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Kinetics of the Tetramerization of the Diaquotetraamminecobalt(III) Ion

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The tetramerization of the monomeric diaquotetraamminecobalt(III) ion has been studied by the pH-Stat method at 20.7° and at different concentrations of the perchlorate counterion (0.30, 1.00, and 2.00 *M*). The reaction has been found to be first order in the monomer. From the pH dependence of the observed pseudo-first-order rate constants, a mechanism is proposed in which the rate-determining step is a dissociative reaction of the *trans*-$Co(NH_3)_4(OH)_2^+$ ion.

Introduction

It has long been known[1] that on the addition of base aqueous solutions of the tetraammine ion $[Co(NH_3)_4(H_2O)_2]^{3+}$ yield a tetrameric product. The condensation reaction may be formulated

$$4Co(NH_3)_4(H_2O)_2^{3+} + 6OH^- \longrightarrow [Co\{(OH)_2Co(NH_3)_4\}_3]^{6+} + 4NH_3 + 8H_2O \quad (1)$$

A hydroxo-bridged dimeric ion, $[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4+}$, has also been prepared.[1] Recently the kinetics of decomposition of both the dimer and the tetramer have been studied.[2] The tetramerization reaction (1) is accompanied by the loss of ammonia,[3] and it is for this reason that the present investigation into the kinetics of this reaction has been undertaken as part of a program of research into the kinetics of formation and breaking of the Co^{III}–NH_3 bond.

Experimental Section

Chemicals.—*cis*-Diaquotetraamminecobalt(III) perchlorate was prepared according to Linhard.[4] The salt was recrystallized from a slightly acidified aqueous solution. pH measurements proved the compound to be acid free. *Anal.* Calcd for $Co(NH_3)_4(H_2O)_2(ClO_4)_3$: Co, 12.8; NH_3, 14.7. Found: Co, 12.8; NH_3, 14.4.

Di-μ-hydroxo-octaamminedicobalt(III) perchlorate and tris-[di-μ-hydroxo-tetraamminecobalt(III)]cobalt(III) perchlorate were prepared as outlined by Hoffman and Taube.[2] The other chemicals used were of reagent grade.

Kinetic Procedure.—The experiments were performed in a glove box filled with nitrogen gas in order to prevent the alkaline solutions from reacting with carbon dioxide. All the solutions used were made up from CO_2-free water. The condensation reactions were followed at a pH fixed by a pH-Stat constructed in our laboratory. The pH-Stat used an Electrofact 36200 pH meter equipped with a 7G 111 glass electrode and a R 111 calomel reference electrode, the latter being connected to the solution by a sodium nitrate bridge. The pH accuracy is ±0.03 and the pH is referred to the NBS standard buffers (phosphate (pH ~7) and borax (pH ~9)). The pH-Stat was made to compensate for the rise in pH due to the alkaline medium analog of reaction 1 by adding a perchloric acid solution. For each run 25 ml of an aqueous solution of *cis*-diaquotetraamminecobalt(III) perchlorate and sodium perchlorate was measured into a closed stainless steel cell (20.7 ± 0.1°) equipped with a stirrer and inlets for the pH-Stat components. The solution was then brought to a pH value a little higher than the preset pH on the pH-Stat by adding a concentrated sodium hydroxide solution in a slight overdose. The volume of the acid added by the pH-Stat was monitored on a recorder as a function of time. The initial concentration of the monomeric cobalt(III) complex was varied between 0.05 and 0.20 *M*, and the corresponding concentrations of the perchloric acid titration solutions were between 0.3 and 1.0 *M*. During the reaction the concentration of the perchlorate ion was kept constant by adding sodium perchlorate to the various solutions. This procedure was chosen for chemical reasons[5] and because in the system studied it is impossible to keep the ionic strength constant.[2] To avoid confusion this "ionic strength" will be given the symbol $I(ClO_4)$. The main experiments were done at $I(ClO_4) = 1.00$. For a comparison a limited number of experiments were done at $I(ClO_4) = 0.30$ and 2.00. Absorption spectra were recorded on a Perkin-Elmer 124 spectrophotometer using 2-mm quartz cells.

Results

Analysis of the pH-Stat Curves.—In the following a_0 (with volume x_0), a_t (x_t), and a_∞ (x_∞) will denote the amount of acid consumed at time zero, t (in min), and infinity, respectively. It should be noted that a_0 differs from zero because of the procedure followed. At any fixed pH a plot of ln ($a_\infty - a_t$) *vs.* time yields a straight line for the first 80% of the reaction. A representative plot is given in Figure 1. After about 80% reaction at the higher pH values a slowing down of the reaction rate due to the ammonia liberated (see eq 1) becomes visible. As the addition of an excess of ammonia was found to stop the reaction completely,[6] this slowing down must be due to the ammonia liberated in the reaction (see eq 1). The a_t values corresponding to 15–75% reaction were therefore analyzed with the help of a computer program (LSG from Detar[7]) using the formula

$$\ln ((a_\infty - a_t)/(a_\infty - a_0)) = -kt$$

in an iterative fit for the parameters a_0, a_∞, and k. The value of a_0 thus obtained was used to calculate the exact quantity of base needed to attain the desired pH (this quantity will be called b_0). The results are in Table I. Figure 2 shows k for $I(ClO_4) = 1.0$ as a function of the pH. The entries b_0 and $b_\infty = (b_0 - a_\infty)$ are referred to in Table I as fractions of the total amount of cobalt present, $c_0 = [Co]$. As expected from the previous results in this section, the total cobalt concentration did not influence the observed rate constant, as shown below ($t = 20.7°$; $I(ClO_4) = 2.00$; pH 8.50).

[Co], *M*	$10^{-1}k$, min^{-1}
0.05	1.56 ± 0.10
0.10	1.37 ± 0.06
0.20	1.47 ± 0.03

For this reason the experiments have been performed at one cobalt concentration of 0.10 *M*.

Acid Dissociation Constants.—The entries in the

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[1] A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, **13**, 1 (1970).

[2] A. B. Hoffman and H. Taube, *Inorg. Chem.*, **7**, 903 (1968).

[3] G. Schwarzenbach, J. Boesch, and H. Egli, *J. Inorg. Nucl. Chem.*, **33**, 2141 (1971).

[4] M. Linhard and M. Wiegel, *Z. Anorg. Allg. Chem.*, **260**, 65 (1949).

[5] B. Perlmutter-Hayman, *Progr. React. Kinet.*, **6**, 239 (1971).

[6] S. Balt, *Recl. Trav. Chim.* **91**, 1026 (1972).

[7] D. F. Detar, Ed., "Computer Programs for Chemistry," W. A. Benjamin, New York, N. Y., 1968, p 117.

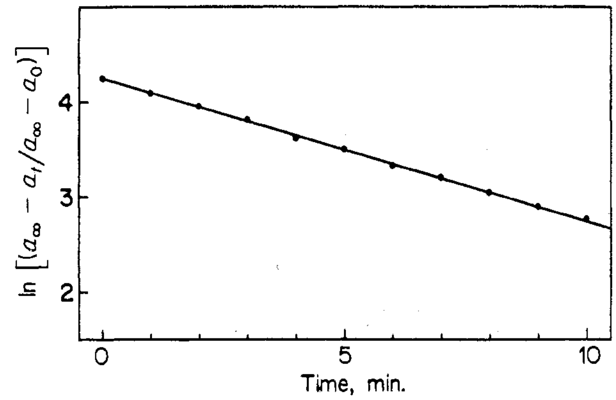

Figure 1.—Representative first-order plot for the acid consumed (a_t) in the tetramerization reaction of the $Co(NH_3)_4(OH_2)_2^{3+}$ ion: [Co] = 0.10 *M*; pH 9.10; $T = 20.7 \pm 0.1°$; $I(ClO_4) = 1.00$.

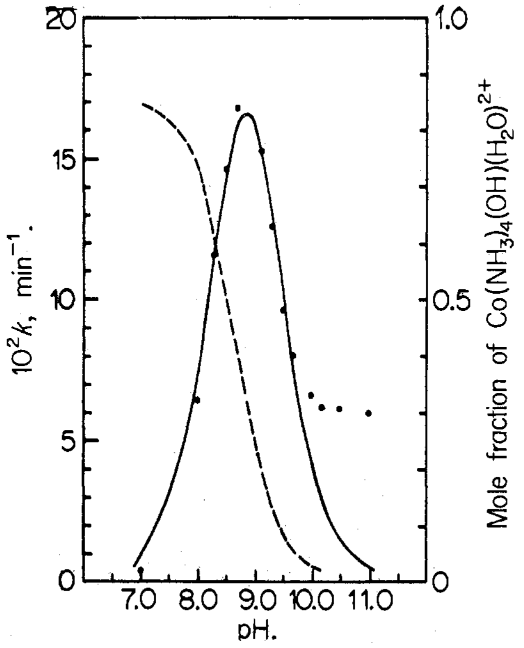

Figure 2.—pH dependence of the observed and calculated pseudo-first-order rate constants for the tetramerization of the $Co(NH_3)_4(H_2O)_2^{3+}$ ion, compared to the measured extent of acid dissociation of the cation: $T = 20.7 \pm 0.1°$, $I(ClO_4) = 1.00$; ●, observed rate constant; ——, calculated rate constant; ----, distribution curve for $Co(NH_3)_4(OH)(H_2O)^{2+}$ plotted as mole fraction from the total amount of cobalt present.

TABLE I

RESULTS OF THE pH-STAT EXPERIMENTS AS A FUNCTION OF pH[a]

pH	$k \times 10$, min^{-1} Obsd[b]	$k \times 10$, min^{-1} Calcd	b_0/c_0 Obsd[c]	b_∞/c_0 Obsd[c]	b_∞/c_0 Calcd[d]
	A. $I(ClO_4) = 1.00$				
7.00	0.04	0.10			
8.00	0.65	0.74	1.20	0.52	0.54
8.30	1.16	1.15	1.40	0.49	0.57
8.50	1.46	1.42	1.46	0.54	0.61
8.70	1.68	1.61	1.61	0.62	0.67
9.10	1.53	1.56	1.81	0.80	0.83
9.30	1.26	1.33	1.82	0.83	0.94
9.50	0.96	1.05	1.94	0.88	1.06
9.70	0.80	0.77	1.94	1.09	1.17
10.00	0.66		1.98	1.22	1.30
10.20	0.61		2.03	1.53	1.36
10.50	0.61		2.03	1.53	1.43
11.00	0.60		2.11	1.53	1.48
	B. $I(ClO_4) = 0.30$				
8.00	1.10	1.18	1.40	0.56	0.54
8.50	2.06	1.95	1.72	0.61	0.61
9.00	2.00	2.03	1.84	0.72	0.79
9.30	1.58	1.66	1.87	0.93	0.94
10.00	0.72	0.59	1.95	1.27	1.30
10.50	0.75		2.01	1.56	1.43
	C. $I(ClO_4) = 2.00$				
8.00	0.44	0.77	1.26	0.55	0.54
8.50	1.37	1.32	1.65	0.62	0.61
9.00	1.58	1.46	1.87	0.72	0.79
9.50	0.95	1.01	1.91	0.95	0.94
10.00	0.61	0.47	1.91	1.31	1.30
10.50	0.59		1.97	1.52	1.43

[a] Temperature 20.7 ± 0.1°, [Co] = 0.10 *M*. [b] The accuracy in the observed *k* is better than 4%. [c] See text. [d] Using ref 8.

fourth column of Table I have been used to calculate the equilibrium constant[3] K_2 of the reaction

$$Co(NH_3)_4(OH)(H_2O)^{2+} \rightleftarrows Co(NH_3)_4(OH)_2^{+} + H^{+} \quad K_2$$

with

$$pK_2 = p\left(\frac{[Co(NH_3)_4(OH)_2^{+}][H^{+}]}{[Co(NH_3)_4(OH)(H_2O)^{2+}]}\right) = p\left(\frac{(b_0/[Co]) - 1}{2 - (b_0/[Co])}\right) + pH \quad (2)$$

(for $(b_0/[Co]) > 1$). The symbol K_2 fits in with the generally used notation for acid dissociation constants.[8] Only $[H^+]$ as obtained from pH measurements represents an activity. The other values in brackets [ ] are concentrations, so that K_2 defined as above for convenience is a mixed constant. As the starting product is in the cis configuration, for the moment we assume that (2) refers to cis complexes only, but we shall come back to this point later. The simple formula (2) could be used because at the pH values in Table I the presence of $Co(NH_3)_4(H_2O)_2^{3+}$ can be neglected.[3] pK_2 has been obtained from a plot of

$$p\left(\frac{2 - (b_0/[Co])}{(b_0/[Co]) - 1}\right) \text{ vs. pH, giving at } 20.7°$$

$I(ClO_4)$	pK_2
0.30	8.2 ± 0.2
1.00	8.5 ± 0.1
2.00	8.3 ± 0.2

The distribution curve for the two complex ions at $I(ClO_4) = 1.00$ is plotted in Figure 2.

End Product of the Reaction.—The spectra of the solutions after seven or more half-lives of the reaction are identical with the spectrum of the tetramer.[2] During this time the reaction product exists in a supersaturated solution from which it eventually precipitates. Only at pH values over 10 is some precipitate of cobalt hydroxide formed. The occurrence of this side reaction is also evident from Table I, where the actual amount of base used to convert the diaquo complex into the end product (b_∞) is compared with the amount calculated on the assumption that eq 1 holds and with the help of the published[8] acidity constants of ammonia (at zero ionic strength) at the same temperature. No exact agreement between the observed and the calculated constants can be expected, but it is seen that the observed values follow the trend of the calculated ones up to pH 10.0. At higher pH values the observed

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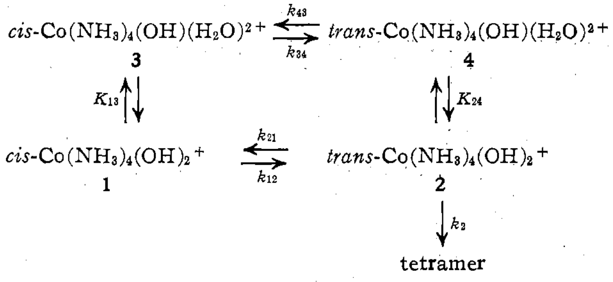
(8) R. G. Bates and G. D. Pinching, *J. Amer. Chem. Soc.*, **72**, 1393 (1950).

ratio is higher than expected, indicating the formation of cobalt hydroxide.

The Dimeric Compound.—Solutions of the dimer $[(NH_3)_4Co(OH)_2Co(NH_3)_4](ClO_4)_4$, brought to pH 8–11, the experimental pH region, decompose instantaneously to give cobalt hydroxide. The same happens when the monomeric compound is added to the dimer solution. This compound consequently cannot be an intermediate in the tetramerization studied.

Discussion

The mechanism of the tetramerization reaction is not obvious. Especially striking features are that at any fixed pH the reaction is found to follow a first-order law and that a plot of the observed pseudo-first-order rate constant *vs.* pH shows a pronounced maximum at pH ~9. The maximum in the rate constant occurs at a pH where no single cis complex has its maximum concentration (Figure 2), so that the singular behavior noted cannot be understood by an extraordinary reactivity of a single cis ion. A consideration of the diverse species of the monomer that may be expected in the solutions used suggest the following mechanism



The ions have been numbered to make the indexing of k obvious. As the acid–base reactions may be expected to be rapid compared to the cis–trans isomerizations,[3,9,10] we may assume a continuous state of equilibrium to subsist between **1** and **3** and also between **2** and **4**. These equilibria are governed by the constants

$$K_{13(24)} = \frac{[cis(trans)\text{-}Co(NH_3)_4(OH)_2^+]}{[cis(trans)\text{-}Co(NH_3)_4(OH)(H_2O)^{2+}][OH^-]}$$

$K_{13(24)}$ is defined as a deprotonation constant for clarity as the polymerization involves the reaction with the hydroxyl ion. The rate-determining step can be thought of as a dissociative reaction of the *trans*-dihydroxo compound **2** to create an as yet undefined intermediate that rapidly reacts with three molecules of the monomer to form the tetramer. A general solution of the kinetic equations involved will express each concentration of the various tetraammine ions as a sum of two exponential functions.[11] The fact that in the case considered one exponential suffices means that a simplification of the scheme worked out above is possible. An obvious way to bring in such a simplification is to apply a steady-state treatment to the total concentration of the supposedly more reactive and thermodynamically less stable trans compounds (compare 6 and 10). Then eq 3 results.

$$k = \frac{4k_2k_{34}K_{24}[OH^-] + 4k_2k_{12}K_{13}K_{24}[OH^-]^2}{\{1 + K_{13}[OH^-]\}\{k_{43} + K_{24}(k_2 + k_{21})[OH^-]\}} \qquad (3)$$

As a consequence of eq 3 the experimental k values were tentatively fitted with the relation

$$k = \frac{a_1[OH^-]}{\{1 + c_1[OH^-]\}\{1 + c_2[OH^-]\}} \qquad (4)$$

(leaving out the $[OH^-]^2$ term in the nominator). This was done by varying the parameters to minimize the sum of squares of the differences between the experimental and the calculated values of k for pH <10. To this end a steepest descent computer program was written by Professor P. Ros and executed on an IBM 1130 computer. The theoretical curve for k at $I(ClO_4) = 1.00$ calculated in this way is plotted in Figure 1 in order to compare it to the observed k. The points at pH over 10 fall outside this curve. As it has been pointed out earlier the reaction does not produce a single product in this region. The values obtained for the parameters are in Table II. In Table I the observed k has been compared with the calculated one at the three ionic strengths. A general idea of the accuracy with which the parameters are determined was obtained by observing the changes in k(calcd) as a function of the change in the parameters. It was found that k(calcd) is not very sensitive to changes in c_1 and c_2; the accuracy in the parameters c_1 and c_2 is *ca.* 20%. The pH of the sharp maximum in Figure 2 is determined by the product c_1c_2; consequently this product is obtained with a higher accuracy (*ca.* 10%) than the individual constants c_1 and c_2. The accuracy of a_1 is 5%. Introduction of a term $a_2[OH^-]^2$ into the nominator of eq 4 did not significantly improve the fit for pH <10.0; neither did it alter the value of the other parameters more than a few per cent. It was therefore concluded that this term could be omitted in the region studied. A comparison between the two terms in the numerator of eq 3 then gives $k_{12} \approx 0$ (assuming that k_2 and k_{34} are of the same order of magnitude). This means that the reaction path *via* the *cis*-dihydroxo compound **1** can be neglected in the present discussion. As k_{12} and k_{21} are of comparable magnitude,[6] for the present purpose we may also set $k_{21} = 0$. A comparison of eq 3 and 4 then gives

TABLE II

BEST FIT PARAMETERS FOR EQ 4

$I(ClO_4)$	$10^{-5}a_1$	$10^{-5}c_1$	$10^{-5}K_{13}{}^a$	$10^{-5}c_2$	a_1/c_2
0.30	2.6	7.2	9.0	0.7	3.7
1.00	1.4	3.4	4.3	1.1	1.3
2.00	1.7	6.6	7.1	0.6	2.8

[a] Determined directly (see text).

$$\begin{aligned} a_1 &= 4k_2k_{34}K_{24}/k_{43} \\ c_1 &= K_{13} \qquad (5) \\ c_2 &= k_2K_{24}/k_{43} \end{aligned}$$

If the proposed mechanism is correct, the directly determined acid dissociation constant (see Results) will refer to an equilibrium between cis compounds. Table II contains a comparison between c_1 values and the directly determined k_{13} values (from pK_2). For-

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(9) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

(10) M. E. Farago, B. A. Page, and C. F. V. Mason, *Inorg. Chem.*, **8**, 2270 (1969).

(11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, Wiley, New York, N. Y., 1961, p 173.

mula 4 is symmetrical in c_1 and c_2. The parameter value closest to the experimental k_{13} value has been chosen for c_1. The agreement is rather good for the three $I(\mathrm{ClO_4})$ series. From the relations 5 it is seen that $k_{34} = {}^1/_4 a_1/c_2$. k_{34} is the only isomerization rate constant that can be calculated directly and in Table II an entry is made of the quotient $a_1/c_2 = 4k_{34}$. The change in k_{34} on varying the ionic strength reflects the uncertainty in c_2. As the sum of the rate constants k_{34} and k_{43} at 20° lies[6] between 1 and 10, the steady-state treatment outlined above is not invalidated by the absolute values obtained for k_{34}.

Alternate Mechanism.—The mathematical formulation of eq 4 is not altered when it is assumed that the rate-determining step is a dissociative reaction of the conjugate base formed by abstracting an ammine proton from the *trans*-$\mathrm{Co(NH_3)_4(OH)(H_2O)^{2+}}$ ion.

$$\mathrm{Co(NH_3)_4(OH)(H_2O)^{2+} + OH^-} \underset{K_c}{\rightleftarrows} \mathrm{Co(NH_3)_3(NH_2)(OH)(H_2O)^+ + H_2O} \quad (6)$$

$$\downarrow k_c$$

$$\text{tetramer}$$

When the proper substitutions are made, the quotient a_1/c_2 still equals $4k_{34}$ and $c_1 = K_{13}$. Finally it must be noted that a direct check on the reactivity of the trans complexes is prohibited by the fact that no trans complex has as yet been isolated.

Conclusion

The most striking result of the present study is the fact that the polymerization reaction of the tetraammine complex is essentially of first order in the concentration of the monomer. In the mechanisms worked out in the preceding section, the rate-determining step must consequently proceed by a dissociative reaction;[12] this can be the splitting off of one ligand from the *trans*-$\mathrm{Co(NH_3)_4(OH)_2^+}$ ion or from the N-conjugated base of the *trans*-$\mathrm{Co(NH_3)_4(OH)(H_2O)^{2+}}$ ion to give a rapidly reacting intermediate. At present nothing can be said about the nature of the intermediate. The expected low concentration of the N-conjugated base probably makes this ion an unlikely reactive species, although this amido complex may have an unusually high reactivity analogous to the amido complex of the SN1cb mechanism for base hydrolysis.[13] The reactivity of the *trans*-dihydroxo ion may be explained from the fact that the hydroxyl ion as a ligand exerts a large cis labilization effect.[14,15] Thus cis labilizations could effect a loosening of the $\mathrm{Co^{III}{-}NH_3}$ bonds in the $\mathrm{CoN_4}$ plane of the *trans*-$\mathrm{Co(NH_3)_4(OH)_2^+}$ ion and result in the splitting off of an ammine group.

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[12] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1966, p 7.

[13] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1961, p 177.

[14] M. L. Tobe, *Sci. Progr. (London)*, **48**, 484 (1960).

[15] Reference 13, pp 170–177.

Notes

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Polarized Single-Crystal Spectrum of a High-Spin Trigonal-Bipyramidal $\mathrm{NiN_5}$ Chromophore

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The high-spin pentacoordinate nickel(II) complexes with the quadridentate ligand $\mathrm{Me_6tren}$ (tris(2-dimethylaminoethyl)amine) having general formula $[\mathrm{Ni(Me_6tren)X}]\,\mathrm{X}$ (X = Cl, Br, I)[2] are known to be trigonal bipyramidal with a C_{3v} symmetry.[3] Despite their high symmetry, the halo complexes are not suitable for anisotropic measurements because they crystallize in the cubic system.[3]

We looked for $\mathrm{Me_6tren}$ derivatives which crystallize in a noncubic system. The thiocyanate derivative has been found to be crystallographically anisotropic, and its electronic spectrum is quite similar to those of the halo analogs. An X-ray structure determination has been undertaken in order to determine the exact geometry of the chromophore and the molecular orientation in the crystal. Such information has been used to discuss the single-crystal polarized spectra.

The aim of this research is (I) the circumstantiated assignment of the electronic transitions of a trigonal-bipyramidal high-spin nickel chromophore and (II) the study of the spectral and magnetic properties of a ^3E ground state which is expected to experience a zero-field splitting.

Experimental Section

Preparation and Characterization of the $[\mathrm{Ni(NCS)Me_6tren}]$-$(\mathrm{SCN})\cdot\mathrm{H_2O}$ Complex.—The complex was prepared by the general method already reported.[2] *Anal.* Calcd for $\mathrm{C_{14}H_{32}N_6ONiS_2}$: N, 19.85; C, 39.72; H, 7.62. Found: N, 20.16; C, 40.00; H, 7.76. The compound is green and paramagnetic

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[2] M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

[3] M. Di Vaira and P. L. Orioli, *ibid.*, **6**, 490 (1967).