absorbancy when a solution of the *cis*-compound is made more acid than pH 2.[9]

As a result of these pieces of information a proton attack which causes ring opening of one oxalate group is suggested as the mechanism of the hydrogen ion dependent reaction. At pH 2 and above the reaction could proceed as previously suggested by water dissociation,[3] while at pH values below 2 a two path mechanism is suggested which can be represented by the equations

$$[Cr(C_2O_4)_2(H_2O)_2]^- \xrightarrow{k_1} [Cr(C_2O_4)_2(H_2O)]^- + H_2O \xrightarrow{\text{rapid}} [Cr(C_2O_4)_2(H_2O)_2]^- \quad (1)$$

$$H^+ + [Cr(C_2O_4)_2(H_2O)_2]^- \xrightarrow{k_2} [Cr(C_2O_4)(OC_2O_3H)(H_2O)_2] \xrightarrow{\text{rapid}} [Cr(C_2H_4)_2(H_2O)_2]^- \quad (2)$$

This mechanism is in agreement with the rate data reported. Reaction 1 would explain the hydrogen ion independent rate above pH 2, and reaction 2 would become more and more important as the hydrogen ion concentration increased below pH 2.

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[9] H. L. Schläfer, private communication.

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CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION,
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# Complexes of 2-Hydroxyethyliminodiacetic Acid

BY RONALD A. KRAUSE[1]

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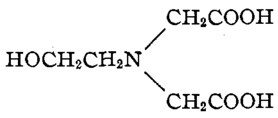
Several complexes of 2-hydroxyethyliminodiacetic acid were prepared and characterized by means of infrared and visible-ultraviolet spectra, magnetic moments, and molar conductivities. The complexes appear to be of two distinct types; the first type consists of $K_2[Ni(HO\text{-}A)_2]$, $Na[Co(HO\text{-}A)_2]$, $Na_2[Co(HO\text{-}A)_2]$, and $K[Cr(HO\text{-}A)_2]$, which appear to be octahedral complexes with the ligand coördinating through the nitrogen and two carboxyl oxygens. $[Ni(HO\text{-}AH)_2]$ and $[Co(HO\text{-}AH)_2]$ are of a second type and appear to coördinate to the alcohol OH group as well as to one carboxylate.

The solution behavior of 2-hydroxyethyliminodiacetic acid (I) ($HO\text{-}AH_2$) toward metal ions has been studied by several workers[2,3]; however, little attention has been directed toward the isolation of complexes of this compound. Vieles and Seguin[4] appear to have reported the only synthetic work with this ligand in the isolation of a copper(II) salt. It was of interest to us to isolate and characterize complexes of 2-hydroxyethyliminodiacetic acid and, in particular, to determine if the alcohol OH group enters the coördination sphere.



I

## Experimental

**Reagents.**—Reagent grade transition metal salts were used as received. A research sample of 2-hydroxyethyliminodiacetic acid was received from the Dow Chemical Company.

**Preparation of Complexes.**—The complexes were prepared as described below and dried *in vacuo* over $P_2O_5$. In Table I analytical data for these compounds are summarized.

**Dihydrogen Bis-(2-hydroxyethyliminodiacetato)-cobalt(II) and Dihydrogen Bis-(2-hydroxyethyliminodiacetato)-nickel(II), $[M(HO\text{-}AH)_2]$.**—Cobalt(II) carbonate (prepared according to Schlesinger[5]) or nickel(II) carbonate was added to a hot aqueous solution containing the theoretical quantity of $HO\text{-}AH_2$. After filtration, the solution was boiled for 1 hr. and the water-insoluble product isolated by filtration and washed with hot water.

**Sodium Bis-(2-hydroxyethyliminodiacetato)-cobalt(II), $Na_2[Co^{II}(HO\text{-}A)_2]$.**—Solution of $[Co(HO\text{-}AH)_2]$ in aqueous sodium bicarbonate, followed by precipitation with ethanol, conveniently afforded this compound.

**Sodium Bis-(2-hydroxyethyliminodiacetato)-cobalt(III), $Na[Co^{III}(HO\text{-}A)_2]$.**—$Na_3[Co(CO_3)_3]\cdot 3H_2O$[6] and the theoretical quantity of ligand were mixed in warm water. After effervescence ceased concentrated perchloric acid was added to pH *ca.* 4. The solution was evaporated to low volume and the purple crystals were isolated by filtration and recrystallized from hot water.

**Potassium Bis-(2-hydroxyethyliminodiacetato)-chromium(III), $K[Cr(HO\text{-}A)_2]$, and Potassium Bis-(2-hydroxyethyliminodiacetato)-nickel(II), $K_2[Ni(HO\text{-}A)_2]$.**—An aqueous solution of $HO\text{-}AH_2$, containing sufficient potassium hydroxide to neutralize one ligand proton, was added to a hot, aqueous solution of the stoichiometric amount of the hydrated metal chloride. The solutions were neutralized with aqueous potassium hydroxide; in the case of the chromium(III) complex neutralization was completed after the color of the solution changed from blue to red. On cooling, $K[Cr(HO\text{-}A)_2]$ crystallized; this complex was recrystallized from hot water. $K_2[Ni(HO\text{-}A)_2]$ was precipitated by the addition of ethanol and recrystallized from ethanol–water.

**Infrared Spectra.**—Infrared spectra were obtained on a Perkin–Elmer Model 21 spectrophotometer using mineral oil and halocarbon mulls.

**Visible-Ultraviolet Spectra.**—Visible-ultraviolet absorption spectra of aqueous solutions of the complexes were obtained using a Cary Model 14 recording spectrophotometer. Reflectance spectra were obtained on $1^1/_8$ in. disks of sample using

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[1] Department of Chemistry, The University of Connecticut, Storrs, Connecticut.

[2] S. Chaberek, R. C. Courtney, and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5057 (1952).

[3] (a) G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955); (b) G. Anderegg and G. Schwarzenbach, *ibid.*, **38**, 1940 (1955).

[4] P. Vieles and J. Seguin, *Compt. rend.*, **238**, 1819 (1954).

[5] G. Schlesinger, *Inorg. Syn.*, **6**, 189 (1960).

[6] H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

TABLE I

CHARACTERIZATION OF HO-$AH_2$ COMPLEXES

| Compound | Color | Yield, % | Calcd. C | Calcd. H | Calcd. N | Found C | Found H | Found N |
|---|---|---|---|---|---|---|---|---|
| $[Co(HO\text{-}AH)_2]$ ($CoC_{12}H_{20}N_2O_{10}$) | Pink | 88 | 35.1 | 4.91 | 6.82 | 35.20 | 4.69 | 6.56 |
| $[Ni(HO\text{-}AH)_2]$ ($NiC_{12}H_{20}N_2O_{10}$) | Blue | 90 | 35.1 | 4.92 | 6.72 | 34.76 | 5.04 | 7.18 |
| $Na_2[Co^{II}(HO\text{-}A)_2]$ ($Na_2CoC_{12}H_{18}N_2O_{10}$) | Purple | . . | 31.6 | 3.98 | 6.17 | 31.34 | 4.02 | 6.30 |
| $Na[Co^{III}(HO\text{-}A)_2]$ ($NaCoC_{12}H_{18}N_2O_{10}$) | Purple | 26 | 33.4 | 4.19 | 6.48 | 33.40 | 4.24 | 6.56 |
| $K[Cr(HO\text{-}A)_2]$ ($KCrC_{12}H_{18}N_2O_{10}$) | Red | 59 | 32.7 | 4.12 | 6.35 | 32.12<br>31.99 | 4.05<br>4.40 | 6.63 |
| $K_2[Ni(HO\text{-}A)_2]$ ($K_2NiC_{12}H_{18}N_2O_{10}$) | Blue | 71 | 29.6 | 3.72 | 5.76 | 29.73 | 3.87 | 5.77 |

TABLE II

PHYSICAL PROPERTIES OF COMPLEXES OF 2-HYDROXYETHYLIMINODIACETIC ACID

| Compound | $\Lambda_M$,[b] mhos ($10^{-3}$ *M* in water) | $X_M \times 10^6$ complex | $\mu_{eff}$ (B.M.) | (Spin-only value) | Infrared assignments,[a] cm.$^{-1}$ Asymm. COO$^-$ stretch | Infrared assignments,[a] cm.$^{-1}$ OH stretch |
|---|---|---|---|---|---|---|
| HO-$AH_2$ | 221 | −93.2 | | | 1700 s | 3300 m, 3160 m |
| $K_2[Ni(HO\text{-}A)_2]$ | 221 | 4180 | 3.25 | (2.8) | 1605 s | 3320 m |
| $Na[Co^{III}(HO\text{-}A)_2]$ | 95.9 | 5 | 0.7 | (0) | 1630 s | 3400 sh, 3300 m |
| $Na_2[Co^{II}(HO\text{-}A)_2]$ | 214 | 9640 | 4.86 | (3.9) | 1605 s | 3240 m |
| $K[Cr(HO\text{-}A)_2]$ | 92.8 | 5930 | 3.84 | (3.9) | 1650 s, 1630 s | 3380 m, 3300 m |
| $[Co^{II}(HO\text{-}AH)_2]$ | . . . | 9120 | 4.73 | (3.9) | 1730 s, 1580 s | 3440 vw, 3050 m |
| $[Ni(HO\text{-}AH)_2]$ | . . . | 4180 | 3.24 | (2.8) | 1730 s, 1585 s | 3340 vw, 3060 m |

[a] s, strong; m, medium; vw, very weak; sh, shoulder. [b] Expected for 1:1 electrolytes, *ca.* 120 mhos. For 1:2 electrolytes, *ca.* 250 mhos. *Cf.* D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Co., New York, N. Y., 1939, p. 339.

a Beckman DK-2A recording spectrophotometer with barium sulfate as a reference.

**Magnetic Susceptibilities.**—The Guoy method was employed to determine the magnetic susceptibility of solid samples at 25°, using ferrous ammonium sulfate 6-hydrate and water as standards. Magnetic moments were calculated using the Curie law after correcting the observed susceptibilities for the diamagnetic contributions of ligand and cations.

**Molar Conductivities.**—Conductivities were determined on $10^{-3}$ *M* aqueous solutions of the complexes at 27°, using a Leeds and Northrup bridge.

## Results

The compounds prepared in this study are listed in Table II along with several of their physical properties. These complexes fall into two groups; the first group, consisting of $K_2[Ni(HO\text{-}A)_2]$, $Na[Co^{III}(HO\text{-}A)_2]$, $Na_2[Co^{II}(HO\text{-}A)_2]$, and $K[Cr(HO\text{-}A)_2]$, comprises complexes which have infrared spectra containing only one asymmetric carboxyl stretching mode, and an OH stretching mode at *ca.* 3300 cm.$^{-1}$.

The second group of complexes consists of $[Ni(HO\text{-}AH)_2]$ and $[Co^{II}(HO\text{-}AH)_2]$. It differs from the first group in that the infrared spectra contain more than one asymmetric carboxyl mode, and the OH stretch appears at *ca.* 3100 cm.$^{-1}$.

Nickel(II) and chromium(III) complexes of the first type may be prepared by neutralizing an aqueous solution of the hydrated metal chloride and ligand. This procedure also may be used for the preparation of the cobalt(II) complex $Na_2[Co^{II}(HO\text{-}A)_2]$, but a cleaner product is realized by neutralizing $[Co^{II}(HO\text{-}AH)_2]$. The cobalt(III) complex, $Na[Co^{III}(HO\text{-}A)_2]$, is conveniently prepared, in low yield, using the reagent of Bauer and Drinkard,[6] $Na_3[Co^{III}(CO_3)_3]\cdot 3H_2O$. With this procedure, large amounts of the cobalt(II) complex also are formed. This observation, and the fact that our preparations of $Na_3[Co^{III}(CO_3)_3]\cdot 3H_2O$ are strongly paramagnetic, leads us to believe that considerable amounts of cobalt(II) are present in the sodium triscarbonatocobaltate(III) and are not necessarily generated in the reaction with HO-$AH_2$.

Complexes of the second type are prepared by slightly different procedures; nickel(II) or cobalt(II) carbonate react with two moles of ligand in aqueous solution to provide a solution in which only two protons per complex have been neutralized. Digestion of these solutions at the boiling point causes the uncharged complexes, $[Ni(HO\text{-}AH)_2]$ and $[Co^{II}(HO\text{-}AH)_2]$, to precipitate.

## Discussion

In complexes of the first type both ligand carboxyl groups coördinate to the central metal ion; this is attested to by the infrared spectra of these complexes (Table II). One asymmetric carboxyl stretching mode indicates all carboxyl groups to be equivalent. The location of this vibration is essentially that predicted on the basis of the covalency of the M–O bond[7]; *i.e.*, the chromium(III) and cobalt(III) complexes absorbing at a higher frequency than the cobalt(II) and nickel(II) compounds. Coördination of all carboxyl and amino

(7) R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, **1**, 174 (1962), and references cited therein.

groups to an octahedral metal ion dictates that the alcohol OH must be free. A strong band in the infrared spectra of these complexes in the neighborhood of 3300 cm.$^{-1}$ indicates a normal OH stretching mode.

From the infrared data tabulated in Table II, it is apparent that complexes of the second type contain two different kinds of carboxyl groups; the absorption at 1730 cm.$^{-1}$ in [Ni(HO-AH)$_2$] and [Co$^{II}$(HO-AH)$_2$] indicates free carboxylic acid while that at 1580 cm.$^{-1}$ implies an essentially ionic carboxyl. The OH stretching mode in these compounds is considerably lower than in K$_2$[Ni(HO-A)$_2$] or Na$_2$(Co$^{II}$(HO-A)$_2$]. From these data a structure in which alcohol groups coördinate seems to be most logical. It is possible that these are actually polynuclear species in which HO-A$^{-2}$ functions in a bidentate fashion (not involving coördination of the alcohol group) but employing bridging carboxyl groups; in this event, it is difficult to rationalize the shift in the OH stretching mode.

Chaberek, Courtney, and Martell[2] have demonstrated that the hydroxyethyl group in HO-AH$_2$ takes part in chelate formation in solution to some extent; it is not difficult to visualize this also occurring in the solid complexes.

If the alcohol group were hydrogen bonded to the free carboxylic acid (and not coördinated) one would expect not only a lowering of the OH vibration, but also a lowering of the asymmetric carboxyl stretching mode from 1730 (observed) to *ca.* 1700 (normally observed in hydrogen bonded acids).

In Table III ultraviolet–visible absorption and reflectance spectral data for the complexes under study are tabulated. Unfortunately, the broadness of the reflectance bands in several of the compounds makes comparison difficult.

TABLE III

ULTRAVIOLET–VISIBLE ABSORPTION AND REFLECTANCE SPECTRA OF HO-AH$_2$ COMPLEXES

| | Reflectance[a] $\lambda_{max}$, m$\mu$ | Solution $\lambda_{max}$, m$\mu$ | (Water) $\epsilon$ |
|---|---|---|---|
| K[Cr(HO-A)$_2$] | *ca.* 245 | 230 sh | 2,340 |
| | 360 | 361 | 27.3 |
| | 500 b | 506 | 39.8 |
| K$_2$[Ni(HO-A)$_2$] | *ca.* 225 | 375 | 7.3 |
| | 350 | 610 | 5.4 |
| | *ca.* 575 | | |
| [Ni(HO-AH)$_2$] | *ca.* 220 | . . . | . . . |
| | 360 | | |
| | *ca.* 600 vb | | |
| Na$_2$[Co$^{II}$(HO-AH)$_2$] | Below 225 | | |
| | *ca.* 480 vb | 516 | 15.8 |
| [Co$^{II}$(HO-AH)$_2$] | Below 225 | . . . | . . . |
| | *ca.* 470 vb | | |
| Na[Co$^{III}$(HO-A)$_2$] | *ca.* 240 | 230 | 20,700 |
| | 520 | 516 | 66.1 |
| | *ca.* 610 sh | | |

[a] b, broad; vb, very broad; sh, shoulder.

The reflectance and solution spectra of K[Cr(HO-A)$_2$] are very similar. If the infrared data on the solid complex is accepted as indicating the presence of uncoördinated alcohol groups in the solid, one must assume that there is little association of this group with the central metal ion in solution on the basis of these data. The same argument may be applied to the cobalt(III) complex, Na[Co(HO-A)$_2$].

From the data in Table II it can be seen that, with the exception of the cobalt(III) complex, Na[Co$^{III}$-(HO-A)$_2$], these compounds possess the expected molar conductivities and magnetic moments. The unusually high magnetic moment for the cobalt(III) complex, 0.7 B.M., is not changed on recrystallization, so apparently does not indicate a cobalt(II) impurity. A small residual paramagnetism in cobalt(III) complexes has been observed in the past. Kernahan and Sienko[8] account for this phenomenon by assuming low lying excited states in cobalt(III). Without further study the cause of the slight paramagnetism observed in Na-[Co$^{III}$(HO-A)$_2$] cannot be ascertained.

The chromium(III) complex ion, [Cr(HO-A)$_2$]$^-$, shows a fair degree of lability. On raising or lowering the pH of an aqueous solution of K[Cr(HO-A)$_2$] the color changes from red to blue; the rate of this reaction varies considerably with pH. In neutral solution several hours elapse before any change is apparent in the visible absorption spectrum, while at high or low pH this reaction is observed to occur within seconds. Although the blue complex has not been isolated it is felt that this reaction involves a displacement of ligand. Since the spectra of the blue complex in acid and base are not identical, this species does not appear to be an isomer of the red compound but rather a hydrolysis product of it.

Since one group of compounds prepared in this study contains uncoördinated alcohol groups, it would be of interest to see if these complexes possess normal alcohol reactivity. Such a study on the chromium(III) complex ion, [Cr(HO-A)$_2$]$^-$, has been completed.[9]

**Acknowledgments.**—The author wishes to express his thanks to the Research Service Department of the Stamford Laboratories of the American Cyanamid Company for performing the measurements reported on these compounds.

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(8) J. L. Kernahan and M. J. Sienko, *J. Am. Chem. Soc.*, **77**, 1978 (1955).

(9) R. A. Krause and S. D. Goldby, paper presented at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962; to be published.