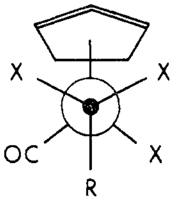
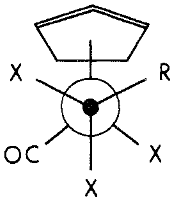
and the high conductivity in acetone (135 ohm$^{-1}$ cm$^2$ mol$^{-1}$) establish that the compound should be formulated as $[C_5H_5bipyCoSnI_3]^+I^-$. A high degree of insolubility in all solvents made it impossible to carry out metathetical reactions (for example with $NH_4^+PF_6^-$) by which the constitution of the cation could have been confirmed. The reaction with bipyridyl is quite analogous to that observed earlier with $C_5H_5COCoI_2$.[3,4]

**Infrared Spectra.**—As pointed out above, compounds of the type $C_5H_5COXCoMX_3$ and $C_5H_5COCo(MX_3)_2$ exhibit the single carbonyl stretching fundamental expected for monocarbonyl molecules. However, the spectra of the organic derivatives $C_5H_5COXCoMRX_2$ and $C_5H_5COCo(MRX_2)_2$, when it is possible to use cyclohexane as solvent, show an unexpected feature in the form of a *second weaker band at higher frequency*. The separation of the two bands ranges from 10 to 20 cm$^{-1}$, and they are not resolved in dichloromethane.

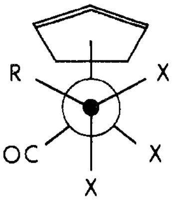
To account for the appearance of two carbonyl stretching bands in a molecule possessing a single carbonyl group, it is necessary to assume that more than one isomer is present. We believe that the isomerism in this case is of conformational origin and that these compounds provide further novel examples of an effect only recently recognized in these laboratories.[16] Thus, for molecules of the $C_5H_5COXCoMRX_2$ type, Newman projections of the three possible staggered conformations are shown in VI, VII, and VIII. Both metal atoms are regarded for this purpose as four-coordinate and tetrahedral, although it is more common in coordination chemistry to regard the π-cyclopentadienyl ligand as occupying three coordination positions. The fact that only two bands are observed could mean that the concentration of one conformer is very low, or that two of the conformers (for example, VI and VIII) have almost identical carbonyl frequencies.



VI



VII



VIII

## Conclusions

Bonds between cobalt and germanium or tin have been formed in several ways: displacement reactions,[17] the insertion of $SnX_2$ or $GeX_2$ into cobalt carbonyl,[18] and what is presumably a cleavage reaction involving $MX_4$ and cobalt carbonyl.[19] The experiments reported in this paper describe an important new method for the synthesis of cobalt–germanium and cobalt–tin bonds, namely, the oxidative elimination reaction with appropriate halides of germanium(IV) and tin(IV). As later papers in this series will show, these cyclopentadienylcarbonylcobalt derivatives are valuable intermediates in the synthesis of more complex metal–metal-bonded species.

**Acknowledgment.**—We thank the National Research Council of Canada for support of this work.

---

[16] W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967).

[17] W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1270 (1957).

[18] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966).

[19] D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967).

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

# Kinetic Study of the Alkaline Hydrolysis of Sulfato and Sulfamato Complexes of Pentaamminecobalt(III)

BY LUISA L. PO AND ROBERT B. JORDAN

*Received August 28, 1967*

The rate of hydrolysis of $(NH_3)_5CoSO_4^+$ was found to be first order in hydroxide ion. The rate constant is $4.9 \times 10^{-2}$ $M^{-1}$ sec$^{-1}$ at 25° ($\mu = 1.00$ $M$ $NaClO_4$) and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 26.3 kcal mole$^{-1}$ and 24.6 cal mole$^{-1}$ deg$^{-1}$, respectively. The rate law for hydrolysis of the sulfamato complex has the form $-d \ln [\text{complex}]/dt = k' + k''[OH^-]$. The rate constant (25°, $\mu = 1.00$ $M$ $NaClO_4$), activation enthalpy, and entropy, respectively, for $k'$ are $8.65 \times 10^{-7}$ sec$^{-1}$, 25.8 kcal mole$^{-1}$, and $-3.5$ cal mole$^{-1}$ deg$^{-1}$ and for $k''$ are $2.5 \times 10^{-7}$ $M^{-1}$ sec$^{-1}$, 41.2 kcal mole$^{-1}$, and 46 cal mole$^{-1}$ deg$^{-1}$. The $k'$ path is attributed to the reaction $(NH_3)_5CoNH_2SO_3^{2+} + OH^-$, and the $k''$ path, to the $(NH_3)_5CoNHSO_3^+ + OH^-$ reaction. The acid dissociation constant ($K_1$) of $(NH_3)_5CoNH_2SO_3^{2+}$ has been measured at low ionic strength and at 0, 13, and 25°, and also in 1 $M$ $NaClO_4$ at 25°. These results are used in the interpretation of the kinetics of the $k'$ path. The value of $K_1$ is also used to estimate the acid dissociation constant of coordinated ammonia.

## Introduction

The alkaline hydrolysis of cobalt(III)–ammine complexes has been widely studied and much of the recent evidence indicates that the S$_N$1CB mechanism best explains the results. This work has been summarized in several recent publications.[1,2]

---

[1] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 3.

[2] N. S. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

For an SN1 type of mechanism the rate-controlling step is bond breaking between cobalt and the leaving group. The results reported here do not constitute further proof of this mechanism but rather demonstrate some of the factors which are important in the bond-breaking process.

Comparison of the hydrolysis behavior of the pentaamminecobalt(III) complexes of $SO_4^{2-}$ and $NHSO_3^{2-}$ will indicate the effect of changing the atom bound to cobalt without changing the net charge and size of the leaving group. The same comparison for the $NH_2SO_3^-$ and $NHSO_3^{2-}$ complexes will reflect the result of changing the charge and thus the basicity of the atom directly coordinated to cobalt.

The measurement of the acid dissociation constant of the coordinared sulfamate ion gives a measure of the large effect of coordination on the acidity of the N–H proton. The latter effect is used to estimate the p$K$ of coordinated $NH_3$, a quantity of some controversy in the SN1CB mechanism.

## Experimental Section

**Preparation and Analysis of Reagents.**—The preparation of $(NH_3)_5CoSO_4(HSO_4)$ has been reported by Jorgenson.[3] However, we found this method always gave at least 20% of the aquopentaamminecobalt(III) complex. The impurity became apparent during attempts to repeat the $^{18}$O-tracer studies reported by Green and Taube.[4,5] Subsequently the product from Jorgenson's preparation has been purified by elution from Dowex 50-X8 ion-exchange resin with 0.4 $M$ sodium perchlorate. The eluent solution containing the sulfato complex and sodium perchlorate was cooled in an ice bath and crystals of $((NH_3)_5CoSO_4)ClO_4$ were collected and washed with methanol and dried under vacuum.

The sulfamato complex was prepared by heating an aqueous solution of $((NH_3)_5CoOH_2)(ClO_4)_3$ with a tenfold molar excess of half-neutralized sulfamic acid. The crude product which separated on cooling was redissolved in water and recrystallized by adding concentrated perchloric acid.

*Anal.* Calcd for $((NH_3)_5CoSO_4)ClO_4\cdot H_2O$: N, 19.6; H, 4.80; $SO_4^{2-}$, 26.85. Found: N, 19.73; H, 4.84; $SO_4^{2-}$, 27.30. Calcd for $((NH_3)_5CoNH_2SO_3)(ClO_4)_2$: N, 19.10, H, 3.90; $SO_4^{2-}$, 21.87. Found: N, 18.91; H, 4.04; $SO_4^{2-}$, 21.55. Sulfate was determined by heating a solution of complex and barium chloride in 1 $M$ perchloric acid for 24 hr at 60°. The barium sulfate was collected and weighed following standard procedures.

Sodium perchlorate and lithium perchlorate solutions were prepared by neutralization of the respective carbonates with perchloric acid. Concentrations are based on the amount of carbonate salt used. Sodium hydroxide solutions were prepared by dilution of ampoules of concentrated reagent (Fisher Certified reagent) or from a 50% solution of NaOH in water. All reagents were prepared in water redistilled from alkaline permanganate in an all-glass apparatus.

Absorbance measurements were made on a Bausch and Lomb Spectronic 505. Temperatures were controlled to ±0.1° with a standard constant-temperature bath.

**Visible and Ultraviolet Spectrum of Complex Ions.**—The visible spectrum of $(NH_3)_5CoSO_4^+$ has peaks at 517 m$\mu$ ($\epsilon$ 65.5) and 357 m$\mu$ ($\epsilon$ 34.8). These values agree with previous results.[6,7]

The sulfamato complex in 0.10 $M$ perchloric acid has peaks at 488 m$\mu$ ($\epsilon$ 60.2) and 345 m$\mu$ ($\epsilon$ 49.6). In 0.10 $M$ sodium hydroxide there is one peak in the visible region at 517 m$\mu$ ($\epsilon$ 115) and one in the near-ultraviolet region at 296 m$\mu$ ($\epsilon$ $1.78 \times 10^3$). The peak expected in the 350-m$\mu$ region is apparently hidden under the 296-m$\mu$ peak.

**Base Hydrolysis Kinetics.**—The solid $((NH_3)_5CoSO_4)ClO_4$ was dissolved in the reaction solution containing appropriate amounts of sodium hydroxide and sodium perchlorate to give an ionic strength of 1.00. The reaction solution was preequilibrated at the required temperature for at least 30 min before the complex salt was added. Aliquots were taken and quenched in sufficient 1 $M$ $HClO_4$ to give a final acid concentration of 0.1 $M$. The absorbance of the samples was determined (at 270 and 290 m$\mu$ in different runs), and the rate constant was calculated from the usual plots of log $(A_t - A_\infty)$ *vs.* time.

Similar solution preparation and sampling procedure were used for the study of the alkaline hydrolysis of $(NH_3)_5CoNH_2SO_3^{2+}$. However, in this case it is necessary to remove the cobalt oxide decomposition product by filtration through a 0.45-$\mu$ filter (Millipore Filter Corp., Bedford, Mass.). The filtered solutions were diluted with sufficient perchloric acid to give a final concentration of 0.01 $M$ NaOH. The absorbance was recorded at 296 m$\mu$, a peak in the spectrum of $(NH_3)_5CoNHSO_3^+$. The solutions can be stored under dilute alkaline conditions at room temperature because of the slow hydrolysis as shown by the results reported here. Recording the spectra under alkaline conditions takes advantage of the large extinction coefficient of $(NH_3)_5CoNHSO_3^+$ at 296 m$\mu$.

In all cases the hydroxide ion was in at least tenfold molar excess over the complex concentration. For $(NH_3)_5CoSO_4^+$ the rate was studied over at least a fourfold change in hydroxide concentration at each temperature, from the lowest value of 0.05 $M$ NaOH at 25° to 0.80 $M$ NaOH at 0°. The sulfamato complex was generally studied between 0.10 and 1.0 $M$ NaOH at all temperatures.

**Acid Dissociation Constant of $(NH_3)_5CoNH_2SO_3^{2+}$.**—The value of the acid dissociation constant ($K_1$) of $(NH_3)_5CoNH_2SO_3^{2+}$ was determined by standard potentiometric titrations of 0.002 $M$ solutions of complex with 0.106 $M$ sodium hydroxide. The sodium hydroxide was added, in increments from a calibrated 1.00-ml syringe, to the sample solution in a 100-ml three-necked flask equipped with the usual glass and calomel reference electrodes. Scrubbed nitrogen was passed through the solution continually during the titration to exclude carbon dioxide and provide mixing.

The pH measurements were made on a Beckman Expandomatic pH meter, calibrated at pH 4 and 7. The p$K$ values were calculated as described by Albert and Sergeant.[8]

## Results

The rate of hydrolysis of $(NH_3)_5CoSO_4^+$ was found to be first order in hydroxide ion between 0.05 and 0.80 $M$ NaOH at 0, 16, and 25°. Typical results at 25° are given in Table I. The calculated first-order rate constants and the activation parameters are given in Table II.

The dependence of the hydrolysis rate of the sulfamato complex on hydroxide ion shows a term independent of hydroxide ion and a term first order in hydroxide ion. In the pH region studied the complex is completely in the basic form. Therefore the rate of hydrolysis is represented by

$$\frac{-\mathrm{d}\ln[(\mathrm{NH_3})_5\mathrm{CoNHSO_3}^+]}{\mathrm{d}t} = k' + k''[\mathrm{OH}^-] \qquad (1)$$
$$= k_{\mathrm{obsd}}$$

---

[3] S. M. Jorgenson, *J. Prakt. Chem.*, **31**, 268 (1885).

[4] M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

[5] H. Taube and R. B. Jordan, unpublished results. Tracer studies on the position of bond breaking during alkaline hydrolysis of $(NH_3)_5CoSO_4^+$ indicate that less than 4% of the events lead to S–O bond breaking, for hydroxide ion concentrations between 0.01 and 0.12 $M$ at 25°.

[6] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[7] W. P. Schmidt and H. Taube, private communication.

[8] A. Albert and E. P. Sergeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, p 33.

TABLE I

RATE OF HYDROLYSIS OF $(NH_3)_5CoSO_4^+$ AT 25° AND $\mu = 1.0\ M$ ($NaClO_4$)

| $[OH^-]$, $M$ | $10^2k_1$,[a] $M^{-1}$ sec$^{-1}$ |
|---|---|
| 0.05 | 4.80 |
| 0.10 | 5.24 |
| 0.12 | 5.00 |
| 0.15 | 4.75 |
| 0.20 | 4.80 |
| | Av $4.92 \times 10^{-2}$ $M^{-1}$ sec$^{-1}$ |

[a] Observed first-order rate constant at 25° divided by $[OH^-]$.

TABLE II

RATE PARAMETERS FOR THE HYDROLYSIS OF $(NH_3)_5CoSO_4^+$ AT $\mu = 1.0\ M$ ($NaClO_4$)

| Temp, °C | $10^2k_1$, $M^{-1}$ sec$^{-1}$ |
|---|---|
| 0 | 0.81 |
| 16 | 1.38 |
| 25 | 4.92 |
| $\Delta H^{\ddagger}$, kcal mole$^{-1}$ | $26.3 \pm 0.5$ |
| $\Delta S^{\ddagger}$, cal mole$^{-1}$ deg$^{-1}$ | $24.6 \pm 3$ |

Since the hydroxide ion concentration is always in large excess over the complex concentration, $k'$ and $k''$ can be obtained from plots of $k_{obsd}$ *vs.* $[OH^-]$. In Table III the experimental $k_{obsd}$ values are compared to those calculated from eq 1 using the values of $k'$ and $k''$ given in Table IV. Table IV also contains values of the apparent activation energies for $k'$ and $k''$.

TABLE III

$(NH_3)_5CoNHSO_3^+$ HYDROLYSIS AT 55° AND $\mu = 1.00\ M$ ($NaClO_4$)

| $[OH^-]$, $M$ | $10^4k_{obsd}$, sec$^{-1}$ | |
|---|---|---|
| | Found | Calcd[a] |
| 0.30 | 1.03 | 1.05 |
| 0.40 | 1.22 | 1.21 |
| 0.50 | 1.42 | 1.38 |
| 0.60 | 1.53 | 1.55 |
| 0.80 | 1.87 | 1.88 |
| 0.90 | 2.04 | 2.04 |

[a] Calculated from eq 1 using the values of $k'$ and $k''$ given in Table IV.

TABLE IV

RATE CONSTANTS[a,b] FOR THE ALKALINE HYDROLYSIS OF $(NH_3)_5CoNHSO_3^+$ AT $\mu = 1.00\ M$ ($NaClO_4$)

| Temp, °C | $10^4k'$, sec$^{-1}$ | $10^4k''$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| 45 | 0.144 | 0.213 |
| 55 | 0.55 | 1.66 |
| 65 | 1.70 | 12.5 |
| $\Delta H^{\ddagger}$, kcal mole$^{-1}$ | $25.8 \pm 1.0$ | $41.2 \pm 0.50$ |
| $\Delta S^{\ddagger}$, cal mole$^{-1}$ deg$^{-1}$ | $-3.5 \pm 5$ | $46 \pm 3$ |

[a] By extrapolation of log $(k/T)$ *vs.* $1/T$ plots at 25°, $k' = 8.65 \times 10^{-7}$ sec$^{-1}$, and $k'' = 2.5 \times 10^{-7}$ $M^{-1}$ sec$^{-1}$. [b] The estimated errors are ±10% in $k'$ and ±3% in $k''$.

It is possible that the sulfamato complex may hydrolyze with either Co–N or N–S bond breaking. The latter path would lead to sulfate ion as a product. Qualitative tests with barium chloride indicate that less than 5% sulfate product is formed when the reaction proceeds either 90% by the $k'$ path (0.10 $M$ NaOH, 35°) or 90% by the $k''$ path (1.0 $M$ NaOH, 70°).

The values of p$K_1$ determined by potentiometric titrations were 5.83, 6.03, and 6.40 at 25, 13, and 0°, respectively, and at low ionic strength (about 0.004). An error of ±0.03 is estimated from the variation in calculated values during one titration and the reproducibility of the results. From the temperature dependence of p$K_1$ the enthalpy and entropy for $K_1$ are calculated as $6.5 \pm 0.5$ kcal mole$^{-1}$ and $-5.5 \pm 2$ cal mole$^{-1}$ deg$^{-1}$, respectively.

Similar titrations in 1 $M$ $NaClO_4$ at 25° give a value of 5.70 for p$K_1$.

## Discussion

The kinetic parameters and rate law for the alkaline hydrolysis of $(NH_3)_5CoSO_4^+$ are quite typical of previous results on other acidopentaamminecobalt(III) complexes. It may be noted that the double negative charge on the sulfate ion does not seem to cause any marked increase in the activation enthalpy for hydrolysis. A similar effect has been noted in the alkaline hydrolysis of dicarboxylic acid complexes[9] and in the aquation of $(H_2O)_5CrSO_4^+$.[10]

Before considering the hydrolysis kinetics of $(NH_3)_5CoNH_2SO_3^{2+}$, it is necessary to give some justification for considering the sulfamate ion as being bonded to cobalt through nitrogen rather than oxygen. Nitrogen bonding is to be expected from the formulation of sulfamic acid as the zwitterion $H_3N^+SO_3^-$, indicating that the nitrogen is the more basic center in the sulfamate ion.[11]

Several features of the visible spectrum of the complex also substantiate the nitrogen bonding formulation. The large difference in peak positions of $(NH_3)_5CoNH_2SO_3^{2+}$ and $(NH_3)_5CoSO_4^+$ would not be predicted if the sulfamate were bonded through oxygen. Also the large spectral change on going from acidic to basic solution would only be expected if a proton were being lost from the atom directly bonded to cobalt. Thus the observed difference is similar to that between $(NH_3)_5CoOH_2^{3+}$ and $(NH_3)_5CoOH^{2+}$, whereas there is very little change on protonation of $(NH_3)_5CoPO_4$ to give $(NH_3)_5CoOPO_3H^+$.[12]

In addition, the acidic behavior of the coordinated sulfamate ion indicates that it is nitrogen bonded and the acidity of the $NH_2$ protons is greatly increased by the inductive effect of the cobalt(III). The $K_a$ of the sulfamate ion[11] is too small to be measured in aqueous solution. Thus the acidity has been enhanced by at least a factor of $10^{10}$ owing to coordination to cobalt(III). For other coordinated oxy anions such as carbonate,[13] phosphate,[12] and oxalate[14] the $K_a$ generally differs by less than $10^2$ from that of the uncoordinated ligand. Thus the large change in $K_a$ is a further indication that the sulfamate ion is bonded through nitrogen.

---

(9) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **6**, 379 (1967).

(10) J. E. Finholt and S. N. Deming, *ibid.*, **6**, 1533 (1967).

(11) H. P. Hopkins, C. H. Wu, and L. G. Hepler, *J. Phys. Chem.*, **69**, 2244 (1965).

(12) W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963).

(13) D. J. Francis and R. B. Jordan, *J. Am. Chem. Soc.*, **89**, 5591 (1967).

(14) C. A. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).

The rate law for the hydrolysis of $(NH_3)_5CoNHSO_3^+$ is consistent with two apparently reasonable reaction paths ((A) and (B)).

$$(NH_3)_5CoNHSO_3^+ + OH^- \xrightarrow{k_1} (NH_3)_5CoOH^{2+} + NHSO_3^{2-}$$
$$(NH_3)_5CoNHSO_3^+ + H_2O \rightleftharpoons (NH_3)_5CoNH_2SO_3^{2+} + OH^- \quad \text{(A)}$$
$$(NH_3)_5CoNH_2SO_3^{2+} + OH^- \xrightarrow{k_2} (NH_3)_5CoOH^{2+} + NH_2SO_3^-$$

The $NHSO_3^{2-}$ product from the $k_1$ path would react rapidly with water to give $NH_2SO_3^-$ and $OH^-$. This scheme leads to the rate expression

$$\frac{-d[\text{complex}]}{dt} = k_1[OH^-][(NH_3)_5CoNHSO_3^+] + k_2[OH^-][(NH_3)_5CoNH_2SO_3^{2+}] \quad (2)$$

Since the complex is completely in the $(NH_3)_5CoNHSO_3^+$ form, eq 2 may be rearranged to give

$$\frac{-d[(NH_3)_5CoNHSO_3^+]}{dt} = \left(k_1[OH^-] + \frac{k_2K_w}{K_1}\right)[(NH_3)_5CoNHSO_3^+] \quad (3)$$

where $K_w = [H^+][OH^-]$, the ion product for water. The specific expressions for $k'$ and $k''$ can be obtained by comparison of eq 1 and 3.

There is an alternate reaction path which also seems reasonable and is consistent with the rate law

$$\left.\begin{array}{l} (NH_3)_5CoNHSO_3^+ + OH^- \xrightarrow{k_1} \\ \qquad (NH_3)_5CoOH^{2+} + NHSO_3^{2-} \\ (NH_3)_5CoNHSO_3^+ + H_2O \xrightarrow{k_3} \\ \qquad (NH_3)_5CoOH^{2+} + NH_2SO_3^- \end{array}\right\} \quad \text{(B)}$$

In this case

$$\frac{-d[(NH_3)_5CoNHSO_3^+]}{dt} = (k_3 + k_1[OH^-])[(NH_3)_5CoNHSO_3^+] \quad (4)$$

The choice between (A) and (B) must be made by considering the hydroxide ion independent term since the other term is the same reaction in both cases. For case A, using the measured value for $pK_1$ of 5.70, the extrapolated value for $k'$ of $8.65 \times 10^{-7}$, and the known value for $pK_w$ of 13.77 (1 $M$ $NaClO_4$, 25°),[15,16] it is possible to calculate a value of 100 for the specific rate constant $k_2$. For pentaamminecobalt(III) complexes in general the ratio of the alkaline hydrolysis to aquation rate constants is about $10^4$ to $10^6$. The calculated value of $k_2$ is then consistent with the measured value of the aquation rate constant for $(NH_3)_5CoNH_2SO_3^{2+}$, $3 \times 10^{-5}$ sec$^{-1}$ [17] ($\mu = 1.00$ $LiClO_4$, 25°). A similar comparison of $k_1$ and $k_3$ serves to eliminate scheme B, since the ratio of $k_1$ to $k_3$ is 0.35 and rises to only about 10 at the highest temperature studied here.

Another difficulty with (B) is the large difference in $\Delta H^{\ddagger}$ for the $k'$ and $k''$ paths. It is generally observed that the activation enthalpy for aquation is within about 5 kcal mole$^{-1}$ of that for alkaline hydrolysis. Thus the observed difference of 16 kcal mole$^{-1}$ would be entirely unexpected. If one of the reaction paths occurs with Co–N and the other with N–S bond breaking, then $k'$ and $k''$ might have entirely different activation energies. However, as reported in the Results section, tests for $SO_4^{2-}$ with $Ba^{2+}$ were negative under conditions where the reaction was proceeding either 90% by the $k'$ or 90% by the $k''$ path.

It is therefore concluded that the kinetic results apply to the reactions given in scheme A. The measured temperature dependence of $K_1$ can be used to calculate an activation energy of 32 kcal mole$^{-1}$ for the specific rate constant $k_2$.

It should be pointed out that hydrolysis of $(NH_3)_5CoNHSO_3^+$ leads to a considerable loss of ammonia from the cobalt, and the final product is mainly cobalt oxide. If the rate-controlling step were loss of ammonia, rather than sulfanate, then reaction schemes similar to (A) and (B) would also explain the kinetics. The initial product would be $Co(NH_3)_4NHSO_3OH$ instead of $(NH_3)_5CoOH^{2+}$. However, it is difficult to rationalize the large difference in activation energies for the two reaction paths if $NH_3$ is being lost in both cases. A similar situation was found in the study of the alkaline hydrolysis of $(NH_3)_5CoCO_3^+$,[13] but in this case it is possible to study the reaction under pH conditions in which either considerable or no ammonia loss occurs. Good agreement was found for rate constants determined under either set of conditions, indicating that carbonate ion loss is always the rate-controlling step in the hydrolysis.

The two systems studied here represent a good illustration of the difficulty in relating electronic factors, as deduced from the spectra, and hydrolysis kinetic parameters. Since the lowest energy transition in both complexes occurs at 517 mμ, simple consideration of crystal or ligand field effects would lead to the conclusion that the hydrolysis rates might be similar. The similarity in charge, size, and electronic configuration of the $SO_4^{2-}$ ligands would further strengthen this prediction. The complete failure of such a prediction is relatively easy to explain in this case and points out factors which may be unnoticed but still important for other systems. The change from $(NH_3)_5CoNH_2SO_3^{2+}$ to $(NH_3)_5CoNHSO_3^+$ results in a shift of the lowest energy transition to lower energy. Since $NHSO_3^{2-}$ is undoubtedly a much stronger base than $NH_2SO_3^-$, the former ligand would give a much stronger $\sigma$ bond, and the empty $\sigma^*$ ($d_{z^2}$, $d_{x^2-y^2}$) level would be of higher energy. Then the spectral transition would be expected to shift to higher energy. However, this effect is apparently offset by the stronger $\pi$ bonding of $NHSO_3^{2-}$, causing an increase in energy of the filled $\pi_{xz}^*$ and $\pi_{yz}^*$ levels. The net result is that the $\pi^* \rightarrow \sigma^*$ transition shifts to lower energy.

As expected, the kinetic results reported here show that $\sigma$-bonding interactions are most important in predicting either relative rates or activation enthalpies. Therefore, the use of spectral correlations will fail unless the spectra are being dominated by the effect of

---

(15) R. Nasanen and P. Merilainen, *Suomen Kemistilehti*, **B33**, 149 (1960), as quoted in ref 16.

(16) "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

(17) R. B. Jordan, results to be published.

the ligand on the energy of the $\sigma^*$ level. The latter condition may hold for the $SO_4^{2-}$ ligand but certainly does not for the isoelectronic and structurally similar $NHSO_3^-$ ligand.

The measured p$K_1$ value gives some indirect support to the S$_N$1CB mechanism for the alkaline hydrolysis of cobalt(III)–ammine complexes. The reaction

$$(NH_3)_5CoNH_2SO_3^{2+} \rightleftharpoons (NH_3)_5CoNHSO_3^{+} + H^+ \qquad K_1$$

is similar to the formation of the conjugate base proposed in the S$_N$1CB mechanism

$$(NH_3)_4CoNH_3X \rightleftharpoons (NH_3)_4CoNH_2X + H^+ \qquad K_a$$

The same type of back $\pi$ bonding can occur with $NH_2^-$ as described above for $NHSO_3^{2-}$; therefore, it should be possible to estimate $K_a$ from $K_1$.

From measured p$K$ values[16] it is known that sulfamic acid is about $10^9$ times a stronger acid than $NH_4^+$. It may then be assumed that the second dissociation constants of these ions also differ by $10^9$ and further that the dissociation constants of the coordinated ions differ by $10^9$. Then using the measured value of $10^{-6}$ for $K_1$, $K_a$ is calculated as $10^{-15}$. This value is quite consistent with the inability to measure the value of $K_a$ in aqueous solution and with previous estimates from deuterium exchange and kinetic studies.[1,18]

[18] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA 15213

# Circular Dichroism of Some Optically Active Rhodium–Amino Acid Complexes[1]

BY STEPHEN K. HALL AND BODIE E. DOUGLAS

*Received August 14, 1967*

Circular dichroism (CD) and electronic absorption spectra are reported for some rhodium(III) complexes of optically active amino acids of the general formula $[Rh(en)_2aa]^{2-}$ (where aa is an amino acid anion). All the $(-)_D$ isomers of $[Rh(en)_2aa]^{2+}$ were assigned the Λ configuration which is related to the absolute configuration of the $(+)_D$-$[Co(en)_3]^{3+}$ ion.

Complexes of the type $[Co(en)_2aa]^{2+}$ (where aa is an amino acid anion) have been prepared and resolved, and the absorption spectra, ORD, and CD curves have been reported.[2] Some rhodium(III) complexes of the type $[Rh(en)_2aa]^{2+}$ have been prepared by Waller, Hu, and Bryant.[3] In the present work, some of these complexes were successfully resolved and their electronic absorption and circular dichroism (CD) spectra were measured.

## Experimental Section

**Reagents.**—All optically active amino acids were purchased from Nutritional Biochemical Corp., Cleveland, Ohio, and used as received. The reported specific rotations at the sodium D line were: (*S*)-alanine, +14.25° in 6 *N* HCl; (*S*)-leucine, +15° in 6 *N* HCl; (*S*)-methionine, +23.5° in 5 *N* HCl; (*S*)-serine, +14.3° in 9 *N* HCl; (2*S*,3*R*)-threonine, −28.3° in water; (*S*)-valine, +27.3° in 6 *N* HCl. (*S*) refers to the absolute configuration of the amino acids, commonly designated as L.

**Measurements.**—The CD spectra were taken in aqueous solutions in 1- or 2-cm cells using a Roussel-Jouan Dichrograph. The concentrations of the solutions were 0.004–0.006 *M*. Measurements of optical rotations were made on the same solutions in a 1-dm cell at the sodium D line, at room temperature. Absorption spectra were recorded on a Cary Model 14 spectrophotometer using 1-cm cells. Results of measurements on the rhodium complexes of optically active amino acids are summarized in Table I.

**Preparation and Resolution of Glycinatobis(ethylenediamine)-rhodium(III) Iodide.**—This compound was prepared by the method of Waller, Hu, and Bryant.[3] A slurry of 3.56 g of *trans*-dichlorobis(ethylenediamine)rhodium(III) nitrate[4] and 0.75 g of glycine in a mixture of 10 ml of 1 *N* NaOH, 15 ml of water, and 5 ml of 95% ethanol was warmed gently on the steam bath until a clear solution resulted. The warm solution was filtered, cooled, and treated with 5 g of solid NaI. It was left in a refrigerator overnight to precipitate. The resulting creamy colored precipitate was filtered, washed with absolute ethanol, acetone, and ether, and air dried. The compound was recrystallized from a minimum amount of hot water.

The racemic complex dissolved in a minimum amount of water at room temperature was resolved using freshly prepared silver antimonyl tartrate. The resolutions were carried out using 0.5–1 g of complex and a slight excess of resolving agent. Silver iodide was removed by filtration after shaking the mixture vigorously for 10–15 min away from direct light. Ethanol (*ca.* 15 ml) was slowly and carefully added while the solution (*ca.* 20 ml) was mechanically stirred to precipitate the less soluble diastereoisomer. When the first cloudiness appeared, the solution was gently warmed on a steam bath to clear the cloudiness. On cooling and standing overnight, the less soluble diastereoisomer precipitated. This was filtered, washed with ethanol, acetone, and ether, and air dried. The more soluble diastereoisomer was obtained by first concentrating the filtrate under a stream of compressed air and by further addition of ethanol.

The diastereoisomer dissolved in water was treated with $AgNO_3$ to precipitate the resolving agent, which was removed by filtration, followed by the addition of excess NaI to precipitate the complex in the iodide form.

**Preparation and Resolution of Complexes of Optically Active Amino Acids.**—These compounds were prepared and resolved by methods similar to that described for the glycine complex. The specific rotations and analytical results are given in Table I.

---

[1] Taken from the Ph.D. Dissertation of S. K. Hall, The University of Pittsburgh, 1967. This work was supported by a research grant (GM10829-09) from the Division of General Medical Studies, U. S. Public Health Service.

[2] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

[3] J. F. Waller, Jr., J. Hu, and B. E. Bryant, *J. Inorg. Nucl. Chem.*, **27**, 2371 (1965).

[4] S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 217 (1966).