in $NiC_4S_4H_4$ is considerably higher than the corresponding frequency near 565 cm^{-1} in $NiC_4S_4(CH_3)_4$. Since the $K(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ values 3.65, 3.40, and 2.70 mdyn/Å for H-, CH_3-, and C_6H_5-substituted nickel dithienes decrease sharply, dithiene substituents could profoundly influence the stability of the carbon–sulfur bonds. It seems that carbon–sulfur bonds are strongest for $NiC_4S_4H_4$ and decrease in strength from $NiC_4S_4(CH_3)_4$ to $NiC_4S_4(C_6H_5)_4$.

The nickel–sulfur asymmetric stretching vibration appears near 420, 435, and 465 and 449 cm^{-1} in the H, CH_3, and C_6H_5 complexes, respectively. The corresponding force constants, $K(\mathrm{Ni{-}S})$, are 1.40, 1.65, and 1.65 mdyn/Å. This order is the reverse of the trend noted for the carbon–sulfur stretching force constants in these compounds.

Vibrations of the B_{3u} Species.—In $NiC_4S_4H_4$ the asymmetric carbon–hydrogen bending mode occurs near 1288 cm^{-1} while a mixed vibration, $\delta(\mathrm{C{-}H}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$, has its normal frequency close to 874 cm^{-1}. In dimethylethylene-1,2-dithienes the vibrations in the same frequency range are $\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ at 1205 and 905 cm^{-1} and in $NiC_4S_4(C_6H_5)_4$ the corresponding modes, $\nu(\mathrm{C{-}C_6H_5}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$, near 1135 and 745 cm^{-1} are shifted to lower frequencies. In addition, $NiC_4S_4H_4$ has a normal mode near 714 cm^{-1} which is assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ + ring deformation. Nickel–sulfur asymmetric stretching vibrations occur near 420, 500, and 465 and 449 cm^{-1} in the H, CH_3, and C_6H_5 chelates, respectively. In $NiC_4S_4(CH_3)_4$ $\nu(\mathrm{Ni{-}S})$ is mixed with the asymmetric in-plane methyl bending vibration; however, a pure Ni—S stretching mode does occur near 333 cm^{-1}. The phenyl group in-plane bending vibration appears near 300 cm^{-1} in $NiC_4S_4(C_6H_5)_4$ and the 400-cm^{-1} band in $NiC_4S_4H_4$ was assigned as $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ + ring deformation.

The out-of-plane vibrations in the metal dithienes were not included in normal-coordinate calculations but can be identified by reference to the position of these vibrations[5,17] in chelates of similar structure and composition. The frequencies and assignments for out-of-plane modes are shown in Table VIII.

TABLE VIII

OUT-OF-PLANE FREQUENCIES (CM^{-1}) OF $M(C_2S_2(CH_3)_2)_2$ AND $Ni(C_2S_2H_2)_2$ AND BENZENE RING VIBRATIONS IN $Ni(C_2S_2(C_6H_5)_2)_2$

Vibration	$Ni(C_2S_2(CH_3)_2)_2$	$Pd(C_2S_2(CH_3)_2)_2$	$Pt(C_2S_2(CH_3)_2)_2$	$Ni(C_2S_2H_2)_2$
CH_3 degen def	1427	1431	1430	. . .
CH_3 sym def	1375	1389, 1375	1379	. . .
CH_3 rock	994	995	998	. . .
C–H out-of-plane bend	. . .	. . .	. . .	754
Phenyl group	1592, 1573, 1409, 1442, 1400, 1309, 1278, 1255, 1175, 1108, 1074, 1025, 998, 983, 962, 910, 900, 836, 762, 691, 650, 613, 526, 493, 350			

Acknowledgment.—The authors thank the National Research Council of Canada for its financial support of this work.

[17] K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 1272 (1961).

CONTRIBUTION NO. 1879 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401,
AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MASSACHUSETTS—BOSTON, BOSTON, MASSACHUSETTS 02116

Hindered-Ligand Systems. V. Stability Constants for Some Metal Complexes of *cis,cis*-1,3,5-Triaminocyclohexane[1]

BY R. F. CHILDERS, R. A. D. WENTWORTH,* AND L. J. ZOMPA

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The acid dissociation constants for the trihydrochloride of *cis,cis*-triaminocyclohexane (*cis,cis*-tach) have been determined in 0.1 *M* KCl at 25.0°. The equilibria which exist between the ligand and the Ni(II), Cu(II), or Zn(II) ions were investigated under identical conditions. A comparison of the formation constants of the 1:1 complexes of *cis,cis*-tach and those of other tridentate amines is presented and discussed. The spectra (electronic and esr) of the new bis complex $\mathrm{Cu}(\textit{cis,cis}\text{-tach})_2^{2+}$ are presented.

Stability constants of some metal complexes containing *cis,cis*-1,3,5-triaminocyclohexane (*cis,cis*-tach) were first reported by Brauner and Schwarzenbach.[2] Among several unusual results associated with this study was the conclusion that measurable quantities of a dicoordinated, singly protonated complex existed. It was suggested that the ligand was probably constrained to the boat conformation because of steric and electrostatic repulsion between the positively charged metal ion and the ammonium groups. Another unusual result occurred when they observed no complex formation with Ni(II).

Subsequent studies[3] have, however, shown that the method of synthesis employed by Brauner and Schwar-

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* To whom correspondence should be addressed.

[1] Part IV: W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *Inorg. Chem.*, **9**, 1825 (1970).

[2] P. A. Brauner and G. N. Schwarzenbach, *Helv. Chim. Acta*, **45**, 2030 (1962).

[3] R. A. D. Wentworth and J. J. Felten, *J. Amer. Chem. Soc.*, **90**, 621 (1968).

zenbach, *e.g.*, the Birch reduction of the trioxime of α-phloroglucinol, does not yield a pure stereoisomer but rather approximately equal proportions of the cis,cis and cis,trans isomers. Consequently, the stability constants of Brauner and Schwarzenbach must be in error because of the presence of both stereoisomers. The synthesis[4] of $Ni(cis,cis\text{-tach})_2^{2+}$ and $Ni(cis,cis\text{-tach})(H_2O)_3^{2+}$ again pointed to the inherent error in the original investigation. In addition, bis complexes of Co(II), Zn(II), and Cd(II) have since been reported.[4] Electronic[4] and infrared[5] spectra were in agreement with tridentate coordination of the ligand. No evidence for the existence of partially protonated complexes was found. In addition, a convenient synthesis of isomerically pure samples of the ligand was devised from the acid dissociation of the bis Ni(II) complex.

This paper describes a reinvestigation of the stability constants of $M(cis,cis\text{-tach})^{2+}$ (M = Ni, Cu, Zn). The synthesis and properties of $Cu(cis,cis\text{-tach})_2^{2+}$ are also described.

Experimental Section

Titrations.—The preparation of *cis,cis*-tach·3HCl·H₂O has been previously described.[4]

All solutions were prepared from distilled water which had been passed through a mixed-resin bed (H^+ and OH^-), purged with prepurified nitrogen, and stored under nitrogen in polypropylene bottles. Metal chloride solutions were standarized with EDTA using methods given by Flaschka.[6]

The titration of the pure ligand was accomplished using 100.0-ml aliquots of a solution which was approximately 10^{-3} *M* in *cis,cis*-tach·3HCl·H_2O and 0.1 *M* in KCl. These solutions were placed in EDTA-leached titration vessels which were thermostated at 25.0 ± 0.1°. Nitrogen, which had been passed through a 0.1 *M* KCl solution, was continuously bubbled through the sample solution. Standard 0.1 *M* KOH solution was added from a buret, and equilibrium was assumed when the pH reading became constant (usually 1–2 min).

Titrations of the metal–ligand systems (M = Cu, Zn) were accomplished in an analogous fashion with equimolar quantities of MCl_2 and *cis,cis*-tach·3HCl·H_2O. For each metal ion, at least two titrations were carried out at each of the following millimolar concentrations of metal ion: 0.18, 0.35, 0.70, and 1.0. With M = Cu equilibrium was not attained beyond the complete formation of $Cu(cis,cis\text{-tach})^{2+}$, even after 1 hr, and equilibrium data are not available at present. Equilibrium was not rapidly attained also during any part of the titration of the Ni–ligand system. Consequently, each titration point was obtained from a separately prepared solution to which had been added the desired quantity of KOH. The solution was then stored under nitrogen for over 100 hr at room temperature (~25°) and thermostated for 1 hr prior to the pH measurement.

A Sargent Model DR digital readout pH meter was used in conjunction with a Sargent combination electrode which contained saturated KCl as an electrolyte. The electrode response was standarized with Fischer buffer solutions at 25° over the pH range of interest.

A value of 1.63×10^{-14} for K_w at 25° in 0.1 *M* KCl was taken from Harned and Owen.[7]

Preparation and Characterization of $Cu(cis,cis\text{-tach})_2(ClO_4)_2$.[8]—The stoichiometric quantity of $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol was added to a solution of *cis,cis*-tach in ethanol, whereupon fine, deep blue crystals of the desired product separated from solution. After filtration, the product was washed with ethanol and dried in air. The compound can be recrystallized from acetone. *Anal.* Calcd for $Cu(cis,cis\text{-tach})_2(ClO_4)_2$: C, 27.7; H, 5.81; N, 16.1. Found: C, 27.7; H, 5.82; N, 16.0. The infrared and electronic spectra of the compound were recorded on a Perkin-Elmer Model 621 spectrometer and a Cary Model 14 spectrophotometer. The esr spectrum was obtained using a Varian E-4 spectrometer from a polycrystalline sample of $(Cu,Zn)(cis,cis\text{-tach})_2(ClO_4)_2$.

Calculations

Preliminary values for the acid dissociation constants of the ligand

$$K_{aj} = \frac{[LH_{j-1}][H]}{[LH_j]} \qquad (j = 3, 2, 1)$$

were obtained by assuming that only LH_3 and LH_2 existed with $0 < a < 0.75$ (where a is the moles of OH added per total moles of L, L is *cis,cis*-tach, and all charges have been omitted for simplicity), while LH_2 and LH coexist in the region $1.25 < a < 1.75$, and only LH and L occur in the region $2.25 < a < 3.00$. If these assumptions are correct, the general equation

$$(j - \bar{n}_H)[H^+] = K_{aj}(\bar{n}_H - j + 1)$$

can be used to obtain the three required dissociation constants. The parameter, a, can be related to $\bar{n}_H$, the average degree of protonation, according to

$$\bar{n}_H = 3 - a - ([H]/L_T - [OH]/L_T)$$

where L_T is the total ligand concentration. The results, obtained from appropriate graphs, were $pK_{a3} = 7.17$, $pK_{a2} = 8.67$, and $pK_{a1} = 10.17$. When compared to the final values in Table I, which were obtained by computer fitting, the agreement is seen to be very good.

TABLE I

ACID DISSOCIATION CONSTANTS OF *cis,cis*-tach AND STABILITY CONSTANTS OF ITS METAL COMPLEXES IN 0.1 *M* KCl AT 25.0°

Reaction	Constant
$LH_3^{3+} \rightleftharpoons LH_2^{2+} + H^+$	$pK_{a3} = 7.17 \pm 0.01$
$LH_2^{2+} \rightleftharpoons LH^+ + H^+$	$pK_{a2} = 8.66 \pm 0.01$
$LH^+ \rightleftharpoons L + H^+$	$pK_{a1} = 10.16 \pm 0.01$
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	$\log K_{NiL} = 9.88$
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	$\log K_{CuL} = 10.55 \pm 0.03$
$CuL^{2+} + OH^- \rightleftharpoons CuLOH^+$	$\log K_{CuLOH} = 6.08 \pm 0.07$
$Zn^{2+} + L \rightleftharpoons ZnL^{2+}$	$\log K_{ZnL} = 6.90 \pm 0.05$
$ZnL^{2+} + OH^- \rightleftharpoons ZnLOH^+$	$\log K_{ZnLOH} = 5.85 \pm 0.02$

Subsequent calculations of all stability constants were performed using a computerized curve-fitting procedure similar to Sillén's "pit mapping" method.[9] The constants were varied, one at a time, in such a way that the function σ_a which is defined as

$$\sigma_a = \frac{\left[\sum_{i=1}^{n} (a_i - a_i')^2\right]^{1/2}}{n - 1}$$

is minimized. In this expression n is the number of

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[4] R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1030 (1968).

[5] F. L. Urbach, J. E. Sarneski, L. J. Turner, and D. H. Busch, *ibid.*, **7**, 2169 (1968).

[6] H. A. Flaschka, "EDTA Titrations," 2nd ed, Pergamon Press, Oxford, 1964.

[7] H. W. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, p 634.

[8] J. J. Felten, M.S. Thesis, Indiana University, 1968.

[9] L. G. Sillén, *Acta Chem. Scand.*, **18**, 1085 (1964), and references contained therein.

data points and a_i and a_i' are the experimental and calculated values of a at any point.

The calculated value of a at a given [H] was obtained from the three mass balance equations

$$L_T = [L] + \Sigma r\beta_{pqr}[H]^p[M]^q[L]^r \quad (1)$$

$$M_T = [M] + \Sigma q\beta_{pqr}[H]^p[M]^q[L]^r \quad (2)$$

$$H_T = [H] + \Sigma p\beta_{pqr}[H]^p[M]^q[L]^r \quad (3)$$

where $[H_pM_qL_r] = \beta_{pqr}[H]^p[M]^q[L]^r$,[10] and the additional equation

$$a_i' = \frac{3L_T - H_T'}{L_T} \quad (4)$$

It should be noted that L_T and M_T are the analytically determined total ligand and metal concentration while H_T' is calculated from the mass balance equations at a given [H]. In practice [L] and [M] are obtained from eq 1 and 2 using the given [H] and the assumed values of the constants. Then H_T' is obtained from eq 3, followed by the calculation of a_i' from eq 4.

Equation 2 is, of course, not required for the titration of the pure ligand, while the terms in eq 1 and 3 are limited to those containing [L] and [H]. The acid dissociation constants which were determined are given in Table I and are in excellent agreement with those determined by the graphical method described above.

The scatter in the titration data of the Ni(II)–ligand system invalidated a search for any stability constants other than that for Ni(*cis,cis*-tach)$^{2+}$. Nevertheless, the experimental and calculated results agree reasonably well.

A titration curve of the Cu(II)–ligand system shows inflections at $a = 3$ and $a = 4$, indicative of the formation of Cu(*cis,cis*-tach)$^{2+}$ and Cu(*cis,cis*-tach)(OH)$^+$. However, we belatedly learned that equilibrium is not reached beyond $a = 3$ until several hours has passed. Consequently, the data are restricted to $0 < a < 3$. Within this region the best fit to the data was sought assuming the presence of Cu(*cis,cis*-tachH)$^{3+}$, Cu(*cis,cis*-tach)$^{2+}$, and Cu(*cis,cis*-tach)(OH)$^+$. Stability constants for the first species were sought between 10^0 and 10^{15}, but an increase in σ_a occurred as the constant was increased. Measurable quantities of the protonated species are then not present. Although the data could be plausibly calculated assuming that only Cu(*cis,cis*-tach)$^{2+}$ was present, a much better fit occurred assuming that the hydroxo species was present in small quantities in this region of the titration curve.

The only inflection in the titration curve of the Zn(II)–ligand system occurs at $a = 4$. All reactions appeared to occur rapidly. Stability constants for Zn(*cis,cis*-tachH)$^{3+}$, Zn(*cis,cis*-tach)$^{2+}$, Zn(*cis,cis*-tach)(OH)$^+$, Zn(*cis,cis*-tach)(OH)$_2$, and [Zn(*cis,cis*-tach)(OH)]$_2^{2+}$ were sought, varying each constant between 10^0 and 10^{15}. A minimum value for σ_a occurred only if the first, fourth, and fifth species were neglected.

A comparison of the experimental and calculated results are given in Figure 1. Table I contains the final results for the pure ligand system as well as the three metal ion–ligand systems.

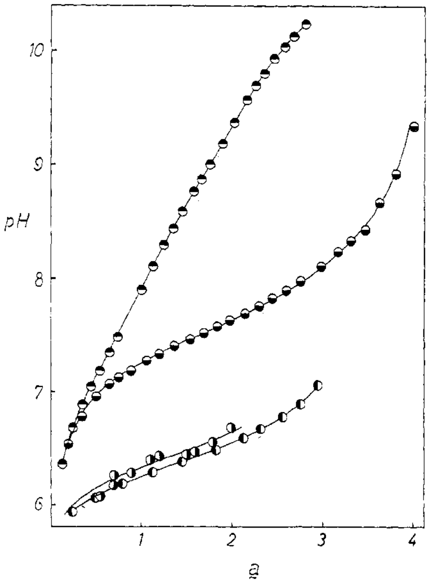
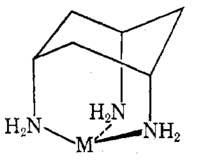


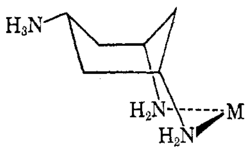
Figure 1.—Titration curves for (◓) *cis,cis*-tach·3HCl·H$_2$O = LH$_3$, (◒) [Zn(II)]:[LH$_3$] = 1:1, (◑) [Ni(II)]:[LH$_3$] = 1:1, and (◐) [Cu(II)]:[LH$_3$] = 1:1. In each case the titration was conducted with 0.1 *M* KOH at 25° in 0.1 *M* KCl with [LH$_3$] = 10^{-3} *M*. The solid lines are the calculated titration curves.

Discussion of Results

It is apparent from the excellent agreement in the calculated and experimental values of a that protonated metal–ligand species are not present in measurable concentrations. Therefore, it can be concluded that *cis,cis*-tach, even in the early stages of titration, is complexed in the chair form (I) and not in the boat form, since a protonated species of the type shown below (II) would probably have been detected. In addition, the previous failure to observe[2] a reaction between the ligand and Ni(II) is clearly a consequence of the slow rate of formation of Ni(*cis,cis*-tach)$^{2+}$.



I



II

The stability of complexes formed by the rigid ligand *cis,cis*-tach, when compared to complexes formed by the more flexible tridentate amine 2-aminomethyl-1,3-diaminopropane (adap),[11] gives an insight into the many factors involved in the formation of *cis,cis*-tach–metal complexes. Both *cis,cis*-tach and adap are restricted to facial coordination when all the nitrogens are attached to an octahedral metal ion.

The pK_a's listed in Table II indicate that adap·3H$^+$

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[10] A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, **5**, 1384 (1966). The overall formation constants, β_{pqr}, were converted to the stepwise constants given in Table I.

[11] G. Anderegg, *Helv. Chim. Acta*, **45**, 1303 (1962).

TABLE II

A COMPARISON OF CONSTANTS[a] FROM VARIOUS METAL–TRIDENTATE LIGAND SYSTEMS

	cis,cis-tach	adap	dien	dpt
$\mathrm{p}K_{a3}$	7.17	6.28	4.25	7.72
$\mathrm{p}K_{a2}$	8.66	8.41	8.98	9.57
$\mathrm{p}K_{a1}$	10.16	10.23	9.70	10.65
$\log K_{\mathrm{NiL}}$	9.88	9.9	10.7	9.19
$\log K_{\mathrm{CuL}}$	10.55	10.9	16.0	14.2
$\log K_{\mathrm{CuLOH}}$	6.08	...	4.5	4.14
$\log K_{\mathrm{ZnL}}$	6.90	...	8.9	7.92
$\log K_{\mathrm{ZnLOH}}$	5.85	...	...	5.23

[a] Each constant is defined in Table I.

is slightly more acidic than *cis,cis*-tach·3H$^+$. This may be explained by the efficiency of charge separation in the latter since both the ligand and protonated form of the ligand are expected to exist in the equatorial conformation thereby restricting the amine groups to a plane in which there is maximum separation. On the other hand, the geometry of adap is not so restrictive and some charge interaction, due to the closer proximity of the protonated amines, does occur making it easier to remove the first and second protons. The above argument (*cis,cis*-tach then is a slightly better base than adap) would favor more stable *cis,cis*-tach complexes.

Another argument can be made in favor of a greater stability for *cis,cis*-tach complexes. The initial and final states in the *cis,cis*-tach system are ordered, whereas adap is randomly oriented and is ordered only after complexes are formed. Therefore, there is a small entropy effect in favor of *cis,cis*-tach complexes.

Since adap complexes appear to be slightly more stable than *cis,cis*-tach complexes (see Table II), it is apparent that one or more effects not yet considered are operating. Since *cis,cis*-tach would exist in the equatorial conformation before complex formation and in the axial conformation after complexation, the enthalpy increase associated with this conversion would tend to destabilize the complex. This enthalpy change was previously estimated[3] to be about 11 kcal/mol based on the assumption that the amine group, with its lone pair of electrons, is sterically similar to a methyl group. Whatever its exact magnitude, this enthalpy increase must be considerably greater than that required to position the randomly oriented $-CH_2-NH_2$ groups in adap for bonding to a metal ion. Thus, the enthalpy associated with the equatorial-to-axial conformational change must be sufficient to outweigh the basicity and entropy factors which were considered above.

An interesting point arises when the interactions of zinc(II) with *cis,cis*-tach and adap are considered. Anderegg[11] has found that hydrolysis occurs in the zinc(II)–adap case before all three nitrogens become bonded to the zinc and therefore a formation constant for Zn(II) adap^{2+} could not be calculated. Although hydrolysis also occurs in the zinc(II)–*cis,cis*-tach system, it apparently takes place with the completely formed complex species ($ZnL^{2+} + OH^- \rightarrow ZnLOH^+$). Therefore our equilibrium studies satisfactorily produced a stability constant for Zn(II)-*cis,cis*-tach.

Stability constants for the tridentate ligands *cis,cis*-tach and adap, which are restricted to facial coordination, are compared in Table II to those obtained from the ligands diethylenetriamine[12] (dien) and 3,3′-diaminodipropylamine (dpt),[10] both of which can bond facially or around the equator. Recent X-ray structural studies of some complexes of dien have shown the ligand to be facially coordinated[13] in Mo(dien)O_3 and Mo(dien)$(CO)_3$ and equatorially coordinated[14] in Cu(dien)$_2Br_2 \cdot H_2O$ and Cu(dien)(ox) (where ox is the oxalate ion). Structural data for dpt complexes are not available but the larger size of the ligand should promote a greater tendency for equatorial coordination than in dien complexes. Two salient features can be obtained from Table II. First, stability constants for an ML species are larger when the ligand is dien or dpt, presumably because the ligand is equatorially coordinated with an attendant decrease in steric hindrance which would otherwise occur in facial coordination. Second, MLOH complexes are most stable when the ligand is facially coordinated. Proton abstraction ($M-OH_2^{n+} + OH^- \rightarrow M-OH^{(n-1)+} + H_2O$) is presumably more hindered in the equatorially coordinated complexes because of the two adjacent amine groups which occupy the same plane.

Cu(*cis,cis*-tach)$^{2+}$.—While the studies described above have not been directed toward equilibria involving the bis complexes M(*cis,cis*-tach)$^{2+}{}_2$, it is clear from synthetic studies[4] that these species do exist in solution with M = Co, Ni, Zn, or Cd. However, it has not been possible to isolate the corresponding Cu(II) complex from aqueous solution and we infer that appreciable quantities of this ion are not present when stoichiometric amounts of the ligand and the metal ion are mixed.

However, Cu(*cis,cis*-tach)$_2$(ClO$_4$)$_2$ can be obtained from alcohol solutions and recrystallized from acetone. The electronic spectrum obtained from an acetone solution has bands at 8790 (ϵ 6) and 15,750 cm^{-1} (ϵ 34). These may be compared to the spectrum of the solid phase which has bands at identical wave numbers with relative intensities comparable to those observed in solution. The esr spectrum of powdered samples of (Cu,Zn)(*cis,cis*-tach)$_2$(ClO$_4$)$_2$ at 80°K shows signals corresponding to $g_{\parallel} = 2.25$ and $g_{\perp} = 2.05$ with $A_{\parallel} = 1.76 \times 10^{-4}$ cm^{-1} and $A_{\perp} < 15 \times 10^{-4}$ cm^{-1}. These data are very similar to those found[15,16] for the Cu(bipy)$_3^{2+}$ ion wherein a dynamic tetragonal distortion has been postulated. However, it should be noted that in the electronic spectrum of that ion the intensities of the two bands are more nearly comparable, *i.e.*, $\epsilon(14{,}900\ \mathrm{cm}^{-1})/\epsilon(7700\ \mathrm{cm}^{-1}) = 2.2$ in

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[12] G. Schwarzenbach and J. E. Prue, *Helv. Chim. Acta*, **33**, 985 (1950); M. Ciampolini and P. Paoletti, *J. Phys. Chem.*, **65**, 1224 (1961).

[13] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964); F. A. Cotton and R. M. Wing, *ibid.*, **4**, 314 (1965).

[14] F. S. Stephens, *J. Chem. Soc.*, 2233, 2493 (1969).

[15] H. C. Allen, G. F. Kokoszka, and R. G. Inskeep, *J. Amer. Chem. Soc.*, **86**, 1023 (1964).

[16] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

CH_3NO_2. A similar ratio of intensities is also found[17] in the reflectance spectra of $Cu(en)_3SO_4$ and the polarized single-crystal spectrum of $Cu(dien)_2Br_2 \cdot H_2O$.

[17] B. J. Hathaway, M. J. Bew, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc.*, 2312 (1969).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

The Rate of Aquation of 1,2,3-Tricyanotriaquochromium(III) in Acidic Aqueous Solution[1,2]

BY D. K. WAKEFIELD AND WARD B. SCHAAP*

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The kinetics of aquation of the 1,2,3-tricyanotriaquochromium(III) complex was studied in aqueous perchloric acid–sodium perchlorate solutions at an ionic strength of 2.0. The aquation was found to be acid assisted and to be well described by the rate law

$$\frac{-\mathrm{d}C_{\mathrm{tri}}}{\mathrm{d}t} = \frac{(k_1K_1[\mathrm{H}^+] + k_2K_1K_2[\mathrm{H}^+]^2)C_{\mathrm{tri}}}{1 + K_1[\mathrm{H}^+]}$$

where C_{tri} is the stoichiometric concentration of the complex, K_1 and K_2 are successive protonation constants, and k_1 and k_2 are first-order rate constants for the singly and doubly protonated species. K_1 was evaluated from direct spectrophotometric measurements as well as from the kinetic data. At 15 and 25°, respectively, $K_1 = 0.9 \pm 0.4$ and 1.1 ± 0.4 l. mol^{-1}, $k_1 = 2.2\ (\pm 1.0) \times 10^{-4}$ and $5.8\ (\pm 2.3) \times 10^{-4}$ sec^{-1}, $k_1K_1 = 2.00\ (\pm 0.12) \times 10^{-4}$ and $6.63\ (\pm 0.15) \times 10^{-4}$ sec^{-1} l. mol^{-1}, and $k_2K_2 = 1.5\ (\pm 0.1) \times 10^{-4}$ and $5.6\ (\pm 0.4) \times 10^{-4}$ sec^{-1} l. mol^{-1}. Calculated values of the pseudo-first-order rate constants obtained with these parameters agree with the experimentally observed rate constants with an overall average deviation of 1.5%. Activation parameters calculated for the aquation of the singly protonated species are $\Delta H^{\ddagger} = 16 \pm 6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19 \pm 9$ eu. The values obtained for the kinetic and activation parameters of the tricyanotriaquo complex are compared with those obtained previously for the cyanopentaaquochromium(III) ion and with recalculated values for the *cis*-dicyanotetraaquochromium(III) ion.

Introduction

Previous work in this laboratory[3-7] has established that in acidic aqueous solutions the hexacyanochromate(III) ion aquates *via* a series of stepwise, stereospecific reactions to give hexaaquochromium(III) cation as the final product. All of the intermediates in this reaction sequence have been isolated.[7]

The complete aquation of the most inert of the intermediate cyanoaquo complexes, the uncharged 1,2,3-tricyanotriaquochromium(III) complex, involves the reactions

$$\text{1,2,3-}\mathrm{Cr(H_2O)_3(CN)_3} + \mathrm{H_3O^+} \longrightarrow cis\text{-}\mathrm{Cr(H_2O)_4(CN)_2^+} + \mathrm{HCN} \quad (1)$$

$$cis\text{-}\mathrm{Cr(H_2O)_4(CN)_2^+} + \mathrm{H_3O^+} \longrightarrow \mathrm{Cr(H_2O)_5CN^{2+}} + \mathrm{HCN} \quad (2)$$

$$\mathrm{Cr(H_2O)_5CN^{2+}} + \mathrm{H_3O^+} \longrightarrow \mathrm{Cr(H_2O)_6^{3+}} + \mathrm{HCN} \quad (3)$$

The results of detailed studies of the kinetics of reactions 2 and 3 are discussed elsewhere.[5,6,8] In this paper, the results of a study of the rate of reaction 1 as a function of acidity and temperature at a constant ionic strength are presented and are compared with the results obtained from studies of reactions 2 and 3.

An interesting feature of the overall acid-assisted aquation sequence of the hexacyanochromate(III) ion is that apparently only one isomer of each of the intermediate cyanoaquochromium(III) complexes is formed at each step. On the basis of the relative aquation rates of the anionic complexes, in comparison with those of the uncharged and cationic species, and a consideration of the spectra,[3,7,9] it is concluded that it is the cis isomers which are formed.

The stereospecific nature of the aquation simplifies the kinetic studies and allows a more straightforward interpretation of aquation rates. In the studies involving the thiocyanatoaquochromium(III) complexes,[10-12] the amineaquochromium(III) complexes,[13] and the chloroaquochromium(III) com-

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* To whom correspondence should be addressed.

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