4:1 chelate; however, the 3:1 2-methyl-8-quinolinol chelate can be prepared. Likewise, the 4:1, and under certain conditions, the 5:1 2-methyl-8-quinolinol thorium chelate can be precipitated from solution while only the 5:1 8-quinolinol chelate can be obtained.

The heats of solvation of the 2-methyl-8-quinolinol thorium and uranium chelates are decidedly more positive than those found for the 8-quinolinol chelates. In fact, the thorium chelate has a positive value. Little can be said about the nature of the interaction between the solvate molecule and the metal chelate because the heat of rearrangement of the complex, after removal of the solvate molecule, is not known.

The structures of the solvated metal chelates remain unknown. It is thought, however, that the structures of the thorium and scandium chelates differ from that for uranium. The exact structural assignment will have to await further studies by X-ray methods.

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[CONTRIBUTION FROM THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA AUSTRALIA]

Rhodium(III) Complexes with Ethylenediaminetetraacetic Acid

BY FRANCIS P. DWYER AND FRANCIS L. GARVAN

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Aquo-(ethylenediaminetriacetatoacetic acid)-rhodium(III) has been obtained from rhodium(III) hydroxide and aqueous ethylenediaminetetraacetic acid at 145–150° and the potassium and ammonium salts of this acidic complex by neutralization. Resolution was effected through the active *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) cation. Racemization occurred at 96° (half-life, 163 min.), and at 20° in Pyrex vessels in sunlight. The dichloro and dibromo complexes, in which the ethylenediaminetetraacetic acid behaved as a quadridentate ligand, were obtained in optically active forms, which did not exhibit photoracemization, but decomposed in aqueous solution very slowly to yield the active aquo complex.

On the basis of photometric studies,[1] complexometric titrations,[2] ion-exchange[3] and chromatographic[4] separations, it was concluded originally that rhodium complexes with ethylenediaminetetraacetic acid were not formed. Recently, however, it has been found that when freshly prepared solutions of rhodium(III) chloride were heated with ethylenediaminetetraacetic acid, the *p*H of the solution slowly decreased, a new absorption band appeared at 353 mμ, and after a time rhodium hydroxide was no longer precipitated by alkali.[5] The previous failures to detect complex formation were ascribed, reasonably enough, to the inertness of the anionic rhodium complexes present in the aged solutions. The composition of the complex was not ascertained.

In the present work, the preparation, properties and resolution of some of the complexes are described. Ethylenediaminetetraacetic acid was found to react in boiling aqueous solution with rhodium(III) chloride and nitrate, and pale yellow solids could be isolated as the ammonium salts. None of the products could be characterized by analysis and they apparently consisted of mixtures. Fractionation of the material obtained from the rhodium(III) chloride reaction gave a series of yellow substances of different solubilities none of which could be identified. With silver nitrate, some silver chloride precipitated slowly, and the infrared curves showed the presence of free carboxylic acid group(s) in all fractions.

Freshly precipitated rhodium(III) hydroxide, free from chloride ion, failed to dissolve in boiling aqueous ethylenediaminetetraacetic acid even after 6 hr., but in an autoclave at 145–150° dissolution was complete in 4 hr. The bright yellow solution was freed from excess acid by concentration and cooling at 4°, and the solid rhodium complex then separated on the addition of ethanol. The infrared spectrum showed a free carboxylic group, and analysis, the presence of a molecule of water, from which the formula [RhH_2O(HEDTA)] has been deduced. From *p*H titrations, for the reactions

$$[\mathrm{RhH_2O(HEDTA)}] \rightleftharpoons \mathrm{H^+} + [\mathrm{RhH_2O(EDTA)}]^- \rightleftharpoons \mathrm{H^+}[\mathrm{Rh(EDTA)OH}]^{-2}$$

we deduce $pK_1 = 2.32 \pm 0.08$ and $pK_2 = 9.12 \pm 0.02$. The aquo group is thus much less acidic than in [Cr H_2O(HEDTA)], ($pK_2 = 7.52$).[6] The color of the hydroxo complex anion [Rh(EDTA)-OH]$^{-2}$ is not visibly different from that of the aquo complex (absorption maxima at 293 and 359 mμ).

The potassium and ammonium salts were obtained by neutralization of the complex acid. Resolution was effected readily with the active *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) cation. Solutions of the active potassium salts retained their rotations unchanged for three months in the dark, but $[\alpha]_{5461}$ had decreased from −180 to −100° in a year. The half life at 96° in the dark was 163 min. which is comparable with the cobalt complex[7] ($t/2 = 168$ min. at 100°). The absorption spectra of various samples collected during racemization showed that apparently little decomposition en-

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(1) W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, **26**, 1768 (1954); **28**, 16 (1956).

(2) W. M. MacNevin and O. H. Kriege, *ibid.*, **27**, 535 (1955).

(3) W. M. MacNevin and E. S. McKay, *ibid.*, **29**, 1220 (1957).

(4) W. M. MacNevin and M. L. Dunton, *ibid.*, **29**, 1806 (1957).

(5) W. M. MacNevin, H. D. McBride and E. A. Hakkila, *Chem. & Ind. (London)*, 101 (1958).

(6) R. E. Hamm, THIS JOURNAL, **75**, 5670 (1953).

(7) F. P. Dwyer, E. C. Gyarfas and D. P. Mellor, *J. Phys. Chem.*, **59**, (1955).

sued. Slow racemization occurred in aqueous solution at room temperature in the diffuse laboratory light, more rapidly in sunlight, and all activity was lost in 2 hr. when irradiated by a 125 watt mercury lamp. No loss in activity occurred when the solid crystalline material was irradiated for 6 hr. In aqueous solution strong absorption commenced at about 450 mμ, with maxima at 348 and 295 mμ. The former maximum was displaced slightly (351 mμ) when photo-racemization was complete. Slow racemization could be detected when the blue-violet lines of mercury (435, 404 mμ), isolated with a filter, were used for irradiation. The rotatory dispersion curve of the levo isomer obtained by Dr. D. H. Busch, The Ohio State University, showed a region of anomalous dispersion with a maximum specific rotation, ($[\alpha] = -300°$) at 440 mμ.

Although probable, it has not been established that the photo- and thermal racemization have the same mechanisms. Two isomeric forms of the $[RhH_2O(EDTA)]^-$ anion are possible: equatorial with the water molecule *cis* to one nitrogen atom and *trans* to the other, and polar in which both nitrogen atoms are *cis*. No evidence for more than one isomer was obtained, and it is likely that the equatorial structure found for the $[NiH_2O(EDTA)]^-$ anion[8] is present. The intramolecular mechanism proposed by Bailar[9] to account for the racemization of the cobalt complex anion $[Co(EDTA)]^-$ cannot be invoked unless the complex actually consists of a mixture of equal amounts of the polar and equatorial isomers, which must also have equal or nearly equal rotatory powers. It can be shown with models that this intramolecular mechanism would convert one geometrical isomer to the other, with inversion. A more feasible mechanism would involve aquation subsequent to the detachment of a further carboxylate group. The resulting diaquo species can exist in four geometrical isomers, but only two of these can yield the symmetrical intermediate, proposed by Bailar.

It should be mentioned that the photo-racemization reaction offers the possibility of effecting an absolute asymmetric synthesis. If the racemic mixture is irradiated with one form of circularly polarized light of the appropriate wave length, it may be possible to racemize one antipode faster than the other and thus enhance the concentration of the more stable form. The photo-racemization appears to be a reversible reaction, since, as will be described later, the rhodium complex of *l*-propylenediaminetetraacetic acid regains its activity completely after standing in the dark for two days. Models show that in one optical isomer of the latter complex, the methyl group of the asymmetric carbon atom interferes with the nearby C=O group. Only isomer (LI) could be isolated.

Treatment of potassium aquo-(ethylenediaminetriacetatoacetate)-rhodium(III) with concentrated hydrochloric and hydrobromic acids at 90° gave the dichloro and dibromo complexes $K[Rh(H_2EDTA)Cl_2]$ and $K[Rh(N_2EDTA)Br_2]$. The infrared spectra of the complexes in Nujol showed two peaks of comparable intensity in the carbonyl region corresponding to two free carboxylic acid groups and two complexed carboxyl groups. The active complexes prepared from active $K[KhH_2O(EDTA)]$ did not undergo photo-racemization in aqueous solution, but, in the dark, the halogen atoms slowly dissociated, and, at the end of two months, the original aqueous complex was obtained with complete retention of configuration.

Attempts to isolate the corresponding iridium(III) complexes were not successful. The hexachloroiridate(IV) and (III) ions reacted with the formation of a mixture of chloro complexes, while iridium(III) hydroxide in the autoclave at 145° was transformed to a mixture of iridium(IV) oxide and iridium. In the presence of a trace of ethanol, iridium(III) or iridium(IV) oxide was reduced to the metal completely. Though crystalline diastereoisomers of the anion $[CrH_2O(EDTA)]^-$ easily were prepared with the active cations *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) and oxalato-bis-(ethylenediamine)-cobalt(III), no activity could be detected in the potassium salts following the elimination of these resolving agents. The failure to effect resolution is ascribed to rapid intramolecular racemization, and it is, perhaps, significant that the structurally analogous anion ethylenediamine-bis-(oxalato)-chromate(III) has a half life of less than four minutes at 20.6°.[10]

Experimental

(All rotations were measured at 20° in a 2 dm. tube.)

dl-**Aquo-(ethylenediaminetriacetatoacetic acid)-rhodium(III).**[11]—Freshly precipitated rhodium(III) hydroxide, prepared from rhodium nitrate solution (containing 0.602 g. Rh) by precipitation at 90° (*p*H 7) by the addition of sodium bicarbonate, was suspended in water (50 ml.) in a Pyrex tube. Ethylenediaminetetraacetic acid (4 g.) was added, the tube sealed and the mixture heated at 145° in an autoclave containing a little water for 6 hr. After cooling to room temperature, the tube was chilled in ice and opened carefully. Sometimes, a small internal pressure had developed, presumably due to some decarboxylation of the ethylenediaminetetraacetic acid. The excess H_4EDTA and a little rhodium metal were removed, and the yellow filtrate evaporated to 15 ml. on a steam-bath in a current of air. A small amount of dark yellow material that separated on the gradual addition of ethanol was rejected. Further addition of alcohol caused the required substance to separate as fine, yellow needles, which were collected, washed with 50% aqueous ethanol, then acetone and air-dried.

The *p*H titration curve was obtained by using a 0.005 *M* solution of substance, 0.1 *N* potassium hydroxide and a Cambridge *p*H meter. For the dissociation of the proton from the complexed EDTA and the aquo group the values were respectively $pK_1 = 2.32 \pm 0.08$ and $pK_2 = 9.15 \pm 0.02$.

Anal. Calcd. for $[RhH_2O(C_{10}H_{13}N_2O_8)]$: C, 29.28; H, 3.69; N, 6.83. Found: C, 29.36; H, 3.82; N, 6.74.

dl-**Potassium and Ammonium Aquo-(ethylenediaminetriacetatoacetate)-rhodium(III) 1-Hydrate.**—The concentrated aqueous solution of the acid complex above (15 ml.) was treated with potassium or ammonium acetate (3 g.) and then ethanol (200 ml.). The viscous yellow oils crystallized on standing and were redissolved in water (15 ml.) in the presence of potassium or ammonium acetate (1 g.) and reprecipitated with ethanol. The pale yellow crystals were washed with alcohol and acetone and air-dried.

Anal. Calcd. for $K[RhH_2O(C_{10}H_{12}N_2O_8)]\cdot H_2O$: C, 25.75 H, 3.46; N, 6.01; for $NH_4[RhH_2O(C_{10}H_{12}O_2O_8)]\cdot H_2O$: C, 26.97; H, 4.53; N, 9.44; Rh, 23.10. Found: C, 25.68; H, 3.74; N, 6.11; C, 27.22; H, 4.58; N, 9.47; Rh, 23.23.

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[8] H. H. Weakliem and J. L. Hoard, THIS JOURNAL, **81**, 549 (1959).

[9] J. C. Bailar, *J. Inorg. & Nuclear Chem.*, **8**, 165 (1958).

[10] F. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939).

[11] For nomenclature see: F. P. Dwyer and F. L. Garvan, THIS JOURNAL, **80**, 4480 (1958).

l-**Potassium Aquo-(ethylenediaminetriacetatoacetate)-rhodium(III) 1-Hydrate.**—The *d,l* salt was dissolved in a solution (35 ml.) of *l-cis*-dinitrobis-(ethylenediamine)-cobalt(III) acetate, prepared from *l*-[Coen$_2$(NO$_2$)$_2$Br,[12] (3.6 g.) and silver acetate (1.67 g.) and the mixture cooled to 5°. The diastereoisomer, *l*-[Coen$_2$(NO$_2$)$_2$]*l*-[RhH$_2$O-(EDTA)]·2H$_2$O. separated as fine golden needles on scratching the sides of the vessel. After 10 hr. at 5° the solid was collected, washed with 50% aqueous ethanol (20 ml.), ethanol and acetone and air-dried (yield, 2.55 g.). A 0.1% solution gave $[\alpha]_{5461}$ −130°.

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$(NO$_2$)$_2$][RhH$_2$O(C$_{10}$H$_{12}$N$_2$O$_8$]·2H$_2$O: C, 23.47; H, 4.78; N, 15.65. Found: C, 23.62; H, 4.55; N, 15.67.

The diastereoisomer (2.5 g.), potassium iodide (6 g.) and water (15 ml.) were ground together in a mortar for 3 min. The insoluble iodide of the resolving agent was filtered off and washed with 10% potassium iodide solution (3 ml.). Addition of alcohol to the filtrate and washings gave the *l*-isomer, which separated as glistening micaceous plates after recrystallization from water (10 ml.) by the addition of alcohol (yield, 1.52 g.). A 0.1% solution gave $[\alpha]_D$ −140°, $[\alpha]_{5461}$ −180°. A 0.07% solution containing one equivalent of potassium hydroxide, (*i.e.*, K$_2$[RhOH(EDTA)] gave $[\alpha]_D$ −79°, $[\alpha]_{5461}$ −93°.

Anal. Found: C, 25.62; H, 3.62; N, 5.83.

d-**Potassium Aquo-(ethylenediaminetriacetatoacetate)-rhodium(III) 1-Hydrate.**—The filtrate from the separation of the *l*-diastereoisomer above was treated with potassium iodide (6 g.) and cooled to 5° for 15 min. After filtration the crude, partially racemic isomer was precipitated with alcohol, separating as a fine yellow powder. It was recrystallized three times from water (15 ml.) by the addition of alcohol. The optical forms were less soluble than the racemate. The characteristic micaceous plates separated on the third recrystallization (yield, 1.3 g.); $[\alpha]_{5461}$+ 180°.

Anal. Found: C, 25.53; H, 3.40; N, 5.95.

Racemization.—The rate of racemization was determined at 96 ± 1° in 0.25% aqueous solution, in the absence of light. Samples (10 ml.) withdrawn at intervals were cooled immediately in an ethanol/solid carbon dioxide mixture. The half life was calculated to be 163 min. from the mean value of the rate constant, $k = 4.26 \times 10^{-3}$ min.$^{-1}$ where k is the rate of racemization which is double the rate of inversion.

dl-**Potassium-(ethylenediaminediacetatodiacetic acid)-dichlororhodate(III).**—The acid *d,l*-[RhH$_2$O(EDTA)], (2.3 g.) was stirred with concentrated hydrochloric acid (1 ml.) to yield a uniform paste and heated, with stirring, on the steam-bath for 7 min., by which time most of the acid had evaporated. The cold orange-yellow solid was ground up with cold water and then ethanol (40 ml.) added. The solid was collected, washed well with ethanol and acetone and air-dried (yield, 2.9 g.). The crude material (1.5 g.) was purified by dissolution in water (9 ml.) containing potassium acetate (1 g.) and after filtration, the addition of concentrated hydrochloric acid (2 ml.). The pale orange leaflets were washed with 50% alcohol and air-dried.

Anal. Calcd. for K[Rh(C$_{10}$H$_{14}$N$_2$O$_8$)Cl$_2$]: C, 23.86; H, 2.80; N, 5.57; Cl, 14.1. Found: C, 23.62; H, 2.96; N, 5.52; Cl, 14.1.

The more soluble monoacidic salt K$_2$[Rh(HEDTA)Cl$_2$] was prepared by suspending the above di-acid salt (0.3 g.) in water (5 ml.), containing potassium acetate, (1.2 g.) and gradually adding alcohol. *Anal.* Calcd. for K$_2$[Rh(C$_{10}$H$_{13}$N$_2$O$_8$)Cl$_2$]·5H$_2$O: C, 19.02; H, 3.67; N, 4.44. Found: C, 18.91; H, 3.46; N, 4.63.

d-**Potassium(ethylenediaminediacetatodiacetate)-di-chlororhodate(III) 4-Hydrate.**—A slurry of *d*-K[RhH$_2$O-(EDTA)]·H$_2$O (0.4 g.) and concentrated hydrochloric acid (0.3 ml.) in a small evaporating dish was stirred until nearly all of the solid had dissolved and then heated on the steam-bath for one minute. The mixture became almost solid, and the excess acid then was removed by intermittent heating in a current of air. The cold solid then was ground up with cold water (0.2 ml.) and potassium acetate (1 g.), to yield a clear orange solution. Ethanol (8 ml.) was added, the sides of the vessel scratched, and after 15 min. the orange-yellow crystals were collected and washed with ethanol (yield, 0.48 g.) ($[\alpha]_D$ +112°). The pale yellow filtrate was inactive. The substance was recrystallized twice from water (3 ml.) containing potassium acetate (1 g.), by adding alcohol (8 ml.) in two portions. The first fraction ($[\alpha]_D$ + 64°) was rejected. The more soluble fraction contained the pure substance, which had $[\alpha]_D$ + 136°, $[\alpha]_{5461}$ + 176° for a 0.125% solution. Solutions containing 0.1% of the tripotassium salt in the presence of one and two equivalents of hydrochloric acid gave, respectively, $[\alpha]_D$ + 71° and + 62°. These values correspond to successive protonations of the free acid groups.

Anal. Calcd. for K$_3$[Rh(C$_{10}$H$_{12}$N$_2$O$_8$)Cl$_2$]4H$_2$O: C, 18.44; H, 3.09; Cl, 10.88. Found: C, 18.90; H, 3.03; Cl, 10.68.

dl-**Potassium-(ethylenediaminediacetatodiacetic acid)-dibromorhodate(III).**—This was prepared in the same manner as the dichloro compound above using constant boiling hydrobromic acid. After purification by dissolution in a little water containing potassium acetate, and reprecipitation with acid, the substance was obtained in bright orange leaflets.

Anal. Calcd. for K[Rh(H$_2$EDTA)Br$_2$]: C, 20.28; H, 2.38; N, 4.73; Br, 27.00. Found; C, 20.09; H, 2.71; N, 4.77; Br, 26.87.

The hydrogen complex H[Rh(H$_2$EDTA)Br$_2$]·H$_2$O was made in a similar manner from [RhH$_2$O(H·EDTA)], or by dissolving K[RhH$_2$O(EDTA)]·H$_2$O in excess of hydrobromic acid and heating on the steam-bath. The bright orange compound separated on cooling.

Anal. Calcd. for H[Rh(C$_{10}$H$_{14}$N$_2$O$_8$)Br$_2$]·H$_2$O: C, 21.37; H, 3.05; N, 4.98. Found: C, 21.56; H, 2.80; N, 4.83.

The monoacidic salt K$_2$[Rh(H·EDTA)Br$_2$]·4H$_2$O was made by dissolving K[Rh(H$_2$EDTA)Br$_2$], (0.3 g.) in water (4 ml.) containing potassium acetate (1.2 g.), and precipitating with alcohol. This orange salt was more soluble in water than the acid salts above.

Anal. Calcd. for K$_2$[Rh(C$_{10}$H$_{13}$N$_2$O$_8$)Br$_2$]·4H$_2$O: C, 16.63; H, 2.93; N, 3.88. Found: C, 16.66; H, 2.96; N, 4.03.

l-**Potassium-(ethylenediaminediacetatodiacetate)-dibromorhodate(III) 4-Hydrate.**—This was prepared and purified in the same manner as the active dichloro compound using *l*-K[RhH$_2$O(EDTA)]·H$_2$O and hydrobromic acid. A 0.125% solution of the pure material gave $[\alpha]_D$ −136°, $[\alpha]_{5461}$ − 164°.

Anal. Calcd. for K$_3$[Rh(C$_{10}$H$_{12}$N$_2$O$_8$)Br$_2$]·4H$_2$O: C, 16.22; H, 2.72; Br, 21.59. Found: C, 16.00; H, 2.65; Br, 21.6.

Aquation of Active Dichloro and Dibromo Complexes.—Aqueous solutions (0.2%), of the active complexes were kept at 20° in the dark for 2 months. At the end of this time both solutions had become very pale yellow, and the absorption curves corresponded to that of [RhH$_2$O(EDTA)]$^-$ ion. The specific rotations ($[\alpha]_{5461}$) had decreased from + 176 to + 124° and from − 184 to − 113°, respectively. From the expected stoichiometry of the reaction and the molecular rotation of active K[RhH$_2$O(EDTA)]·H$_2$O the calculated values are + 129° and − 113°. Hence within experimental error there is complete retention of configuration in the aquation of the complexes.

Attempted Resolution of the [CrH$_2$O(EDTA)]$^-$ Anion.—The acidic substance [CrH$_2$O(H·EDTA)] was prepared by the method of Hamm.[6] This violet complex (9 g.) in water (50 ml.) was stirred with potassium acetate (8 g.) until dissolution was complete. Ethanol (250 ml.) was added, and a violet oil separated which became crystalline upon warming the mixture on the water-bath for 20 min. The solid was recrystallized from water by adding ethanol to yield purple micaceous plates.

Anal. Calcd. for K[CrH$_2$O(C$_{10}$H$_{12}$N$_2$O$_8$)]·H$_2$O: C, 28.95; H, 3.88; N, 6.75. Found: C, 28.5; H, 3.9; N, 6.76.

Debeye-Scherrer powder photographs (Fe Kα and 114.6 mm. camera diameter) showed the isomorphism of [CrH$_2$O(H·EDTA)] and [RhH$_2$O(H·EDTA)], and the two potassium salts. The diastereoisomers were prepared from barium aquo-(ethylenediaminetriacetatoacetic acid)-chromium(III), (from Ba(OH)$_2$·8H$_2$O.(1.6 g.); [CrH$_2$O-(H·EDTA)], (3.3 g.) in aqueous solution, by adding *d*[Coen$_2$(NO$_2$)$_2$]$_2$SO$_4$,[12] (3.8 g.) or *d*=[Coen$_2$(C$_2$O$_4$)]$_2$SO$_4$,[13] (3.2 g.). After removing the precipitate of barium sulfate, the solution was concentrated at 60° to 30 ml., and methanol

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[12] F. P. Dwyer and F. L. Garvan, "Inorganic Syntheses," E. G. Rochow, Ed., Vol. VI. in publication.

[13] A. Werner, *Ber.*, **45**, 3281 (1912).

(30 ml.) added. The crude solid was fractionally crystallized from water by adding alcohol. The resolving agent then was removed from a concentrated aqueous solution of each fraction by the addition of potassium iodide. After removal of the iodide precipitate, the potassium salt of the chromium complex was caused to crystallize by the addition of alcohol. All fractions were inactive.

Infrared Spectra of Rhodium(III) and Chromium(III) Complexes.—The spectra of $[RhH_2O(H{\cdot}EDTA)]$ and $[CrH_2O(H{\cdot}EDTA)]$ were almost identical, showing peaks at 1742, 1643 and 1742, 1650 cm.$^{-1}$ in the carbonyl region. The peak at 1742 cm.$^{-1}$ has been assigned to the free carboxylic acid group, and the higher frequencies to the three coördinated carboxyl groups. The relative intensities of the peaks are in conformity with these assignments. No peak could be assigned unequivocally to the coördinated water molecule.

As expected, the spectra of $K[Rh(H_2{\cdot}EDTA)Cl_2]$ and $K[Rh(H_2{\cdot}EDTA)Br_2]$ were very similar. In the carbonyl region two peaks of comparable intensity and breadth were found, at 1720 cm.$^{-1}$ (two free carboxylic acid groups) and 1598 cm.$^{-1}$ (two coördinated carboxyl groups) for the former substance and at 1717 cm.$^{-1}$ and 1595 cm.$^{-1}$ for the latter.

Acknowledgments.—The authors are indebted to Mr. E. P. Serjeant and Dr. J. E. Fildes for assistance with the *pK* determinations and the microanalyses.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Polynuclear Complex Formation Between Nickel(II) and Mercaptoacetate Ions[1]

BY D. L. LEUSSING, R. E. LARAMY AND GENE S. ALBERTS

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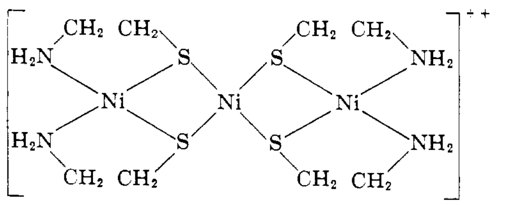
Nickel(II) and mercaptoacetate ions react to form a series of polynuclear complexes of the composition $Ni[Ni(RS)_2]_n{}^{2-2n}$. The monomeric $Ni(RS)_2^{=}$ is also formed. The coexistence of both polynuclear and monomeric species in solution makes difficult an exact description of the system, but to a good approximation the solution equilibria can be described in terms of the species $Ni_4(RS)_6^{-4}$ and $Ni(RS)_2^{=}$. The stabilities of these species and also their heats and entropies of formation were determined from the temperature dependence of the formation function in the range 0 to 40°.

The formation of polynuclear complexes has been demonstrated in several systems with nickel(II) ions and mercaptide containing ligands. Jicha and Busch[2] have isolated tetrakis-(2-aminoethanethiol)-trinickel(II) dichloride. The nickel(II) ions in this complex were found to be diamagnetic[2] and therefore are in a tetragonal (square-planar) ligand field.[3] Jicha and Busch also found that analogous compounds could be prepared in which one of the nickel(II) ions is replaced by Co(II) or Cu(II). They propose the structure



where the central nickel ion is replaceable.

The ligand 2,3-dimercapto-1-propanol has been shown[4] to form a dimeric complex, $Ni_2(DMP)_3OH^{-4}$. Similarly, 1,2-ethanedithiol reacts[5] to form $Ni_2es_3^{=}$. Jensen[6] has attributed the high insolubility of bis-(*o*-aminothiophenolate)-nickel(II) to a network structure in which sulfur bridges join adjacent nickel ions.

In an earlier work with mercaptoacetate,[7] the formation function has been interpreted in terms of the mononuclear complexes $NiSCH_2CO_2$ and $Ni(SCH_2CO_2)_2^{=}$. This function describes $\bar{n}$, the average number of ligands complexed per metal ion in a system, as a function of the concentration of uncombined ligand. The present work represents a continuation of this earlier study. An attempt was made to determine the heats and entropies of the formation of the originally proposed complexes. To do this, the formation function was obtained at various temperatures. At the lower temperatures studied it was obvious that the simple explanation originally proposed did not fit the results. Polynuclear complexes appeared to be present in this system also. A detailed study was made to determine the nature of these complexes.

Experimental

The preparation of reagents and solutions and the procedures used were essentially the same as described earlier.[7] The formation function was calculated from the results of potentiometric titrations in which solutions of nickel nitrate (or chloride) and mercaptoacetic acid in 0.10 *M* potassium chloride were titrated with standard 1.0 *M* potassium hydroxide. During titration, the solutions were thermostated in a water-bath and were protected from air by vigorously bubbling a stream of nitrogen through them. The beakers which contained the solutions were capped by stoppers through which close fitting holes had been drilled for the electrodes, buret and bubbling tube.

Titrations were made at temperatures of 0, 15, 35 and 40°. In addition to being 0.10 *M* in KCl and 0.00206 *M* in nickel nitrate, the following solutions contained mercaptoacetic acid at concentrations of 0.00978 *M* at 0°, 0.01145 *M* at 35° and 0.00990 *M* at 40°. The effect of variation of the nickel concentration was studied at 15° also in 0.10 *M* potassium chloride. Solutions were titrated which contained 0.00255 *M* mercaptoacetic acid, 0.000489 *M* nickel chloride; 0.00259 *M* mercaptoacetic acid, 0.000978 *M* nickel chloride; 0.01020 *M* mercaptoacetic acid, 0.00254 *M* nickel chloride; and 0.01028 *M* mercaptoacetic acid, 0.00397 *M* nickel chloride. The ionic strengths in the regions of interest in these solutions varied from about 0.10 to 0.12 *M*.

The glass and saturated calomel electrode system was standardized at each temperature against a solution of 0.025 *M* disodium hydrogen phosphate, 0.025 *M* potassium dihydrogen phosphate made up with National Bureau

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[1] Financial assistance for this work was made available by grants from the National Science Foundation and the Wisconsin Alumni Research Foundation.

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