[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

# Mechanism of Racemization of Complex Ions. I. Kinetics of the Dissociation and Racemization of Tris-(1,10-phenanthroline)-nickel(II) and Tris-(2,2′-dipyridyl)nickel (II) Complexes[1]

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The rates of dissociation and racemization of tris-(1,10-phenanthroline)-nickel(II) and tris-(2,2′-dipyridyl)-nickel(II) ions were determined under similar conditions. Since in each case the complex was found to dissociate and racemize at the same rate and with the same activation energy, it was concluded that the racemization takes place by a dissociation mechanism. This is believed to be the first example where it has been demonstrated that racemization may result from the dissociation of a chelate group from the complex.

There has been considerable interest in the mechanism of racemization of optically active complex ions. In general two types of mechanisms have been considered: (1) an intramolecular rearrangement, and (2) a dissociation process. The intramolecular process was first suggested by Werner,[3] with some modification recently being offered by Ray and Dutt.[4] The dissociation mechanism was suggested by Thomas,[5] and it has definitely been shown not to apply to the tris-(oxalato) complex ions of cobalt(III) and chromium(III).[6]

Recent studies have been made of the rates of racemization of the tris-(1,10-phenanthroline)-nickel(II)[7] and tris-(2,2′-dipyridyl)-nickel(II)[8,9] ions, and the conclusion reached was that these ions racemize by an intramolecular process. This mechanism was suggested because the rates of racemization were not altered by the presence of excess chelating agent. However, if dissociation were involved and the dissociated product were either symmetrical or lost its optical activity very rapidly, then the presence of chelating agent would not be expected to change the rate of racemization.

A comparison of the rates of racemization and dissociation should indicate which of the two possible mechanisms is operative. Both of these nickel(II) complex ions are colored and thus it is possible to study the rates of dissociation by a spectrophotometric method. The dissociation is observable in solutions of relatively high acid concentration as a consequence of the fact that the 1,10-phenanthroline or 2,2′-dipyridyl formed in dissociation[10]

$$[Ni(AA)_3]^{+2} \longrightarrow [Ni(AA)_2]^{+2} + (AA)$$

reacts rapidly with the acid

$$H^+ + (AA) \longrightarrow H(AA)^+$$

Since the products formed have a different color than the reactants, the rate of dissociation is conveniently followed. The experimental observations reported in this paper indicate the racemization of tris-(1,10-phenanthroline)-nickel(II) and tris-(2,2′-dipyridyl)-nickel(II) ions proceeds by a dissociation mechanism.

## Experimental

**Preparation of Compounds.**—The complex compounds used in these studies were all prepared as described by Pfeiffer and Tappermann.[11] Chloride analyses for these compounds were in accord with the theoretical values.

| Compound | Chlorine, % Calcd. | Chlorine, % Found |
|---|---|---|
| $Ni(ophen)_3Cl_2 \cdot 7H_2O$ | 8.9 | 9.0 |
| $Ni(ophen)_2Cl_2 \cdot 5H_2O$ | 12.2 | 12.1 |
| $Ni(dipy)_3Cl_2 \cdot 6H_2O$ | 10.1 | 10.2 |
| $Ni(dipy)_2Cl_2$ | 16.0 | 15.8 |

Potassium antimonyl *d*-tartrate was used to resolve $[Ni(ophen)_3]^{+2}$ which was finally isolated as the perchlorate with an optical rotation of $[\alpha]^{25}\text{D}$ +1550°.[12] The complex $[Ni(dipy)_3]^{+2}$ was resolved using ammonium *d*-tartrate as the resolving agent and the complex had a specific rotation of $[\alpha]^{25}\text{D}$ +567°.[13]

The complex $Ni(dipy)_2Cl_2$ is obtained by heating the salt $[Ni(dipy)_3]Cl_2 \cdot 6H_2O$ in a vacuum oven at 140° for approximately two hours. It appeared to be of some interest to remove the one molecule of 2,2′-dipyridyl from the optically active salt and then determine whether the resulting product is optically active. This was done and it was found that neither an aqueous nor alcoholic solution of the $Ni(dipy)_2Cl_2$ produced gave any evidence of being optically active.

**Spectra of Complexes.**—The spectra of the following species, related to tris-(1,10-phenanthroline)-nickel(II), were obtained by direct measurement with a Beckman Model DU spectrophotometer: $[Ni(ophen)_3]^{+2}$, $[Ni(ophen)_2]^{+2}$, $Ni^{+2}$ and $Hophen^+$. The measurements were made at 10 mμ intervals in the range 400–1000 mμ. The spectra of equilibrium mixtures containing $Ni^{+2}$ and 1,10-phenanthroline in the molar ratios of 1:1 and 1:2 were also obtained in the same way, allowing calculation of the spectrum of $[Ni(ophen)]^{+2}$. The spectra of the individual complexes, plus that of $Ni^{+2}$ are shown in Fig. 1. Molar absorbancy indexes,[14] *a*, were calculated from the equation $\log_{10} I_0/I = abc$, where *b* is the cell length and *c* is the molar concentration.

The spectrum of $[Ni(dipy)_3]^{+2}$ was determined in like manner, as was the spectrum of the solution of $Ni(dipy)_2Cl_2$. It is felt that the latter compound rapidly comes to an equilibrium between the various complexes, and that the

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[1] Presented at the Los Angeles Meeting of the American Chemical Society, March, 1953.

[2] Taken in part from a thesis submitted by John C. Hayes in partial fulfillment of the requirements for the M.S. degree, 1953.

[3] A. Werner, *Ber.*, **45**, 3061 (1912).

[4] P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

[5] W. Thomas, *J. Chem. Soc.*, **119**, 1140 (1921).

[6] C. H. Johnson, *Trans. Faraday Soc.*, **31**, 1612 (1935); N. W. D. Beese and C. H. Johnson, *ibid.*, **31**, 1632 (1935); F. A. Long, THIS JOURNAL, **61**, 570 (1939); E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939).

[7] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **48**, 244 (1952).

[8] G. K. Schweitzer and J. M. Lee, *J. Phys. Chem.*, **56**, 195 (1952).

[9] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **49**, 180 (1953).

[10] The following symbols are used: ophen, 1,10-phenanthroline; dipy, 2,2′-dipyridyl; (AA), 1,10-phenanthroline or 2,2′-dipyridyl; tris, $[Ni(AA)_3]^{+2}$; bis, $[Ni(AA)_2]^{+2}$; mono, $[Ni(AA)]^{+2}$.

[11] P. Pfeiffer and F. Tappermann, *Z. anorg. allgem. Chem.*, **215**, 273 (1933).

[12] F. P. Dwyer and E. C. Gyarfas, *Proc. Roy. Soc. N. S. Wales*, **83**, 232 (1950).

[13] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2213 (1931).

[14] The nomenclature and symbolism used here for spectrophotometric terms is that given in Letter Circular LC-857 of the National Bureau of Standards.

spectrum is not that of $[Ni(dipy)_2]^{+2}$, but is that of the equilibrium mixture. The two spectra were strikingly similar to those of $[Ni(ophen)_3]^{+2}$ and the 1:2 equilibrium mixture of $Ni^{+2}$ and ophen.

It should perhaps be mentioned that the complexes in aqueous solutions designated throughout this paper as $[Ni(AA)_2]^{+2}$ and $[Ni(AA)]^{+2}$ are probably the aquo ions $[Ni(AA)_2(H_2O)_2]^{+2}$ and $[Ni(AA)(H_2O)_4]^{+2}$. Furthermore the anhydrous compound $Ni(dipy)_2Cl_2$ is perhaps $[Ni(dipy)_2Cl_2]$, while $[Ni(ophen)_2]Cl_2 \cdot 5H_2O$ appears to be $[Ni(ophen)_2(H_2O)_2]Cl_2 \cdot 3H_2O$. However, the exact structure of these compounds is of no significance in this present investigation.

**Rate of Racemization.**—Measurements of optical rotation were made with a Bellingham and Stanley polarimeter. The salt *d*-$[Ni(ophen)_3](ClO_4)_2 \cdot 3H_2O$ was dissolved in an appropriate solution to yield a concentration of approximately $1 \times 10^{-4}$ *M*. This solution was immediately transferred to a 1-dm. polarimeter tube and maintained at constant temperature (±0.1°) by keeping the tube in a thermostated water-bath. The tube was then removed only briefly to make intermittent measurements of optical rotation.

Since *d*-$[Ni(dipy)_3]Cl_2$ racemizes much more rapidly than the 1,10-phenanthroline complex, this same technique could not be employed. Instead it was necessary to use a 4-dm. polarimeter tube equipped with a water jacket and maintained at constant temperature (±0.1°) with circulating water. In order to obtain a maximum rotation at the start of a run, an excess of the complex was shaken in the appropriate solution at 0° for approximately 5 min. The excess salt was removed on a chilled Hirsch funnel and the clear filtrate collected in a filter flask surrounded by an ice–salt-bath. This cold solution was then poured into the polarimeter tube and measurements were taken as soon as the equilibrium temperature was reached.

The data collected were plotted in the usual fashion of log $\alpha$ *vs.* time. Duplicate determinations were usually made, and the results obtained have a precision of better than 5%.

**Rate of Dissociation.**—In the case of the 1,10-phenanthroline complex, a weighed portion, generally about 0.3 g., of $[Ni(ophen)_3]Cl_2 \cdot 7H_2O$ was dissolved in 25 ml. of HCl of the appropriate concentration. Concentrations used were 2, 3 and 5 *M*. The acid solution was maintained at the chosen temperature (±0.1°) before and after mixing. After various reaction periods, portions of the reaction mixture were removed and the absorbancy determined at several wave lengths. Wave lengths used in various experiments were 400, 420, 440, 520, 780, 940 and 1000 mμ. The first four wave lengths gave data of sufficient accuracy for quantitative rate measurements, the remainder giving qualitative information only.

The rapidity of the dissociation of $[Ni(dipy)_3]^{+2}$ required that a different technique be adopted. A stock solution of the chloride (about 0.07 *M*) was made up and thermostated at the reaction temperature. The optical cell was filled with 3 ml. of acid, and maintained at the reaction temperature by means of a water jacket. To commence the reaction 0.05 to 0.20 ml. of the complex solution was added by means of a micropipet and syringe, and mixing was achieved by bubbling air through the solution. Readings of the absorbancy were taken continuously at a wave length of 400 mμ. The first reading could be obtained within 50 sec. after addition of the complex. The most likely source of error in this method arises from the difficulty of temperature measurement. Although the stock solution of complex was maintained at the reaction temperature, and the pipet was chilled prior to use, the pipet warms rapidly in the air, and during the operation of adding the complex to the reaction its temperature may well rise above that of the acid. As a result there is an uncertainty, amounting to about 0.4°, in the true reaction temperature. Consideration of a possible temperature increase resulting from dilution of the acid shows this effect leads to a negligible temperature change.

### Mathematical Treatment of Dissociation Data

The analysis of the rate data is complicated by the fact that there are really three consecutive dissociation reactions taking place, *viz.*

$$[Ni(AA)_3]^{+2} \xrightarrow{k_1} [Ni(AA)_2]^{+2} + (AA) \qquad (1)$$

$$[Ni(AA)_2]^{+2} \xrightarrow{k_2} [Ni(AA)]^{+2} + (AA) \qquad (2)$$

$$[Ni(AA)]^{+2} \xrightarrow{k_3} Ni^{+2} + (AA) \qquad (3)$$

We wish to obtain a quantitative value for the rate of the first reaction, but the observed change in absorbancy will be dependent also on the values of $k_2$ and $k_3$. The absorbancy, $A$, at any time is given by

$$A = a_{\text{tris}}[\text{tris}] + a_{\text{bis}}[\text{bis}] + a_{\text{mono}}[\text{mono}] + a_{\text{Ni}}[\text{Ni}] + a_{\text{HAA}}[\text{HAA}]$$

and the change of absorbancy with time by

$$\frac{dA}{dt} = a_{\text{tris}}\frac{d[\text{tris}]}{dt} + a_{\text{bis}}\frac{d[\text{bis}]}{dt} + a_{\text{mono}}\frac{d[\text{mono}]}{dt} + a_{\text{Ni}}\frac{d[\text{Ni}]}{dt} + a_{\text{HAA}}\frac{d[\text{HAA}]}{dt}$$

If we make some simplifying assumptions in regard to $k_2$ and $k_3$, the mathematics becomes relatively simple, and the observed data can be used as a test for the validity of any particular assumption.

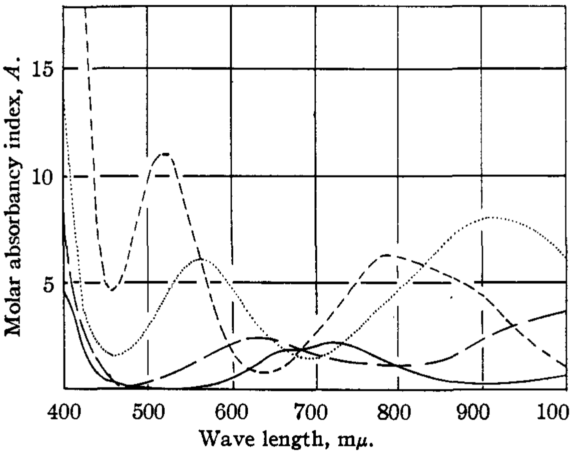

Fig. 1.—Absorption spectra of 1,10-phenanthroline complexes of Ni(II). Experimental results were obtained with a Beckman Model DU spectrophotometer at 25°, using a cell of 1 cm. length. The slit width was varied to give a spectral band width of 2.0 mμ for wave lengths in the region 400–550 mμ, and a band width of 3.5 mμ in the region 550–1000 mμ. Species and concentrations used: – – –, $[Ni(ophen)_3]^{+2}$, 0.018 *M;* ........, $[Ni(ophen)_2(H_2O)_2]^{+2}$, 0.024 *M;* — —, $[Ni(ophen)(H_2O)_4]^{+2}$, calcd.; —, $[Ni(H_2O)_6]^{+2}$, 0.086 *M*.

**Assumption I.**—Reactions 2 and 3 very slow.

$$[\text{bis}] = [\text{HAA}] = [\text{tris}]_0 - [\text{tris}]$$

where $[\text{tris}]_0$ is the initial concentration of $[Ni(AA)_3]^{+2}$.

$$A = (a_{\text{tris}} - a_{\text{bis}} - a_{\text{HAA}})[\text{tris}] + (a_{\text{bis}} + a_{\text{HAA}})[\text{tris}]_0$$

If we let

$$A_{\text{I}} = A - (a_{\text{bis}} + a_{\text{HAA}})[\text{tris}]_0$$
$$A_{\text{I}} = (a_{\text{tris}} - a_{\text{bis}} - a_{\text{HAA}})[\text{tris}]_0 e^{-k_1 t}$$
$$\ln A_{\text{I}} = \ln A_{\text{I}}^0 - k_1 t$$
$$\log_{10} A_{\text{I}} = \log_{10} A_{\text{I}}^0 - 0.4343 k_1 t$$

A plot of log $A_{\text{I}}$ *vs.* $t$ then gives a straight line of slope $(-0.4343\ k_1)$. $A_{\text{I}}$ may be considered a "corrected absorbancy" for this assumption.

**Assumption II.**—Reaction 2 very rapid, reaction 3 very slow. A similar treatment shows that the "corrected absorbancy" $A_{\text{II}}$ is given by

$$A_{\text{II}} = A - (a_{\text{mono}} + 2a_{\text{HAA}})[\text{tris}]_0$$

and its dependence on time by

$$\log_{10} A_{\text{II}} = \log_{10} A_{\text{II}}^0 - 0.4343 k_1 t$$

**Assumption III.**—Reactions 2 and 3 very rapid. For this case

$$A_{\text{III}} = A - (a_{\text{Ni}} + 3a_{\text{HAA}})[\text{tris}]_0$$
$$\log_{10} A_{\text{III}} = \log_{10} A_{\text{III}}^0 - 0.4343 k_1 t$$

For each dissociation reaction $\log_{10} A_{\mathrm{I}}$, $\log_{10} A_{\mathrm{II}}$ and $\log_{10} A_{\mathrm{III}}$ were plotted as a function of time. Each of these functions was linear during the initial portion of the reaction, curving away at later times to approach asymptotically the horizontal line that corresponds to the equilibrium absorbancy for the reaction mixture. Figure 2 shows examples of the type of data obtained. Deviations from the straight line result when the rate of the reverse reaction, *i.e.*, formation of $[\mathrm{Ni(AA)_3}]^{+2}$ is no longer negligible, and this deviation takes place earlier the lower the acidity. The value of $k_1$ is determined from the slope of the straight line portion of the curve.

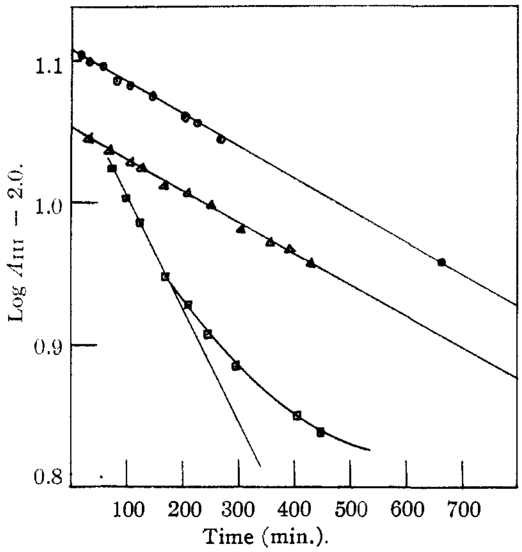

Fig. 2.—Determination of rate of dissociation of $[\mathrm{Ni(ophen)_3}]^{+2}$: ⊙, 3 *M* HCl, 25.0°; ◬, 5 *M* HCl, 25.0°; ⊡, 2 *M* HCl, 35.0°.

## Results

**Rate of Dissociation.**—In general the values of $k_1$ obtained from the three assumptions for a given experiment will be different. However, for a given reaction and assumption the values of $k_1$ obtained from data at different wave lengths should agree if the assumption is valid. This principle was utilized to test the various assumptions, and establish the correct value of $k_1$. The procedure is illustrated in Table I, where the values of $k_1$ arising from the separate assumptions are given for a particular reaction of $[\mathrm{Ni(ophen)_3}]^{+2}$. The agreement shown at the four wave lengths by values of $k_1$ derived from assumption III indicates this assumption to be most nearly correct.

TABLE I

RATE OF DISSOCIATION OF $[\mathrm{Ni(ophen)_3}]^{+2}$ DETERMINED SPECTROPHOTOMETRICALLY IN 3 *M* HYDROCHLORIC ACID

Assumption I: $k_2$, $k_3$ slow. Assumption II: $k_2$ fast, $k_3$ slow. Assumption III: $k_2$, $k_3$ fast.

| λ | $k_1 \times 10^4$ (min.$^{-1}$) I | II | III |
|---|---|---|---|
| 400 | 6.1 | 5.7 | 5.3 |
| 420 | 5.8 | 5.5 | 5.3 |
| 440 | 6.6 | 6.0 | 5.8 |
| 520 | 8.6 | 6.3 | 5.3 |

Additional support for this assumption comes from a determination of the rate of dissociation of $[\mathrm{Ni(ophen)_2}]^{+2}$, performed in an exactly analogous fashion. Measurement of this rate indicates $k_2$ to be ten times $k_1$, and also $k_3 >> k_2$.

For the case of $[\mathrm{Ni(dipy)_3}]^{+2}$ all evidence points to the same relationship between the rate constants, *i.e.*, $k_3 > k_2 > k_1$. The rapidity of these dissociations makes it impossible to study them in the detail possible with the 1,10-phenanthroline complexes. It also means that $k_2$ has a large enough value such that solutions of $\mathrm{Ni(dipy)_2Cl_2}$ react before the spectrum of $[\mathrm{Ni(dipy)_2}]^{+2}$ can be measured. This interpretation is consistent with our observations on this compound.

Considering the experimental limitations on these rate determinations it is felt that a more rigorous mathematical treatment is not necessary. For the reasons already indicated assumption III has been used in the calculation of the values of $k_1$ for all the reactions performed. The results of the dissociation measurements are summarized in Table II.

TABLE II

RATE OF DISSOCIATION OF TRIS-(1,10-PHENANTHROLINE)-NICKEL(II)

| Solution | Temp., °C. | $k_1 \times 10^4$, min.$^{-1}$ |
|---|---|---|
| 2 *M* HCl | 14.9 | 1.52 |
| 2 *M* HCl | 34.5 | 22 |
| 3 *M* HCl | 24.5 | 5.4 |
| 5 *M* HCl | 14.9 | 0.96 |
| 5 *M* HCl | 24.5 | 4.7 |
| 5 *M* HCl | 34.5 | 15.2 |

RATE OF DISSOCIATION OF TRIS-(2,2′-DIPYRIDYL)-NICKEL(II)

| Solution | Temp., °C. | $k_1 \times 10^2$, min.$^{-1}$ |
|---|---|---|
| 1 *M* HCl | 10.5 | 9.5 |
| 2 *M* HCl | 10.5 | 11.4 |
| 1 *M* HCl + 1 *M* LiCl | 1.0 | 2.5 |
| 1 *M* HCl + 1 *M* LiCl | 10.6 | 9.1 |
| 1 *M* HCl + 1 *M* LiCl | 15.7 | 18.7 |
| 5 *M* HCl | 13.0 | 24 |
| 0.5 *M* HCl | 13.0 | 9.9 |

**Rate of Racemization.**—The rates of racemization of these complexes had been studied fairly extensively prior to this work.[8,9] We have primarily studied the racemization under conditions similar to those used in the dissociation studies. These results are given in Table III. The values tabulated are in a form allowing direct comparison with the rates of dissociation, and hence are twice the values stated by some workers. The reaction is viewed as

$$d\text{-}[\mathrm{Ni(AA)_3}]^{+2} \underset{}{\overset{k}{\rightleftarrows}} \text{optically inactive products} \underset{k}{\rightleftarrows} l\text{-}[\mathrm{Ni(AA)_3}]^{+2}$$

The rate constant, $k$, is then obtained from the slope, $m$, of the log $\alpha$ *vs.* $t$ plot by the relationship $k = -2.303\ m$. Alternatively, if the reaction is considered a direct inversion

$$d\text{-}[\mathrm{Ni(AA)_3}]^{+2} \overset{k'}{\rightleftarrows} l\text{-}[\mathrm{Ni(AA)_3}]^{+2}$$

$k'$ is found from the same plot to be given by $k' = -{}^1/_2(2.303m)$. For purposes of comparison with rates of dissociation use of the first method has apparent advantages, so values tabulated are for $k = 2k'$. It should perhaps be mentioned that Schweitzer and Lee[8] report values of $k$, while Davies and Dwyer[9] list their results in terms of $k'$.

TABLE III

RATE OF RACEMIZATION OF TRIS-(1,10-PHENANTHROLINE)-NICKEL(II)

| Solution | Temp., °C. | $k \times 10^4$, min.$^{-1}$ | $k/k_0$ |
|---|---|---|---|
| $H_2O$ | 24.5 | 6.01 | 1.00 |
| 0.020 *M* NaCl + 0.0003 *M* $NiCl_2$ | 24.5 | 6.39 | 1.06 |
| .115 *M* NaCl + 0.0002 *M* $NiCl_2$ | 24.5 | 6.28 | 1.05 |
| .18 *M* LiCl | 24.0 | 5.96 | 1.06[a] |
| 1 *M* HCl | 24.0 | 5.61 | 1.00[a] |
| 2 *M* HCl | 24.5 | 5.82 | 0.97 |
| 2 *M* LiCl | 24.5 | 6.05 | 1.01 |
| 5 *M* HCl | 24.5 | 4.90 | 0.82 |
| 2 *M* HCl + 3 *M* LiCl | 24.0 | 5.27 | .94[a] |
| 5 *M* $HClO_4$ | 24.5 | 5.47 | .91 |
| $H_2O$ | 35.0 | 30.6 | |
| 2 *M* HCl | 40.2 | 45.1 | |
| $H_2O$ | 12.5 | 1.04 | |
| 2 *M* HCl | 12.5 | 0.97 | |

RATE OF RACEMIZATION OF TRIS-(2,2′-DIPYRIDYL)-NICKEL(II)

| Solution | Temp., °C. | $k \times 10^2$, min.$^{-1}$ | $k/k_0$ |
|---|---|---|---|
| 1 *M* HCl + 1 *M* LiCl | 15.4 | 16.2 | 4.2 |
| 1 *M* HCl + 1 *M* LiCl | 1.9 | 2.48 | 4.1 |
| 1 *M* HCl + 1 *M* LiCl | 9.4 | 6.98 | 4.1 |
| 0.5 *M* HCl | 13.1 | 10.3 | 3.6 |
| 5 *M* HCl | 13.3 | 22 | 7.5 |
| 2 *M* LiCl | 15.1 | 4.44 | 1.2 |

[a] Rate in water at 24.0° calculated from rate at 24.5° and activation energy of 25.0 kcal.

The column labeled $k/k_0$ gives the ratio of the rate in the particular solution to the rate in water at the same temperature.

**Conclusions.**—Comparison of the rates of racemization and dissociation under the same conditions shows them to be equal within experimental error. This is best illustrated in Fig. 3, which shows plots of $k$ (obtained from both racemization and dissociation) *vs.* $1/T$. All the data for $[Ni(ophen)_3]^{+2}$ fall on the same straight line, giving an activation energy of 25.0 kcal. The same value is obtained for the racemization in water, and the dissociation in 5 *M* HCl, and is in agreement with the value reported by Davies and Dwyer.[7]

The agreement between dissociation and racemization data for $[Ni(dipy)_3]^{+2}$, also shown in Fig. 3, is within 5%, but the fact that the racemization rate invariably is slower than the dissociation rate seems more than coincidental. This could be accounted for if the temperatures of the reaction mixtures in the dissociation runs were actually about 0.5° above the temperature of the cell holder. For the reasons indicated in the Experimental section it is easily possible that the temperature of the reaction was higher than the measured temperature, although 0.5° is about the maximum possible error. For this reason the small difference in the two rates is not felt to be significant. The activation energy is 21.8 kcal.; to be compared with 21.9 kcal. reported by Schweitzer and Lee,[8] and 24.0 kcal. reported by Davies and Dwyer.[9]

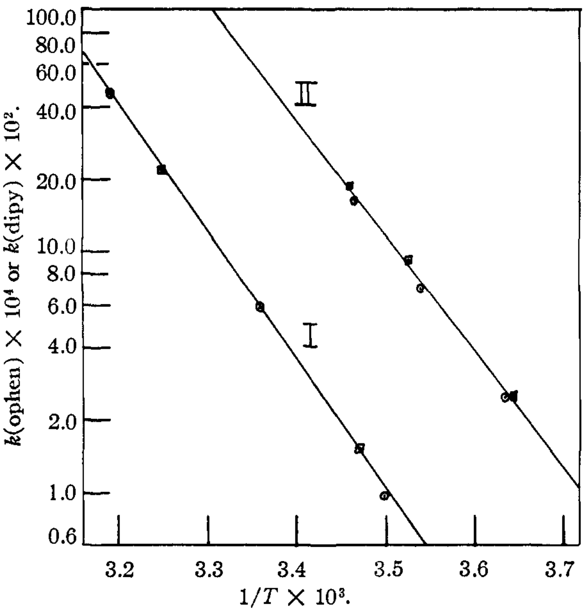

Fig. 3.—Temperature dependence for reactions of $[Ni(ophen)_3]^{+2}$ and $[Ni(dipy)_3]^{+2}$; ⊙, racemization; ⊡, dissociation; I, $[Ni(ophen)_3]^{+2}$; II, $[Ni(dipy)_3]^{+2}$.

It is quite clear then that in these acid solutions the racemization proceeds *via* dissociation. The question then arises as to whether this is still true in neutral solution where the dissociation cannot be measured. The fact that the activation energies for dissociation in acid and for racemization in water are the same would indicate there is no change in mechanism with acidity. The continuous behavior of the two rates as a function of acidity is also consistent with this interpretation. This continuity is most apparent for $[Ni(ophen)_3]^{+2}$, where $k$ for racemization shows only little variation with acid strength, the influence of hydrogen ion probably resulting only from a salt effect. The dissociation and racemization of $[Ni(dipy)_3]^{+2}$ show a pronounced acid dependence, the acid dependence of the racemization at low acidities having been demonstrated previously by Schweitzer and Lee.[8] It might be pointed out that the behavior of $[Ni(dipy)_3]^{+2}$ is similar to the dissociation behavior of $[Fe(dipy)_3]^{+2}$ reported by Baxendale and George.[15] It seems reasonable to conclude that racemization results from dissociation over the entire acid range, although it is not clear why these two similar nickel complexes should show such a difference in acid dependence.

In regard to the actual configuration of the complex ion resulting from dissociation, several hypotheses are consistent with the observations. The only limitation on such a species is that it be either optically inactive, or that it lose its activity rapidly with respect to the rate at which recombination occurs. This restriction is imposed by the observation that excess complexing agent does not affect the rate of racemization, as mentioned earlier. If the intermediate is optically active and itself racemizes by a first-order reaction we estimate the half-time for this reaction need only be less than 2 sec. to account for the failure of excess ligand to change

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[15] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950).

the rate. Such an intermediate might be $[Ni(AA)_2(H_2O)_2]^{+2}$, and it could racemize rapidly in the way suggested for $[Co(en)_2(H_2O)Cl]^{+2}$ by Mathieu.[16] It is also possible that the diaquo $[Ni(AA)_2(H_2O)_2]^{+2}$ is the *trans* isomer and therefore symmetrical. Another possible, but less likely, intermediate would be the tetracovalent and optically inactive $[Ni(AA)_2]^{+2}$.

Formation of the transition state then probably results from expansion of the ion to include two water molecules, resulting in the observed activation energies.[15] This expansion, leading to increased degrees of freedom, also leads to an entropy increase. The entropies calculated for racemization in water at 24.5° are, respectively, 2.6 e.u. for $[Ni(ophen)_3]^{+2}$ and 2.7 e.u. for $[Ni(dipy)_3]^{+2}$.

EVANSTON, ILL.

[16] J. P. Mathieu, *Bull. soc. chim.*, [5] **4**, 687 (1937).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Partial Resolution of the Tris-(oxalato)-germanate(IV) Ion

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Preparation and characterization of strychnine and quinine salts of the tris-(oxalato)-germanate(IV) ion have been effected. The covalent nature and octahedral distribution of the bonds in this ion were confirmed chemically by its partial resolution as the quinine salt. The tris-(oxalato)-germanate(IV) ion is an example of a relatively stable "outer orbital" complex involving d-electrons.

## Introduction

The orbital hybridization essential to octahedral geometry in 6-coördinate covalent inorganic complex species is most commonly of the type $(n-1)d^2nsnp^3$. Complexes based upon this kind of electron arrangement are often relatively stable with respect to the displacement of one ligand by another and, if asymmetric, are frequently resolvable into optical isomers. Because of the nature of the hybridization, Taube[1] has referred to these materials as "inner orbital" complexes. With cations of elements following the transition series, however, the $(n-1)$d-orbitals are completely occupied, and any hybridizations in the 6-coördinate complexes must of necessity be of the $ns\ np^3\ nd^2$ type. Since $n$d-orbitals are inherently more energetic than $(n-1)$d-orbitals, such "outer orbital" complexes[1] may be expected to be somewhat less covalent in character than the inner orbital species and as a result to undergo more rapid displacement reactions and to be less likely to be resolvable in asymmetric combinations. Such is indeed the case, and many of the reported resolutions of materials of this type must be questioned.[1] Taube points out, however, that as the charge of the metal ion increases, enhanced stability does result.[1]

A case in point is the tris-(oxalato)-germanate(IV) ion. This ion was obtained in solution by reaction of germanium(IV) oxide with either oxalic acid or ammonium hydrogen oxalate[2] but could not be isolated as a simple salt. In solution, it was found to be stable toward hydrogen sulfide, although germanium(IV) sulfide is very insoluble, and to be decomposed only by hot, concentrated sulfuric acid. The stability of the species toward sulfide ion has been used in the processing of germanite as a means of removing other metal ions from germanium.[3] Treatment of the species in solution with solutions of quinine oxalate and strychnine oxalate gives slightly soluble crystalline compounds which were formulated[3,4] $QH_2[Ge(C_2O_4)_3]$ and $(StH)_2[Ge(C_2O_4)_3]$, where Q = quinine, $C_{20}H_{24}O_2N_2$, and St = strychnine, $C_{21}H_{22}O_2N_2$. Infrared data for the species are comparable with those for other oxalato complexes.[5]

The apparent stability of the tris-(oxalato)-germanate(IV) ion and its ability to form salts with optically active bases suggested the feasibility of its resolution through established crystallization and precipitation techniques. This resolution has in fact been accomplished with the quinine compound, providing apparently the first recorded resolution of a 6-coördinate outer orbital complex of a tetrapositive ion. Some comparative X-ray diffraction data have been obtained also.

## Experimental

**Materials and Apparatus.**—The germanium(IV) oxide used was a chemically pure sample obtained from the Indium Corporation of America. Other chemicals were chemically pure reagents and were used without further purification.

All measurements of rotation were made at 30° with a Franz Schmidt and Haensch Polarimeter, using a 2-m. tube and sodium-D light. X-Ray diffraction patterns were taken with a Hayes X-Ray Diffraction unit using cobalt and chromium targets.

**Preparation of Alkaloid Salts.**—Quinine and strychnine salts of the tris-(oxalato)-germanate(IV) ion were prepared exactly as described previously,[3,4] using 0.35–2.00-g. samples of germanium(IV) oxide. In addition, several samples of the quinine salt (samples 1-1 through 1-4, Table I) were prepared from the parent acid solution by adding quinine in absolute ethanol rather than as oxalate. The compounds were obtained in *ca.* 85% yields, based upon the germanium used, and compared well in properties with those previously described.[3,4] The quinine compound was notably hygroscopic, but the strychnine derivative could be dried and recrystallized. In contrast to the results of Tchakirian,[3,4] analysis showed the presence of two moles of the alkaloid in the quinine derivative.

*Anal.* Calcd. for $(C_{21}H_{22}O_2N_2{\cdot}H)_2[Ge(C_2O_4)_3]$: Ge. 7.21; C, 57.22; H, 4.57; N, 5.56. Found: Ge,[6] 7.40; C, 57.19; H, 4.80; N, 5.46. Calcd. for $(C_{20}H_{24}O_2N_2{\cdot}H)_2[Ge(C_2O_4)_3]$: Ge, 7.35; C, 55.95; H, 5.08; N, 5.67. Calcd. for $(C_{20}H_{24}O_2N_2{\cdot}H_2)[Ge(C_2O_4)_3]$: Ge, 10.95; C, 47.09; H, 3.92; N, 4.22. Found: Ge, 7.06[6]; C, 57.80; H, 5.75; N, 6.24.

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[1] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[2] J. Bardet and A. Tchakirian, *Compt. rend.*, **189**, 914 (1929).

[3] A. Tchakirian, *Ann. chim.*, [11] **12**, 415 (1939).

[4] A. Tchakirian, *Compt. rend.*, **204**, 356 (1937).

[5] F. Douville, C. Duval and J. Lecomte, *ibid.*, **212**, 697 (1941).

[6] Calculated from $GeO_2$ residue.