N-hydroxyethylethylenediamine with copper(II) and nickel(II) have been reported⁹ but apparently attempts to prepare the cobalt(II) and cobalt(III) salts were unsuccessful. In this work a compound with cobalt(III) was obtained but only after considerable difficulty, presumably due to the marked resistance to oxidation of a cobalt(II) solution containing N-hydroxyethylethylenediamine. This same difficulty in the preparation of cobalt(III) complexes was encountered with N-(3-hydroxypropyl)-ethylenediamine and N-(2-hydroxypropyl)-ethylenediamine. The following solid cobalt(III) and nickel(II) complexes were prepared: $[\text{Co}(\text{etol-en})_3]\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}$), $[\text{Co}(\text{prol-en})_3]\text{Cl}_3$, $[\text{Co}(\text{iprol-en})_3]\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}$), $[\text{Co}(\text{me-en})_3]\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}$), $[\text{Co}(\text{et-en})_3]\text{Cl}_3$, $[\text{Co}(\text{pr-en})_3]\text{Cl}_3$, $[\text{Ni}(\text{etol-en})_3]\text{Br}_2$, $[\text{Ni}(\text{iprol-en})_3]\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) and $[\text{Ni}(\text{me-en})_3]\text{Br}_2$.

Chemical Nature of the OH Groups in $[\text{Co}(\text{etol-en})_3]\text{X}_3$.—In an effort to bring about reaction on the hydroxyl groups of the coordinated diamine molecules without rupturing the coordinate bonds, samples of $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$ were treated in a variety of ways. Refluxing the solid complex with benzoyl chloride, acetyl chloride, acetic anhydride, phosphorus tribromide and thionyl chloride resulted in no change in the composition of the solid and gave no evidence that a reaction had occurred between these reagents and the coordinated diamine alcohol molecules. Refluxing this complex with concentrated hydrochloric acid for periods of time up to ten hours gave no indication of reaction nor was any decomposition of the compound detectable by analysis of the treated solid. The corresponding ethylenediamine salt decomposed within 15 minutes when boiled with concentrated hydrochloric acid. Attempts to replace the hydroxyl groups in $[\text{Co}(\text{etol-en})_3]\text{Br}_3$ with bromine by refluxing the bromide with 48% hydrobromic acid were unsuccessful. Only after several hours of refluxing was there any evidence at all of decomposition of the complex. Similar treatment of tris-ethylenediamine cobalt(III) bromide resulted in almost complete decomposition of the complex after about five minutes of heating.

A solution of $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$ in concentrated nitric acid (70%) was refluxed in an attempt either to oxidize or nitrate the alcohol groups. No evidence of decomposition or reaction with the hydroxyl groups could be observed even after boiling for 52 hours with additional acid being added at intervals to maintain the high acid concentration. The only change that had occurred was the oxidation of the chloride anions. The corresponding tris-ethylenediamine cobalt(III) salt, when subjected to similar treatment, decomposed within a few minutes.

(9) J. G. Breckenridge, *Can. J. Research*, **26B**, 11 (1948).

A solution of $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$ in aqua regia was refluxed for several hours and then chlorine was bubbled through the solution and the mixture again refluxed. This treatment was repeated several times and the complex was finally recovered by slowly concentrating the mixture. The nitrate salt of the tris-complex was the only crystalline product obtained although slight decomposition of the complex had occurred.

The reaction of the tris-N-hydroxyethylethylenediamine Co(III) complex with sodium hydroxide is worthy of note. A solution of this compound in 15% sodium hydroxide when boiled changes gradually from its characteristic orange color to pink, which increases in intensity to a dark red. That the complex has been changed is evidenced by the fact that addition of the $[\text{Co}(\text{CN})_6]^{-3}$ ion to the basic solution no longer yields a precipitate. Continued boiling of the sodium hydroxide solution does not result in a precipitate until just before going to dryness at which point the solution quickly turns black. The black solid which is formed liberates chlorine from hydrochloric acid, indicating the presence of cobalt(III). These basic solutions may contain complexes in which the hydroxyl groups of the coordinated diamine molecules have reacted with the sodium hydroxide. Under similar treatment the tris-ethylenediamine cobalt(III) compounds appear to be very much less stable with decomposition to the black solid occurring even without boiling.

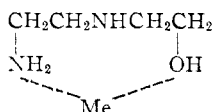
Discussion

The outstanding chemical property noted among the metal complexes containing N-monosubstituted ethylenediamines is the extreme inertness of the tris-N-hydroxyethylethylenediamine cobalt(III) compound toward most common reagents. Also, with the possible exception of the reaction with sodium hydroxide, the hydroxyl groups in this complex appear entirely immune to attack by all reagents tried. Further investigation is under way to ascertain whether strongly basic solutions of this and other hydroxyl-containing diamine complexes may conceivably contain ions in which the hydroxyl groups of the coordinated molecules have reacted with the sodium hydroxide.

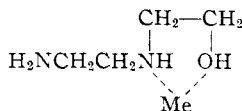
None of the other solid compounds containing N-monosubstituted ethylenediamines appear to approach $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$ in chemical unreactivity. The compound $[\text{Co}(\text{iprol-en})_3]\text{Cl}_3$ was intermediate in reactivity between $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$ and $[\text{Co}(\text{en})_3]\text{Cl}_3$. Monosubstitution of an alkyl group on the nitrogen in ethylenediamine appears to result in no exceptional change in the properties of the metal complexes derived from the substituted diamine as compared with the corresponding ethylenediamine complexes. From the limited data available on the hydroxy-derivatives of ethylenediamine, the greatest stability of the coordination compounds is attained when the hydroxyl group is two carbon atoms removed from the nitrogen.

The marked inertness of the tris-cobalt(III) complex of N-hydroxyethylethylenediamine presents a perplexing problem. It is not at all clear why the hydroxyl group in the coordinated diamine

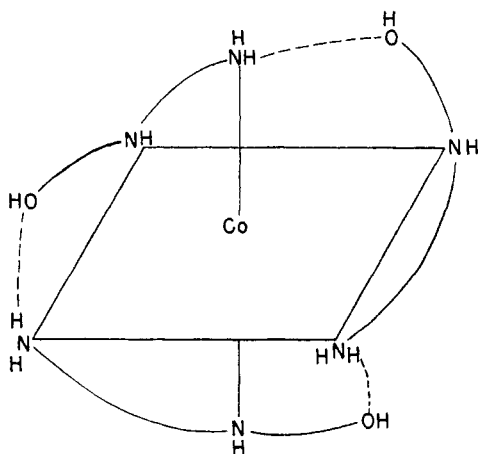
molecule, if it is "free" as pictured (see Introduction) should be so extremely unreactive chemically. Inasmuch as the complex with cobalt(III) was shown by analysis and the freezing point depression method to be the tris-compound, it is difficult to devise any reasonable structure in which the hydroxyl groups are involved in coordination to the metal ion. If coordination occurred through the nitrogen of the primary amino group and the oxygen of the hydroxyl group



the resulting eight-membered ring would surely be unstable. On the other hand, if the nitrogen of the secondary amino group and the oxygen of the hydroxyl group were involved in coordination,



then the primary amino group, which is ordinarily the strongest coordinator, would be left free. It is conceivable that intramolecular hydrogen-bonding might occur in the tris-complex in the following manner



However, it would hardly be expected that hydrogen bonds of this type would greatly enhance the over-all stability of the complex.

Any deep-seated change in the structure of the amine-alcohol molecules as a result of coordination seems ruled out by the regeneration of these molecules unchanged when the complex is split with hydrogen sulfide.

Preliminary infrared studies on the compounds, $[\text{Co}(\text{etol})_3]\text{Cl}_3$ and $[\text{Co}(\text{iprol-en})_3]\text{Cl}_3$, are inconclusive. Tentative conclusions, however, appear to point to the existence of essentially "free" hydroxyl groups in these complexes.

Further study of these compounds is necessary before a decision can be reached as to whether their apparent chemical inertness is a rate of reaction phenomenon or is the reflection of a very small instability constant.

Experimental

Analytical Procedures.—*Halides:* Chloride and bromide were determined by potentiometric titration with standard silver nitrate solution (0.08 *N*). *Nitrogen:* The usual Kjeldahl method for the determination of nitrogen requires modification if the sample contains large amounts of cobalt or other strong complex-forming metal ions. In the procedure for the nitrogen values reported here, about 50 mg. of the metal complexes was digested for one hour with solid potassium sulfate and copper(II) sulfate to which an excess of concentrated sulfuric acid had been added.¹⁰ In order to prevent any complex formation between the metal ion of these compounds and the liberated ammonia, a solution saturated with both sodium sulfide and sodium hydroxide was added to the acid-digested samples. The liberated gases, consisting mainly of hydrogen sulfide and ammonia, were passed into a boric acid solution and the resulting solution titrated with standard hydrochloric acid (ca. 0.05 *N*) using a methyl red-methylene blue indicator. Best results were obtained by maintaining an ice mixture about the reagent flask, which contained 25 ml. of a boric acid solution (40 g. boric acid per liter). It is not necessary to measure an exact volume of boric acid since the indicator reflects only the titration of the ammonium salt present. Samples of acetanilide and an excess of cobalt(II) chloride were used to standardize the method. *Nickel:* All of the nickel analyses were made by the customary gravimetric method using dimethylglyoxime. *Cobalt:* This element was determined potentiometrically.¹¹ About 50-mg. samples of the solid complexes were carefully weighed and successively evaporated to dryness three times with concentrated nitric acid. About 100 ml. of distilled water was added to the cobalt(II) nitrate residue and the percentage of cobalt determined on an aliquot of this solution.

Molecular Weights.—The molecular weights were calculated from freezing point depression measurements on solutions containing 50 to 75 mg. of the solid complex in about 10 g. of water. A Beckmann thermometer of 6.2 degree range was used for the temperature measurements and could be read within 0.003°. The average depression of the freezing point was of the order of 0.1°.

N-Hydroxyethylethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$.—This derivative of ethylenediamine, which was obtained commercially,¹² was purified by a single distillation *in vacuo* in an all-glass apparatus (b.p. 123° at 10 mm.).

N-(2-Hydroxypropyl)-ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}(\text{OH})\text{CH}_3$.—This compound was prepared from ethylenediamine and propene oxide according to the method of Kitchen and Pollard¹³ and was purified by distillation under vacuum (b.p. 112° at 10 mm.).

N-(3-Hydroxypropyl)-ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{OH}$.—This substance was prepared by the dropwise addition of 50 g. (0.36 mole) of trimethylenebromohydrin to a well-stirred solution of 129 g. (2.15 moles) of anhydrous ethylenediamine in 150 g. of isopropyl alcohol as solvent, the reaction mixture being maintained at about 50°. The mixture was refluxed for one hour and then distilled at atmospheric pressure until the temperature reached 85°; distillation was then continued at 10 mm. pressure. The viscous oil remaining in the flask after the distillation was treated with a saturated aqueous sodium hydroxide solution and an excess of solid sodium hydroxide. The amine layer that separated from the aqueous phase was distilled at 10 mm. pressure from solid sodium hydroxide. Fractionation of the distillate yielded 18.5 g. (43.5% yield based on the trimethylenebromohydrin) of N-(3-hydroxypropyl)-ethylenediamine boiling at 126–127° at 5 mm. pressure.

Anal. Calcd. for $\text{C}_3\text{H}_{14}\text{N}_2\text{O}$: N, 23.69. Found: N, 23.6.

The neutral equivalent of this compound was 57 (theoretical, 59) and the dipicrate melted at 222°.

N-Alkylethylenediamines, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHR}$.—N-Methylethylenediamine, N-ethylethylenediamine and N-(*n*-propyl)-ethylenediamine were prepared by the general method

(10) In the case of $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$ a digestion time of 2.5 hours was used.

(11) R. C. Chirnside, H. J. Cluley and P. M. C. Proffitt, *Analyst*, **72**, 354 (1947).

(12) A research sample from Carbide and Carbon Chemical Co.; later purchased from Matheson Chemical Company.

(13) L. J. Kitchen and C. B. Pollard, *J. Org. Chem.*, **8**, 842 (1943).

suggested by Aspinall¹⁴ in which N-benzenesulfonyl-N'-acetylenediamine, prepared as an intermediate, was treated with the appropriate alkyl iodide and the resulting compound hydrolyzed in acid medium.

Tris-N-hydroxyethylethylenediamine Co(III) Chloride, $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$.—When aqueous cobalt(II) chloride solutions are treated with N-hydroxyethylethylenediamine an immediate color change occurs and a dark orange-red solution results. All attempts to obtain a solid material from this solution were unsuccessful. Treatment with either air or hydrogen peroxide resulted in no visible color change, and further studies indicated the cobalt(II) solution to be extremely resistant to oxidation. Finally, it was discovered that in the presence of active carbon¹⁵ and a slight excess of N-hydroxyethylethylenediamine the cobalt(II) solution can be successfully oxidized by air at the steam-bath temperature. The procedure as ultimately worked out follows. To a solution of 4.8 g. (0.02 mole) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 20 ml. of water were added 10.8 g. (0.1 mole) of N-hydroxyethylethylenediamine, 1 ml. of concentrated hydrochloric acid, and about 0.5 g. of activated charcoal (Norite). The mixture, in a 50-ml. flask fitted with a water-cooled reflux condenser and a capillary air inlet tube, was heated on the steam-bath for a minimum of 6 hours during which time a vigorous stream of air was bubbled through the solution to oxidize the cobalt. Small quantities of water were added to maintain the original volume of the solution. A very dark brown sirup was obtained from which the carbon catalyst was removed by filtration while the solution was still hot. The carbon residue was washed with the minimum amount of water (3–5 ml.) in one-half ml. portions and the combined filtrate and washings poured very slowly with stirring into about six times the volume of absolute ethyl alcohol. The yellowish-orange precipitate obtained was filtered off and recrystallized from 95% ethyl alcohol to which sufficient water had been added that solution of the crystals just occurred at the steam-bath temperature. The yield varied from about 19 to 47% based on the cobalt(II) chloride but usually averaged about 40%.

Anal. Calcd. for $\text{CoC}_{12}\text{H}_{30}\text{N}_6\text{O}_3\text{Cl}_3$: N, 17.58; Co, 12.32; Cl, 22.30. Found: N, 17.7; Co, 12.3; Cl, 22.7.

The compound melted with decomposition at 245–250°. From the freezing point depression of an aqueous solution, the molecular weight was calculated to be 452 (theoretical value for $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$, 478).

The substitution of hydrogen peroxide for air as the oxidizing agent in the preparation of this compound resulted in a lower yield and seemed to increase the tendency toward the formation of oils. When absolute ethyl alcohol solutions of the anhydrous reagents were used, the complex that precipitated was identical to that described above but the time required for its formation and the low yield made this method unsuitable.

On occasions when persistent oily residues only could be obtained it was found that treatment of these oils with a dilute solution of $\text{Na}_2\text{Co}(\text{NO}_2)_6$ produced a bright yellow solid. This solid was collected on a fritted glass buchner funnel, washed with water, and decomposed with dilute hydrochloric acid. From the acid filtrate by treatment with absolute ethyl alcohol an excellent yield of $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$ was obtained.

The remarkable resistance of this compound to reduction of the metal ion, oxidation of the organic components, and attack by acidic reagents has already been mentioned. However, hydrogen sulfide gas when bubbled through a suspension of this complex in absolute ethyl alcohol caused its complete decomposition with the formation of a black metal sulfide residue. From the alcohol solution, freed of cobalt sulfide, the dipicrate of N-hydroxyethylethylenediamine was obtained. Its melting point indicated that the diamine had been recovered without change.

Tris-N-hydroxyethylethylenediamine Co(III) Bromide, $[\text{Co}(\text{etol-en})_3]\text{Br}_3$.—This compound was prepared in a manner entirely analogous to that employed for the corresponding chloride except for the use of cobalt(II) bromide and hydrobromic acid. Yields of about 25–30% were obtained.

Anal. Calcd. for $\text{CoC}_{12}\text{H}_{30}\text{N}_6\text{O}_3\text{Br}_3$: N, 13.74; Co, 9.66; Br, 39.37. Found: N, 13.7; Co, 9.6; Br, 39.7.

The bromide complex, of a somewhat darker shade of

orange than the chloride, melted with decomposition at 230–234°. Its molecular weight, calculated from the freezing point depression of an aqueous solution, was found to be 587 (theoretical value for $[\text{Co}(\text{etol-en})_3]\text{Br}_3$, 611).

The properties of $[\text{Co}(\text{etol-en})_3]\text{Br}_3$ closely parallel those of $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$.

Tris-N-(2-hydroxypropyl)-ethylenediamine Co(III) Chloride and Bromide, $[\text{Co}(\text{iprol-en})_3]\text{X}_3$, and **Tris-N-(3-hydroxypropyl)-ethylenediamine Co(III) Chloride**, $[\text{Co}(\text{prol-en})_3]\text{Cl}_3$.—These complexes were prepared by heating aqueous solutions of the cobalt(II) halide and the amine in the ratio of 1:5 with Norite in a manner similar to that described above for $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$. However, more satisfactory results were obtained by prolonging the heating period during the air oxidation to a minimum of 10 hours for the N-(2-hydroxyethyl)-ethylenediamine solution and to between 72 and 120 hours for the N-(3-hydroxyethyl)-ethylenediamine solution. These complexes were purified by recrystallization from aqueous ethyl alcohol.

Anal. Calcd. for $\text{CoC}_{15}\text{H}_{42}\text{O}_3\text{N}_6\text{Cl}_3$: N, 16.15; Co, 11.33; Cl, 20.5. Found for $[\text{Co}(\text{iprol-en})_3]\text{Cl}_3$: N, 16.2; Co, 11.3; Cl, 20.6. Found for $[\text{Co}(\text{prol-en})_3]\text{Cl}_3$: N, 16.2; Cl, 20.7.

When heated, $[\text{Co}(\text{iprol-en})_3]\text{Cl}_3$ melts with decomposition at 235°. The molecular weight, calculated from the freezing point depression of an aqueous solution, was found to be 499 (theoretical value, 519.5).

Samples of $[\text{Co}(\text{iprol-en})_3]\text{Cl}_3$ were refluxed with concentrated nitric acid (70%) in the same manner as for the corresponding $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$. After several hours of this treatment, the orange solution turned red indicating that decomposition of the complex to cobalt(II) had taken place. When the cool acid solution was treated with an excess of acetone, only a very small amount of the complex could be isolated. Refluxing samples of $[\text{Co}(\text{iprol-en})_3]\text{Br}_3$ with 48% hydrobromic acid for about 40 minutes resulted in almost complete decomposition of the complex and the formation of cobalt(II). The original complex was isolated without change after refluxing with hydrobromic acid for 15 to 20 minutes. No significant change in constitution could be detected by analysis of samples of $[\text{Co}(\text{iprol-en})_3]\text{Cl}_3$ that had been refluxed with benzoyl chloride, acetyl chloride or acetic anhydride.

Hydrogen sulfide decomposes these complexes to give the metal sulfide and unchanged hydroxydiamine.

Tris-N-alkylethylenediamine Co(III) Halides, $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHR})_3]\text{X}_3$.—Exactly the same procedure as described above for $[\text{Co}(\text{etol-en})_3]\text{Cl}_3$ was employed in the preparation of $[\text{Co}(\text{me-en})_3]\text{Cl}_3$, $[\text{Co}(\text{me-en})_3]\text{Br}_3$, $[\text{Co}(\text{et-en})_3]\text{Cl}_3$ and $[\text{Co}(\text{pr-en})_3]\text{Cl}_3$ with the exception that the duration of the air oxidation in these cases could be cut down to four hours. Furthermore, because of relatively little tendency for oil formation, solid complexes were more easily isolated. These solids, all yellowish-orange in color, were almost identical in appearance to the corresponding ethylenediamine complex $[\text{Co}(\text{en})_3]\text{Cl}_3$.

Anal. Calcd. for $\text{CoC}_9\text{H}_{30}\text{N}_6\text{Cl}_3$: N, 21.65; Co, 15.2; Cl, 27.5. Found: N, 21.6; Co, 15.3; Cl, 27.7. Calcd. for $\text{CoC}_9\text{H}_{30}\text{N}_6\text{Br}_3$: N, 16.12. Found: N, 16.1. Calcd. for $\text{CoC}_{12}\text{H}_{36}\text{N}_6\text{Cl}_3$: N, 19.55. Found: N, 19.5. Calcd. for $\text{CoC}_{15}\text{H}_{42}\text{N}_6\text{Cl}_3$: N, 17.82. Found: N, 17.8.

Tris-N-hydroxyethylethylenediamine Ni(II) Bromide, $[\text{Ni}(\text{etol-en})_3]\text{Br}_3$.—Breckenridge⁹ has reported the preparation of $[\text{Cu}(\text{etol-en})_2]\text{Cl}_2$, $[\text{Cu}(\text{etol-en})_2]\text{Br}_2$, $[\text{Cu}(\text{etol-en})]\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$ and $[\text{Ni}(\text{etol-en})_2]\text{Cl}_2$. In this investigation, the corresponding nickel bromide complex was prepared by mixing absolute ethyl alcohol solutions of the anhydrous metal salt and the amine using either a 1:3 ratio or an excess of the amine. An 80% yield (based on nickel bromide) of $[\text{Ni}(\text{etol-en})_3]\text{Br}_3$ was obtained after recrystallization from 95% ethyl alcohol. The purple compound melted sharply at 175°.

Anal. Calcd. for $\text{NiC}_{12}\text{H}_{30}\text{N}_6\text{O}_3\text{Br}_3$: N, 15.83. Found: N, 15.9.

Tris-N-(2-hydroxypropyl)-ethylenediamine Ni(II) Halides, $[\text{Ni}(\text{iprol-en})_3]\text{X}_3$.—The chloride and bromide complexes were prepared by a method analogous to that used for $[\text{Ni}(\text{etol-en})_3]\text{Br}_3$.¹⁶ Formation of the minute light-

(14) S. R. Aspinall, *THIS JOURNAL*, **63**, 852 (1941).

(15) *Inorganic Syntheses*, **2**, 216 (1946).

(16) A compound corresponding to the formula $[\text{Cu}(\text{iprol-en})_2]\text{Br}_2$ was prepared in a similar fashion by mixing ethyl alcohol solutions of

purple crystals did not occur until the solutions had stood for about 24 hours. The chloride complex precipitated much more slowly than did the bromide. After recrystallization from 95% ethyl alcohol the chloride melted at 168° and the bromide at 135°.

Anal. Calcd. for $\text{NiC}_{15}\text{H}_{42}\text{N}_6\text{O}_3\text{Cl}_2$: N, 17.39; Cl, 14.69. Found: N, 17.2; Cl, 14.8. Calcd. for $\text{NiC}_{15}\text{H}_{42}\text{N}_6\text{O}_3\text{Br}_2$: N, 14.68; Br, 27.95. Found: N, 14.5; Br, 28.0.

anhydrous copper(II) bromide and N-(2-hydroxypropyl)-ethylenediamine in the ratio of 1:2. Dark blue crystals formed within several hours after mixing. The complex, after recrystallization from 95% ethyl alcohol, melted without decomposition at 208–209°. *Anal.* Calcd. for $\text{CuC}_6\text{H}_{12}\text{N}_4\text{O}_2\text{Br}_2$: N, 12.19. Found: N, 12.2. A very small amount of a chloride complex was also isolated. This was presumably the bis-complex inasmuch as the color was identical to that of $[\text{Cu}(\text{etol-en})_2]\text{Cl}_2$. No analysis was made.

Tris-N-methylethylenediamine Ni(II) Bromide, $[\text{Ni}(\text{me-en})_3]\text{Br}_2$.—A concentrated absolute ethyl alcohol solution of nickel(II) bromide was treated with an excess of N-methylethylenediamine, the resulting mixture cooled to 0°, and anhydrous ether added until the point of precipitation was just reached. From the clear solution, stoppered at room temperature for about six weeks, very large deep purplish-blue crystals of the tris-complex, $[\text{Ni}(\text{me-en})_3]\text{Br}_2$, were slowly deposited.¹⁷

Anal. Calcd. for $\text{NiC}_9\text{H}_{30}\text{N}_6\text{Br}_2$: N, 19.05. Found: N, 19.0.

(17) Fine purplish-blue needles of $[\text{Cu}(\text{me-en})_2]\text{Br}_2$ were obtained in an analogous manner. This compound, after recrystallization from 95% ethyl alcohol, melted at 238°. *Anal.* Calcd. for $\text{CuC}_6\text{H}_{12}\text{N}_4\text{Br}_2$: N, 15.19. Found: N, 15.1.

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pH Change as an Index to Reaction Mechanisms¹

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A preliminary report on the pH changes of oxidation-reduction reactions is presented. Several of the observed curves for different types of reactions are included. The Landolt reaction (iodate oxidation of sulfite) is discussed in some detail to show how the pH-time curve correlates with the known stoichiometries and rate laws from other investigations.

Introduction

When the experimentally determined pH of the unbuffered Landolt reaction⁴ (the oxidation of sulfite by iodate in acid solution, in the presence of starch) is plotted as a function of the time, a curve of the form of line 1 in Fig. 1 is obtained. The sharp break in this curve (point C) occurs at the exact time that the blue color appears. When bromate is substituted for iodate in this reaction, curve 2 of Fig. 1 is observed. Where the break in the iodate curve is followed by a pronounced rise in pH there is no change in pH following the break in the bromate curve. Thus, the pH-time curves for these reactions are distinctly different.

For the reaction of iodide with iodate, the pH-time curves have the form illustrated in Fig. 2, whereas the bromate-bromide reaction has only a slight change in pH under these conditions. The time dependence of the pH of the sulfite-permanganate reaction varies with the starting pH in the fashion reflected in Fig. 3. A similar sort of dependence on starting pH is shown by the nitrite-permanganate, the selenite-permanganate and the arsenite-permanganate reactions, although the last named reaction gives a sudden pH drop at all initial pH's. In Fig. 4, the pH changes in the oxidation of thiosulfate by bromate are presented. The pH change is markedly dependent on the initial pH and the curves cross, so that one can immediately say that the reaction is complex. Similar curves were found in the iodate-thiosulfate reaction.

The thiosulfate-iodide-hydrogen peroxide reaction is accompanied by very pronounced and

striking changes in pH (Fig. 5). The regular change in the pattern of pH change as the hydrogen ion concentration is varied is noticeable; in addition there is a distinct change in character when the sulfuric acid concentration is greater than 0.0112 M for this series of runs.

It is evident from the examples given that oxidation-reduction reactions are, very commonly, accompanied by characteristic pH changes. In some reactions these pH changes are both pronounced and striking; in others they are small and relatively unspectacular. The question is whether an observation of these pH changes can be useful in probing the mechanism of the particular reaction.

To try to find an answer to this question we will examine the results of detailed studies made on one of these reactions, the oxidation of sulfite by iodate. This reaction was probed by the conventional method of varying one factor while holding other factors constant.

Experimental Procedure

The pH measurements were made with a Beckman model G pH meter; the readings were standardized with a potassium hydrogen phthalate buffer. All chemicals used were of analytical reagent quality. For each reagent, the same batch was used throughout to eliminate any effect of variation in purity. All water was doubly distilled and preserved in CO₂-free air. All reducing solutions were preserved in an atmosphere of nitrogen, and reactions involving reagents susceptible to air oxidation were carried out in a nitrogen atmosphere.

The reactions were carried out in a 300-ml., closed, tall-form beaker with a free flowing pipet suspended overhead. The reaction vessel, the nitrogen gas and the solutions were thermostated at 25°. In the case of the Landolt reaction sulfite solution was measured out in the pipet and was then run into the beaker. Sulfuric acid was added to bring its pH to that of the iodate-starch solution. The iodate-starch solution was quickly added, the pH noted, the time-clock started and the pH-time values recorded.

Discussion of the Landolt Reaction

The presence of starch is necessary to give the sharp, blue end-point characteristic of the Landolt

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(4) H. Landolt, *Ber.*, 249 (1885); 193 (1886); 21 (1887).