dqp complexes of ruthenium and osmium compared to those of terpy allow the conclusion that the dqp complexes are low spin like those of terpy. Thus, benzo substitution cis to the coordinating nitrogen atoms of the ligand and the resulting steric hindrance causes a red shifting of the observed spectra but, in contrast to the effect observed for the iron complex, it is not sufficient to form high-spin complexes with the heavier metals. This result is not surprising in view of the fact that the ligand field strength, Δ, is expected to increase by a factor of 1.45 and 1.75 on passing from metal ions in the first transition series to metals in the second and third transition series, respectively.[19] Further studies of ruthenium and osmium complexes with other sterically hindering ligands is currently under way.

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Registry No. $K_2[RuCl_5(H_2O)]$, 14404-33-2; K_2OsCl_6, 16871-60-6; dqp, 2176-51-4; $[Ru(dqp)_2](ClO_4)_2$, 56258-91-4; $[Os(dqp)_2](ClO_4)_2$, 56258-93-6.

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Isomerization Reactions of Tetracyanodiaquocobaltate(III)

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The thermal and the photochemical isomerization reactions of $Co(CN)_4(H_2O)_2^-$ in aqueous solution are investigated as a function of pH and temperature. Rate constants and quantum yields are reported. The thermal and the photochemical reactions are explained by independent mechanisms. At 2°C and unit ionic strength, the pK_a values are about 9.5 and 11.7 for the cis isomer and 7.7 and 10.4 for the trans isomer.

Recently the formation of the tetracyanodiaquo and -dihydroxo complexes of Co(III) by irradiation of the corresponding pentacyanoaquo and -hydroxo complexes was reported.[1-3] Similar to the pentacyano complexes of Co(III) these tetracyano complexes can undergo thermal as well as photochemical substitution reactions. Either cyanide or H_2O (or OH^-) can eventually be replaced by another ligand. Specific however for the tetracyano complexes is the observation of isomerization reactions. Indeed, at room temperature the cis form is found to be the stable conformation, but under the influence of light a very efficient isomerization reaction yields almost exclusively the trans form.[3] At reduced temperature this trans structure can be preserved for a limited time.

In this paper we will discuss the kinetics of these thermal and photochemical isomerization reactions. These data evidence the importance of the stereospecific excitation, possible in photochemical reactions, and the consequences for the further course of the reaction.

Experimental Section

Preparation of the Different Complexes. The starting material was $K_3Co(CN)_6$ as prepared by Poskozim.[4] A solution of 5×10^{-3} *M* $Co(CN)_6^{3-}$ in 10^{-1} *M* $HClO_4$ was irradiated in a Pyrex vessel with a mercury high-pressure immersion lamp at a temperature of 1°C. The HCN, produced during the irradiation, was continuously removed by means of a stream of nitrogen. After some 10 hr of irradiation, the cold reaction mixture was passed through an anionic-exchange resin. The tetracyanodiaquocobaltate(III) complex is eluted as the trans isomer. The cis isomer is obtained upon standing at room temperature. Solutions containing the aquohydroxo and the dihydroxo complexes were obtained by adding either NaOH, a borax, or a phosphate buffer to the solution of *trans*- and *cis*-diaquo complexes. A detailed discussion of the preparation and the separation of the various tetracyano complexes is to be published elsewhere.[3] In Figures 1 and 2 the spectra of the *cis*- and *trans*-tetracyanodiaquo and -dihydroxo complexes are given. The assignments of the cis and the trans structures were made on the basis of the electronic absorption spectra. Thus the first ligand field absorption band of the trans species is expected to be considerably shifted toward the red as compared to the band of the cis species.[5]

For all the subsequent experiments the ionic strength of the solutions was adjusted to unity by means of $NaClO_4$ (Merck, p.a.).

Thermal Isomerization. The trans form of the tetracyano complexes is not stable and converts thermally into the cis form. At reduced temperature this isomerization can be slowed down enough in order to allow a kinetic investigation.

The reaction was monitored spectrophotometrically using a Unicam SP 700 C recording spectrophotometer. The solutions were thermostated in the sample holder.

In acid medium a clean isomerization reaction is observed and no secondary products can be detected. The two intersections of the spectra represent isosbestic points over the entire course of the isomerization reaction.

In alkaline solutions, isosbestic points are only observed in the beginning of the reaction. This is due to the formation of polynuclear compounds when the reaction proceeds.[6] At any pH the rate of the latter reaction is considerably slower than the rate of the isomerization

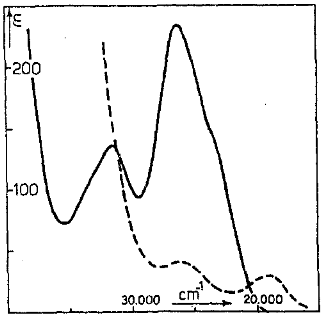

Figure 1. Absorption spectra for cis (——) and trans (- - -) complexes of $Co(CN)_4(H_2O)_2^-$.

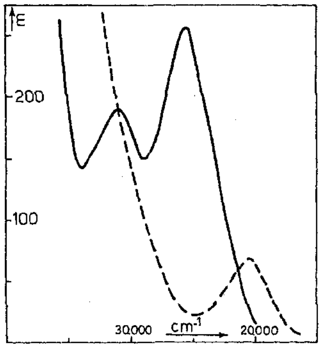

Figure 2. Absorption spectra for cis (——) and trans (- - -) complexes of $Co(CN)_4(OH)_2^{3-}$.

reaction. Thus correct isomerization rate constants could be calculated using kinetic data from the first percents of isomerization.

Photochemical Isomerization. The photochemical isomerization reactions were performed using a monochromatic light source, consisting of a mercury high-pressure arc, a high-intensity monochromator, and a supplementary filter.

The incident flux depends on the photolysis wavelength and varies between 10^{-9} and 5×10^{-9} einstein cm^{-2} sec^{-1} for the different wavelengths used. The reaction was followed spectrophotometrically. The experimental setup has been described elsewhere.[2] Quantum yields are calculated from the initial experimental data (less than 10% conversion).

All of the photochemical isomerization reactions were studied at a temperature of 1°C.

As was the case for the thermal isomerization no side reactions are observed in acid solutions. In alkaline solutions polymerization interferes for large conversion ratios.

Results and Discussion

pK_a's of Tetracyanodiaquocobaltate(III). Depending on the pH either one or both the water ligands of $Co(CN)_4(H_2O)_2^-$ can become deprotonated. The reactivities of the diaquo, the aquohydroxo, and dihydroxo forms are quite different. This is the case for both the cis and the trans isomers.

The acid dissociation constants of the cis isomer were determined by a colorimetric titration. At a temperature of 2°C and unit ionic strength, the pK_a values were found to be about 9.5 and 11.7. The determination of the pK_a values at higher temperatures was rendered very difficult by the occurrence of a fast thermal reaction of the *cis*-$Co(CN)_4(OH)(H_2O)^{2-}$ species. This interference is due to a dimerization reaction, resulting in the formation of oxygen-bridged compounds. Analogous reactions are reported for several hydroxo-containing complexes in alkaline solutions.[6] The direct determination of the acid dissociation constants of the trans isomer by a titration procedure is excluded, due to the fast isomerization reaction of *trans*-$Co(CN)_4(OH)(H_2O)^{2-}$, even at reduced temperatures. As will be discussed below, it is however possible to obtain the pK_a values from kinetic measurements.

Thermal Trans–Cis Isomerization. The first-order rate constants for the thermal trans–cis isomerization reaction at 2°C and unit ionic strength are given in Figure 3 as a function of the pH of the solution. In the case of unbuffered solutions, the isomerization rate changes during the trans–cis conversion, due to a simultaneous change of the pH. Indeed the pK_a values for the cis and trans isomers are quite different. The rate constant, at the indicated pH, is in these cases calculated by extrapolation of the apparent rate constant at each moment, to complete reaction, in which condition the pH is experimentally determined.

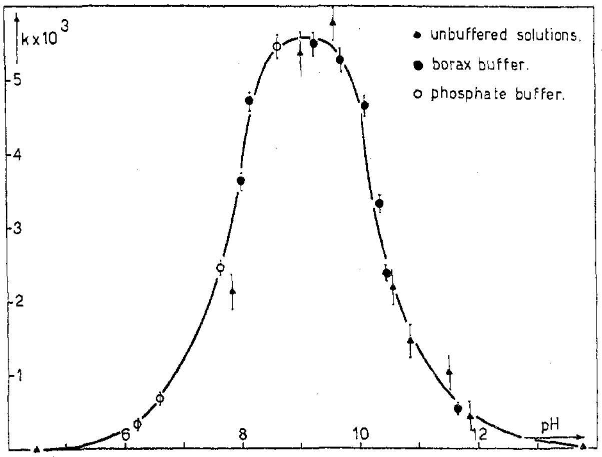

Figure 3. Rate constants of trans–cis isomerization as a function of pH (2° C, $\mu = 1$).

Table I. Kinetic Data for the Thermal Trans–Cis Isomerization at 25°C

Reaction conditions	k, sec^{-1}
1 M HClO	1.04×10^{-3}
10^{-3} M $HClO_4$, 1 M $NaClO_4$	9.0×10^{-4}
0.2 M NaOH, 0.8 M $NaClO_4$	4.5×10^{-4}
0.5 M NaOH, 0.5 M $NaClO_4$	2.1×10^{-4}
0.9 M NaOH, 0.1 M $NaClO_4$	1.0×10^{-4}

The change of the reaction rate in Figure 3 can be considered as a combination of two titration-like curves. It is obvious to correlate this behavior with the two acid dissociation steps of *trans*-$Co(CN)_4(H_2O)_2^-$. The pK_a values can be estimated from this figure to be 7.7 and 10.4 (2°C, $\mu = 1$).

The isomerization rate for the aquohydroxo complex appears to be approximately 10^3 times greater than for the diaquo and the dihydroxo complexes. This behavior is not exceptional: many substitution reactions are reported to be catalyzed by the presence of a hydroxo ligand in the complex. An almost identical dependence has been reported for the trans–cis isomerization of $Co(en)_2(H_2O)_2^{3+}$.[7,8]

The high reactivity of *trans*-$Co(CN)_4(OH)(H_2O)^{2-}$ can be ascribed[9] to the electron-donating power of the OH^- ligand, favoring the release of the loosely bound H_2O ligand.

The much slower isomerization rate of *trans*-$Co(CN)_4(OH)_2^{3-}$ is probably due to two effects. In the first place, the expulsion of an OH^- ligand is rendered more difficult, since the Co–OH bond is much stronger as compared to the Co–OH_2 bond. The second effect is brought in evidence by the inhibition of the isomerization reaction by OH^- in strong alkaline medium (see Table I). This effect can be explained by the following considerations. If one considers as the primary step the formation of a $Co(CN)_4OH^{2-}$ species with a tetragonal-pyramidal structure, the formation of the cis isomer can only occur after rearrangement to a trigonal bipyramid.[9] It is known that in all similar reactions OH^- behaves as a very reactive nucleophilic substituent.[10] There will be a competition between rearrangement of the tetragonal-pyramidal structure and reaction with OH^- before a rearrangement has taken place. The rate of this competitive reaction will of course be

Table II. Activation Energies for the Thermal Trans-Cis Isomerization

Reaction conditions	E, kcal/mol
0.1 M $HClO_4$, 0.9 M $NaClO_4$	29.3
0.2 M NaOH, 0.8 M $NaClO_4$	26.9
0.9 M NaOH, 0.1 M $NaClO_4$	27.0

Table III. Photochemical Isomerization at 1°C

Reaction conditions	Direction	λ_{excit}, nm	ϕ
10^{-3} M $HClO_4$, 1 M $NaClO_4$	Cis → trans	405	0.34
10^{-3} M $HClO_4$, 1 M $NaClO_4$	Cis → trans	365	0.34
10^{-3} M $HClO_4$, 1 M $NaClO_4$	Cis → trans	313	0.30
10^{-3} M $HClO_4$, 1 M $NaClO_4$	Cis → trans	254	0.25
10^{-3} M $HClO_4$, 1 M $NaClO_4$	Trans → cis	546	0.004
10^{-3} M $HClO_4$, 1 M $NaClO_4$	Trans → cis	313	0.04
0.2 M NaOH, 0.8 M $NaClO_4$	Cis → trans	405	0.045
0.9 M NaOH, 0.1 M $NaClO_4$	Cis → trans	405	0.045

increased by an increase of the pH.

As an alternative explanation for the inhibiting effect of OH^- one could propose that at each pH the reaction rate is only governed by the concentration ratio of *trans*-$Co(CN)_4(OH)(H_2O)^{2-}$ and *trans*-$Co(CN)_4(OH)_2{}^{3-}$. This assumption can be rejected since the observed decrease in reaction rate is much larger than the one calculated using the second K_a value of the trans isomer.

The activation energies for the trans-cis isomerization have been calculated both in acid and in alkaline medium. The numerical values are collected in Table II.

The activation energy for the isomerization of the diaquo species is 2 kcal higher than for the reaction of the dihydroxo complex. Although it is easier to abstract an H_2O ligand than an OH^- ligand, this effect must be compensated by the fact that the inductive effect of an H_2O ligand trans to the leaving group is much smaller as compared to that of an OH^- ligand in this position. The present experimental results on the trans-cis isomerization reactions of $Co(CN)_4(H_2O)_2{}^-$, $Co(CN)_4(OH)(H_2O)^{2-}$, and $Co(CN)_4(OH)_2{}^{3-}$ are best interpreted in terms of a dissociative mechanism. The thermal activation of the complexes results in the formation of a $Co(CN)_4H_2O^-$ or a $Co(CN)_4OH^{2-}$ species with a square-pyramidal structure. Competitive with the restoration of the octahedral structure by the capture of an H_2O or an OH^- ligand from the solvent, there is a possibility of transformation into a trigonal-bipyramidal intermediate. One can expect that this species will have a much lower electron density in the vicinity of the H_2O or OH^- ligand as compared to the four electron-accepting CN^- groups. This situation favors considerably the entrance of an H_2O or OH^- group near the oxygen-bonded ligand, leading to the cis configuration.

The nature of the heteroligand is important for the relative stability of the two isomers. Thus in the reaction of either *cis*- or *trans*-$Co(CN)_4H_2O^-$ with $SO_3{}^{2-}$, the *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ is the only reaction product.[1]

Photochemical Isomerization Reaction. In Table III some data for the photochemical isomerization reactions are collected. A systematic investigation of the pH dependence of the isomerization quantum yield could not be done due to the important thermal back-reaction once part of the product is in the aquohydroxo form.

Especially the isomerization of *cis*-$Co(CN)_4(H_2O)_2{}^-$ is a very efficient process. The quantum yield shows only a minor wavelength dependence in the ligand field absorption region. The reaction proceeds also upon excitation in the charge-transfer band but with a smaller quantum yield.

Although some photochemical trans-cis isomerization can be observed, it is clear that photochemical excitation leads mainly to the thermally more labile trans configuration. The dissociative mechanism, responsible for the thermal trans-cis isomerization, cannot be invoked for these photochemical reactions. Ligand field excitation results primarily in a labilization of the metal-ligand bond. Theoretical considerations for these octahedral complexes[11,12] lead to the conclusion that the axis having the lowest mean ligand field strength will be labilized preferentially. For the cis isomer this is the H_2O-Co-CN axis. On this axis, CN^-, being a π acceptor, will be the most labilized ligand. Removal however of this labilized CN^- is improbable: since no excess CN^- is present in the solution, CN^- abstraction would mainly lead to the formation of $Co(CN)_3(H_2O)_3$. Although some aquation is observed,[3] its quantum yield is very low ($<10^{-3}$ at 313 nm).

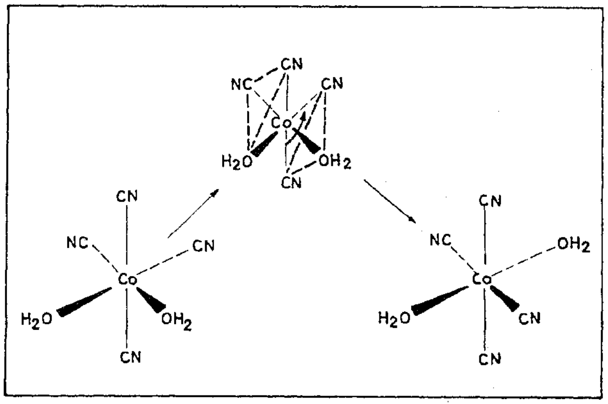

Figure 4. Intramolecular cis-trans isomerization.

Supposing on the other hand a removal of H_2O upon photoexcitation, one would have a pentacoordinated intermediate identical with the one considered in the thermal isomerization reaction. As demonstrated earlier, this finally leads to the formation of a cis product.

Therefore a nondissociative mechanism must be invoked: one has to accept that the photochemical labilization creates the possibility of an interchange of the ligands without their removal. This could be visualized as a twist of one of the triangular surfaces relative to the other as shown in Figure 4. Similar thermal intramolecular racemization reactions are found for complexes such as $Co(C_2O_4)_3{}^{3-}$, $Cr(C_2O_4)_3{}^{3-}$, and $Fe(phen)_3{}^{2+}$.[13] For $Fe(phen)_3{}^{2+}$ such a twist mechanism is discussed by Bailar.[14]

The lower quantum yield for the photoisomerization of *cis*-$Co(CN)_4(OH)_2{}^{3-}$ as compared to the one for $Co(CN)_4(H_2O)_2{}^-$ fits into this scheme. Since the Co-OH bond in the complex, whether excited or not, is much stronger than the Co-OH_2 bond, the rigidity of the octahedral frame is expected to be much larger, and this should be reflected in a lower probability for isomerization. On the other hand, since OH^- is a π donor, the CN^- will be more labilized in the excited hydroxo complex and dissociation will be more probable. Indeed a higher quantum yield is found for the formation of $Co(CN)_3(OH)_3{}^{3-}$ ($\phi \simeq 5 \times 10^{-2}$ at 313 nm).

Photoexcitation of the trans tetracyano complexes at the lowest ligand field transition (546 nm) labilizes the H_2O-Co-OH_2 or the HO-Co-OH axis.[11,12] The very low isomerization quantum yield is in accordance with the proposed interchange mechanism. No exchange of the H_2O with a neighboring CN^- is expected due to the very high strength of the Co-CN bond. Indeed before any twisting of the octahedral configuration can be expected to occur, a labilization of the strong Co-CN bond is required. Excitation with 313-nm light results in a labilization of the NC-Co-CN bond.[11,12] Although a rapid conversion of the energy to the lowest level (H_2O-Co-OH_2 axis) is expected, there seems to be a possibility of reaction prior to this conversion. The quantum yield for the trans-cis isomerization is 10 times larger than for 546-nm excitation.

Conclusions

A comparison of the results for the thermal and the photochemical isomerization of $Co(CN)_4(H_2O)_2^-$ and $Co(CN)_4(OH)_2^{3-}$ proves that two different mechanisms are involved. The thermal trans–cis isomerization is in accordance with an SN1 type mechanism. The data on the photochemical cis–trans isomerization can only be explained by accepting a nondissociative mechanism, in which ligands exchange place without bond breaking.

The photochemical reactions evidence also the specificity of the interaction with light: excitation of a specific axis in the complex results in a preferential subsequent reaction pattern.

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Registry No. *cis*-$Co(CN)_4(H_2O)_2^-$, 56403-82-8; *trans*-$Co(CN)_4(H_2O)_2^-$, 56403-83-9; *cis*-$Co(CN)_4(OH)_2^{3-}$, 53797-83-4; *trans*-$Co(CN)_4(OH)_2^{3-}$, 53769-69-0; $Co(CN)_6^{3-}$, 14897-04-2.

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Kinetics and Mechanisms of Chromium(II)-Catalyzed Nitrosyl Ligand Transfer Reactions

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The reaction of nitrosylbis(ethylenediamine)cobalt(III) ion with chromium(II) was studied in an aqueous perchlorate medium. The electron-transfer reaction involving $Co(en)_2(H_2O)NOH^{3+}$ (the dominant species in highly acidic solution) and chromium(II) can be represented by the rate expression

$$\frac{d[Cr(H_2O)_5NO^{2+}]}{dt} = k_{et}Q\frac{[Co(en)_2(H_2O)NOH^{3+}][Cr^{2+}]}{[H^+]}$$

The activation parameters reported for this reaction are in accord with those previously reported for a series of Co(III)–Cr(II) inner-sphere electron-exchange reactions. The cobalt(III) nitrosyl–chromium(II) reaction product, $Cr(H_2O)_5NO^{2+}$, was observed to undergo a further Cr(II)-catalyzed ligand exchange reaction to yield $Cr(H_2O)_6^{3+}$. Mechanisms are proposed for all reactions studied and chloride ion dependencies for both the electron-transfer and aquation reactions are discussed.

Introduction

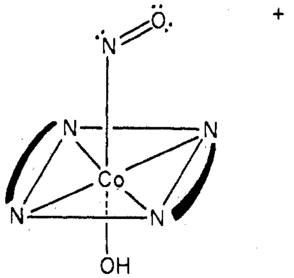
Although the literature contains numerous reports of the synthesis of a variety of metal–nitrosyl complexes,[2–7] only a few[8–15] report data concerning the reactions that these species undergo. Of the reactions that have been reported most include direct oxidations and/or reductions of the nitrosyl ligand itself by various reagents. Armor and Taube[15] have shown that the nitrosyl ligand of nitrosylpentaammineruthenium(III) can be reduced by chromium(II) to yield an amine. Their reaction sequence was shown to generate $Ru(NH_3)_6^{2+}$ and 6 equiv of chromium(III) as products. Armor[9] reported that the reaction of chromium(II) and $Co(NH_3)_5NO^{2+}$ in acidic aqueous chloride media produces $Cr(H_2O)_5NO^{2+}$ and cobalt(II), although he did not report the complete kinetic data for the reaction. Armor and Buchbinder[8] further found that chromium(II) reacts with $Cr(H_2O)_5NO^{2+}$ to yield hydroxylamine and a chromium(III) dimer, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4$. Additional work[9] indicated that the nitrosyl ligand, when coordinated to a transition metal, can undergo a series of successive reduction reactions to yield such species as NO^-, N_2, NH_3OH^+, N_2H_4, or NH_3.

The study reported here concerns the chromium(II)-catalyzed nitrosyl ligand "transfer" reactions of nitrosylbis(ethylenediamine)cobalt(III) via an oxidation–reduction mechanism.

In the cobalt complex shown in I, the basal position, trans to the NO group, may be occupied by either H_2O or OH^-, depending on the pH. The dominant species at high pH is $Co(en)_2(OH)NO^+$. Acidification of this complex results in the formation of the protonated aquo species represented by the equation

$$Co(en)_2(OH)NO^+ + 2H^+ \rightleftharpoons Co(en)_2(H_2O)NOH^{3+}$$

Also, the nitrosyl ligand is bent in this complex (see I) as was



I

found to be the case in similar nitrosyl complexes,[16] thereby allowing a chromium(II) ion the option of attacking the lone pair of electrons on the nitrogen atom or one of the lone pairs of electrons on the oxygen atom. In an inner-sphere redox reaction of this type, either one of the two modes of attack