3722 *Inorg. Chem.* **1981**, *20*, 3722-3727

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trans- and *cis*-Dicyanotetraamminechromium(III) and Some Related Monocyano Complexes

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Received November 5, 1980

The *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ ions were synthesized by reaction of cyanide with (dimethyl sulfoxide)tetraamminechromium(III) complexes, both in Me_2SO and in H_2O. In the former solvent, stereorearrangements complicate the preparative procedure, yielding mixtures of the two dicyano isomers. In aqueous medium, substitution appears to be stereoretentive. The new species were precipitated as perchlorate salts and characterized by conductance, ion-exchange chromatography, and electronic and infrared spectroscopy. Their electronic structures are atypical among the other known diacidotetraammines of chromium(III). The ligand field spectra are compared with theoretical predictions in the literature. The charge-transfer bands exhibit a vibrational sequence, consistent with a $t_{2g}(Cr) \rightarrow \pi^*(CN^-)$ transition. Both complexes undergo acid-catalyzed, stepwise release of cyanide. Aquation is totally stereorigid, and the terminal species are *trans*- and *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$, respectively. The products of the first solvation stage, *trans*- and *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, as well as the $Cr(NH_3)_4(OH)(CN)^+$ counterparts, were isolated chromatographically and analyzed in solution. Also the *cis*-$[Cr(NH_3)_4(Me_2SO)(CN)](ClO_4)_2$ synthetic intermediate is described.

Introduction

Diacidotetraamine complexes are of particular relevance to the stereochemistry of chromium(III) substitutions both in the ground state[1,2] and in the excited states.[3] Known members of the *trans*- and/or *cis*-$Cr(NH_3)_4X_2^{z+}$ families are those with X = H_2O,[1,4] F^-,[5,6] Cl^-,[4,6] Br^-,[6] NCS^-,[7,8] DMF,[9] Me_2SO,[9] ONO^-,[8] $^1/_2C_2O_4^{2-}$[8] (the last two only cis). The ligand field (LF) absorption spectra of these ions have been treated theoretically,[10,11] and the electronic transitions of species yet to be prepared have been quantitatively predicted.[11]

The unusual bonding and spectroscopic properties of the cyanide ligand make the compounds with X = CN^- especially important, and our interest for the thermal and photochemical reactivity of tetragonal chromium(III)–ammine systems prompted us to synthesize these two isomers by extending the procedure that proved successful with $Cr(NH_3)_5(CN)^{2+}$.[12] This paper deals with the preparation, characterization and spectra of the *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ complexes. We also describe other new species that were isolated in the course of the present investigation, namely, *trans*- and *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ and *cis*-$Cr(NH_3)_4(Me_2SO)(CN)^{2+}$. Previous literature reports on mixed-ligand, chromium(III) cyano complexes concern the analogous *trans*-[13] and *cis*-$Cr(en)_2(CN)_2^+$ cations,[13,14] the $Cr(H_2O)_{6-n}(CN)_n^{3-n}$ series,[15] and the $Cr(CN)_5(NO)^{2+}$ anion[16] and its aquation products.[17]

Experimental Section

Materials. Dimethyl sulfoxide, Me_2SO (Erba RPE), was dried with 4-Å molecular sieves (Merck), distilled under nitrogen atmosphere at reduced pressure, and stored over anhydrous Na_2SO_4.[18] All other chemicals and solvents employed were of reagent grade.

***trans*- and *cis*-Diaquotetraamminechromium(III) perchlorate** salts were prepared and recrystallized by literature methods.[4] The LF absorption spectra in 10^{-2} M $HClO_4$ solution exhibit maxima at 475 (ϵ 21) and 368 nm (ϵ 30 M^{-1} cm^{-1}) for the trans isomer and at 495 (ϵ 36) and 366 nm (ϵ 27 M^{-1} cm^{-1}) for the cis form, both in agreement with reported values.[1,4]

***trans*- (A) and *cis*-Bis(dimethyl sulfoxide)tetraamminechromium(III) (B) perchlorates** were obtained as reported elsewhere.[9] The maxima of the LF bands in aqueous solution occur at 560 (ϵ 24), 465 (ϵ 16), and 385 nm (ϵ 35 M^{-1} cm^{-1}) for the trans species[9] and at 515 (ϵ 51) and 382 nm (ϵ 33 M^{-1} cm^{-1}) for the cis analogue.

***trans*- (C) and *cis*-Chloro(dimethyl sulfoxide)tetraamminechromium(III) (D) perchlorates** were synthesized as described previously.[9] The LF spectral maxima of aqueous samples are observed at 576 (ϵ 24), 470 (ϵ 15), and 392 nm (ϵ 36 M^{-1} cm^{-1})[9] and at 524 (ϵ 42) and 390 nm (ϵ 31 M^{-1} cm^{-1}), respectively. In Me_2SO solution, both the positions and the intensities of the absorption bands of A–D are modified to some extent.[9]

Caution: Cyanide solutions were handled in a ventilated hood. Excessive heating of Me_2SO solutions containing large amounts of $NaClO_4$ may be hazardous.

Analytical Procedures. The complexes were treated with 1 M $HClO_4$ at room temperature to facilitate removal of CN^- by acid catalysis. The samples were then made alkaline with NaOH and heated in order to complete decomposition. Chromium was measured spectrophotometrically at 374 nm (ϵ 4760 M^{-1} cm^{-1}) after oxidation to chromate by alkaline hydrogen peroxide. Ammonia was determined by a semimicro Kjeldahl technique, distilling NH_3 from the above basic solutions. Cyanide was analyzed potentiometrically by means of an Amel Model 201-CN Sens-Ion electrode coupled with a Radiometer Model PHM 84 research pH meter. Samples were buffered at pH ca. 12.5, and standardization plots were constructed in parallel with each analysis using KCN. Carbon, hydrogen, and nitrogen were determined by standard organic microanalysis.

Ion-exchange separations were carried out by using either Sephadex SP-C25 cationic resin in the sodium form or De-Acidite FF-IP anionic exchanger in the perchlorate form. Dependent upon the types and amounts of products to be treated, the column lengths varied between 2 and 15 cm and the diameters were either 1 or 2 cm. Elution was performed with sodium perchlorate at the desired pH. Typical $NaClO_4$ concentrations displacing 1+, 2+, and 3+ complex ions were 0.02, 0.05, and 0.15 M, respectively.

Electrical conductance of aqueous samples at 20 °C was determined by a Philips PW 9501 conductivity meter connected with a PW 9512 cell. Electronic absorption spectra were obtained with either Shimadzu UV 200 S or Cary 17 double-beam instruments, while optical densities at given wavelengths were measured by a Beckman DU spectrophotometer. Luminescence spectra were measured on argon-saturated solutions by means of a Perkin-Elmer MPF 44A spectrofluorimeter equipped with an R 446 photomultiplier. Infrared spectra were taken

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as Nujol mulls on a Perkin-Elmer 521 grating spectrophotometer.

Preparative Procedures. Exploratory work was carried out spectrophotometrically by following the absorption changes of 0.3-mL samples contained in thermostated cells of 1-mm path length and made up with the same reagent concentrations as in the batch preparations. The ligand substitution reactions were thus monitored semiquantitatively so as to optimize the preparative conditions. In some instances, ion-exchange separations were performed on mixtures at various reaction stages in order to verify the relative amounts of the possible products. All the operations were carried out in dim light.

Synthesis of Dicyanotetraamminechromium(III) Ions in Me_2SO. The yields and the isomeric composition of products were essentially the same, regardless the starting complex was A, B, C, or D (see Results). The use of reactants of cis configuration may be advantageous since their obtainment involves less preparative steps than required for the trans counterparts.

A typical preparation was as follows. A 1.7-g amount of NaCN (ca. 35 mmol) was dissolved on heating in the minimum volume (ca. 15 mL) of Me_2SO and 4.0 g of B (ca. 7 mmol) was then added. The mixture was kept at 70 °C for 30 min and was occasionally stirred. The color progressively turned from purple to deep orange. After cooling, the solution was treated with 50 mL of 3 M $LiClO_4$ in ethanol and was kept in a refrigerator for at least 2 days. A yellow salt slowly separated and was collected by filtration, washed with ethanol and ether, and vacuum dried over P_2O_5. The precipitate consisted of an approximately equimolar mixture of the $[Cr(NH_3)_4(CN)_2]ClO_4$ isomers. The yields ranged between 0.4 and 0.6 g or 20–30% of the theoretical.

***trans*-Dicyanotetraamminechromium(III) Perchlorate.** Owing to the relative insolubility of this salt, the pure trans isomer may be obtained by dissolution of 0.5 g of the above crude product in 100 mL of water, filtration, and slow addition of 5 mL of 8 M $NaClO_4$. Long standing in a refrigerator (at least overnight) favored precipitation, and the recovery was about 90%. The lemon yellow crystals were filtered off and then washed and dried as above. Further recrystallization may be accomplished by dissolving the complex salt in water at 40 °C and reprecipitating it upon ice cooling. Anal. Calcd for $[Cr(NH_3)_4(CN)_2]ClO_4$: Cr, 19.15; NH_3, 25.08; CN, 19.16; C, 8.84; H, 4.45; N, 30.94. Found: Cr, 19.0; NH_3, 25.1; CN, 19.4 ± 0.3; C, 8.7; H, 4.3; N, 30.8.

***cis*-Dicyanotetraamminechromium(III) Perchlorate.** Only ion-exchange chromatography led to isolation of the pure complex. The product mixture (0.4 g) was dissolved in water and loaded into a 15-cm column of the cation exchanger. Elution with neutral 0.02 M $NaClO_4$ separated the two isomers into two distinct yellow bands. The nonpolar trans species was displaced at a faster rate than the polar cis form. As a precaution, the front part of the second fraction was discarded so as to eliminate possible residual amounts of the less soluble trans compound. The solvent was then gently evaporated from each fraction by means of a rotory evaporator at ca. 30 °C, and the residues were repeatedly washed with ethanol to remove $NaClO_4$. *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$ was recovered by dissolution in water of the residue of the first eluate and was reprecipitated as mentioned above.

The more soluble salt contained in the second fraction (ca. 0.2 g) was dissolved in 9 mL of water at room temperature. After centrifugation, the solution was cooled at −15 °C for 2–3 h. About 70 mg of *cis*-$[Cr(NH_3)_4(CN)_2]ClO_4$ precipitated as yellow crystals and were collected by filtration. Addition of 2 mL of 8 M $NaClO_4$ to the mother liquor and further standing at −15 °C for 2 days led to precipitation of another 70 mg of complex salt. The precipitates were washed with ethanol and then with ether and air-dried. Anal. Calcd for $[Cr(NH_3)_4(CN)_2]ClO_4$: Cr, 19.15; NH_3, 25.08; CN, 19.16; C, 8.84; H, 4.45; N, 30.94. Found: Cr, 19.2; NH_3, 25.0; CN, 18.9 ± 0.3; C, 8.7; H, 4.2; N, 30.6.

Synthesis of *trans*-Dicyanotetraamminechromium(III) Perchlorate in Water. A larger molar excess of NaCN than employed in Me_2SO and a lower temperature were necessary to ensure precipitation of the product as the cyanide salt. This protects the complex from successive anation, which appears to be more efficient in aqueous medium than in dimethyl sulfoxide. Preparation in water of the cis isomer was not possible.

To an aqueous solution (ca. 15 mL) of 3.4 g of NaCN (ca. 70 mmol) was added 2.0 g of A (3.5 mmol), and the mixture was warmed at 35 °C for 8–9 h under continuous stirring. While the reactant slowly dissolved, a yellow solid started to separate from the deep purple solution. The reaction vessel was then kept in the dark at ca. 20 °C for 2 days. More product precipitated during this period. *trans*-$[Cr(NH_3)_4(CN)_2]CN$ was filtered off, washed with ethanol and ether, and vacuum dried over P_2O_5. The yield was 0.20 g or 25%. The cyanide was converted into the perchlorate salt by precipitation from aqueous solution (ca. 50 mL) with 8 M $NaClO_4$ (5 mL) and long standing in a refrigerator. Recrystallization was accomplished as already described. Analysis of Cr, NH_3, and CN^- confirmed the complex composition, and the LF absorption spectrum was identical with that of the product obtained in Me_2SO.

***cis*-Cyano(dimethyl sulfoxide)tetraamminechromium(III) perchlorate** was isolated as an intermediate product during cyanide anation of A and B in Me_2SO and of B (but not of A) in water. The same reagent amounts as in the preparations of the dicyano complexes were employed. The conditions were 15 min at 70 °C for reaction in Me_2SO and 2 h at 40 °C for reaction in H_2O. Addition of 60 mL of 3 M $LiClO_4$ in ethanol in the former case and of excess solid $NaClO_4$ in the latter caused precipitation of an orange-red mixture, the main constituent of which was *cis*-$[Cr(NH_3)_4(Me_2SO)(CN)](ClO_4)_2$. After 2–3 h of cooling, the crude product was filtered off and repeatedly washed with ethanol to eliminate $NaClO_4$. The solid was then dissolved in water and adsorbed in a 3-cm cationic column. Elution with neutral 0.02 M $NaClO_4$ revealed the absence of any 1+ (dicyano) species. Successive treatment with 0.05 M $NaClO_4$ displaced the orange cyano(dimethyl sulfoxide), 2+ ion. The purple band remaining at the top of the column consisted of unreacted tripositive parent complex. The eluate was brought to dryness by using a rotovapor at room temperature and the residue was again washed with ethanol for removal of $NaClO_4$. The complex salt was recrystallized by dissolution in the minimum volume of water, filtration, and addition of 8 M $NaClO_4$ to the ice-cold solution. The orange crystalline powder was washed with ethanol and then ether and vacuum dried. Anal. Calcd for $[Cr(NH_3)_4(C_2H_6SO)(CN)](ClO_4)_2$: Cr, 12.29; NH_3, 16.10; CN, 6.15; C, 8.51; H, 4.29; N, 16.55. Found: Cr, 12.5; NH_3, 16.2; CN, 6.3 ± 0.2; C, 8.4; H, 4.1; N, 16.3.

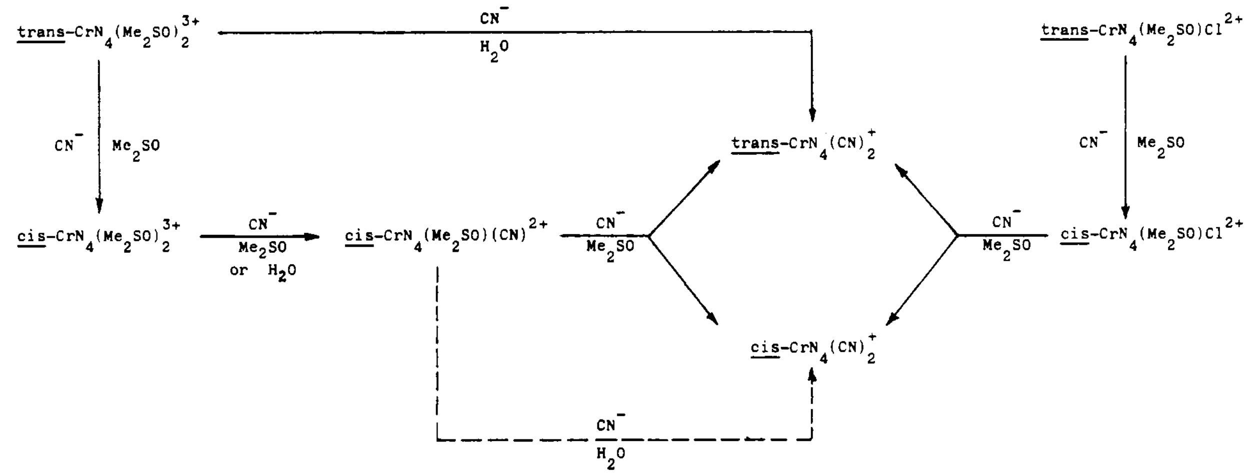
***trans*-Cyanoaquotetraamminechromium(III)** was obtained by acid-catalyzed aquation of the *trans*-dicyano complex and was isolated in solution by an ion-exchange technique. A 10^{-2} M solution of *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$ was made 3×10^{-2} M in $HClO_4$ and was kept at ca. 25 °C for 30 min. The pH was increased to 12 (NaOH) so as to quench the reaction and to have all uncoordinated cyanide in the ionic form. The solution was then eluted through a 6-cm column of anionic resin at pH 12 in order to remove CN^-. After the pH was adjusted to 3.5 ($HClO_4$), the sample was adsorbed on a 3-cm cationic column and eluted, first with 0.02 M $NaClO_4$ and then with 0.05 M $NaClO_4$, both at pH 3.5. Since the first cyanide ligand is lost at a faster rate than the second one (vide infra), virtually all the monopositive reactant had disappeared and only traces of the tripositive diaquo complex resulted as a retained, faint red band. The second eluant displaced the 2+ cyanoaquo ion. The complex was characterized by its absorption spectrum (vide infra) and by analysis in solution. The CN^-:Cr ratio was found to be 1.00 ± 0.02.

***cis*-Cyanoaquotetraamminechromium(III)** was prepared in a similar manner by controlled acid hydrolysis of *cis*-$[Cr(NH_3)_4(CN)_2]ClO_4$. While the reagent concentrations and the eluants were the same as for the trans isomer, the reaction conditions differed (40 min at 35 °C) as the *cis*-dicyano cation aquates more slowly (vide infra). In this case, because of the similarity of the rates of successive aquation, mixtures of dicyano (ca. 30%), cyanoaquo (ca. 40%), and diaquo (ca. 30%) complexes were obtained. Free CN^- was eliminated by anion exchange at pH 12, as above. The dipositive product was then selectively eluted by 0.05 M $NaClO_4$ at pH 3.5 after the starting complex was displaced with 0.02 M $NaClO_4$. Characterization in solution was again accomplished through the absorption spectrum and the CN^-:Cr ratio (1.01 ± 0.02).

Results and Discussion

Synthesis in Dimethyl Sulfoxide. The synthetic method already adopted for $Cr(NH_3)_5(CN)^{2+}$[12] consists of cyanide anation of dimethyl sulfoxide–ammine complexes. While one common preparative route to acidoamminechromium(III) ions is replacement of H_2O ligands by anionic groups,[1] CN^- cannot be coordinated by such a procedure. Deprotonation of bound water by this strongly basic anion hinders substitution both by increasing the nucleophilicity of the ligand to be replaced and by making the complex decomposition highly competitive

Scheme I



with anation. On the contrary, if the departing group is Me_2SO, entry of CN^- in the coordination sphere becomes relatively easy. Also the solvent seems to play an important role. Anation proceeds more cleanly in dimethyl sulfoxide and results in a larger product yield than in water. In addition, one of the dicyano isomers cannot be obtained in aqueous solution. Several factors facilitate coordination of CN^- in the dipolar aprotic solvent with respect to aqueous media. (1) Ion association is intensified.[19] (2) The entering anion is less solvated.[20] (3) No cyanide is subtracted by hydrolysis. The general pattern of reactivity is summarized in Scheme I (where $N = NH_3$) and, unlike the synthesis of cyanopentaamminechromium(III), presents some stereochemical complexities.

Reaction in dimethyl sulfoxide leads to approximately equimolar mixtures of *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$, irrespective of the isomerism of the $Cr(NH_3)_4(Me_2SO)_2^{3+}$ starting compound. While the *trans*-bis(dimethyl sulfoxide) complex is stable in Me_2SO for several hours at room temperature, addition of NaCN causes swift and essentially complete trans → cis isomerization, even at 20 °C, before anation takes place. The LF spectrum rapidly loses its typical shape (i.e., the large splitting of the low-energy band of trans-disubstituted tetraammines), and two maxima appear at ca. 410 and 380 nm, identifying the cis isomer. This species can be, in fact, recovered by precipitation and authenticated. Stereochemical change of chromium(III) systems in this solvent is not novel,[21,22] and a possible explanation for its occurrence is that ion pairing of the tripositive complex with CN^- drives the isomeric equilibrium toward the polar cis form. The same rearrangement was observed upon addition of hydroxide (as NaOH) but not in the presence of Cl^-, Br^-, and NCS^- ions. So, only strongly basic anions seem able to induce fast isomerization, suggesting a rapid acid–base equilibrium step perhaps involving an amido complex as intermediate.

Stepwise replacement of Me_2SO by CN^- is indicated by a progressive blue shift of the LF spectral maxima. The low-energy band is finally stabilized around 450 nm. The CN^-:Cr ratio leading to the highest product amount is about 5:1. A larger molar excess of cyanide and prolonged reaction times cause coordination of more CN^- groups, as evidenced by a further displacement of the spectrum to shorter wavelengths, to end up with $Cr(CN)_6^{3-}$.

An unexpected result is that, after coordination of the first cyanide group, access of the second one is accompanied by partial cis → trans isomerization. Such a rearrangement appears to be rather uncommon for chromium(III) systems that in nonaqueous solvents are generally prone to stereochemical change in the opposite (trans → cis) direction.[21,22] In this stage, the decreased (1+) complex charge should not favor ion pairing stabilization of the cis configuration with respect to mutual repulsion of bound cyanides in a trans configuration. That cis → trans isomerization occurs either simultaneously or subsequently to entry of the second CN^- ligand is confirmed by chromatographic separations at various conversion times. Reaction mixtures in Me_2SO, quenched before anation was complete (see Experimental Section), were, in fact, found to contain only the *cis*-$Cr(NH_3)_4(Me_2SO)(CN)^{2+}$ species and not the trans analogue. The *cis*-cyano(dimethyl sulfoxide) cation was even isolated by precipitation as the perchlorate salt.

Attempts to prepare cyanochloro complexes by using either *trans*- or *cis*-$Cr(NH_3)_4(Me_2SO)Cl^{2+}$ as reactants were unsuccessful. Only mixtures of $Cr(NH_3)_4(CN)_2^+$ isomers could be obtained without substantial differences from those described above. Both the Cl^- and the Me_2SO ligands are readily replaced by CN^- with little selectivity. Also in these cases, fast trans → cis rearrangement upon addition of CN^- precedes any substitution.

It is noteworthy that while separation of the two dicyanotetraamminechromium(III) cations is achieved by ion-exchange chromatography, the large difference in solubility of the perchlorate salts allows obtainment of pure *trans*-$Cr(NH_3)_4(CN)_2^+$ by simple precipitation from aqueous solution.

Definite stereochemical evidence for all the new compounds is provided by the known spectra[1,4] of the terminal aquation products *trans*- and *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$ (vide infra). In fact, acid hydrolysis occurs in all cases with complete retention of configuration.

Synthesis in Water. Anation of the bis(dimethyl sulfoxide) species by CN^- is also possible in H_2O. There are several indications for stereorigidity in these preparations in conformity with the well-established behavior of chromium(III) in aqueous media.[1,23] The fairly insoluble perchlorate salt of *trans*-$Cr(NH_3)_4(CN)_2^+$ precipitates only when the starting complex is trans, whereas *cis*-$Cr(NH_3)_4(Me_2SO)(CN)^{2+}$ can be isolated only if the parent compound has the cis configuration. In either of these systems, further coordination of CN^- reduces the products, resulting mainly in anionic species.

Chromatographic analyses yielded no evidence for the presence of even small amounts of *trans*-$Cr(NH_3)_4(Me_2SO)(CN)^{2+}$ in the former case and of *cis*-$Cr(NH_3)_4$-

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Table I. Electronic Spectra of the $Cr(NH_3)_4(CN)_2^+$ Complex Ions in Aqueous Solution

isomer	obsd features λ, nm	obsd features ε, M^{-1} cm^{-1}	predicted max[a] λ, nm	assignt[b]
trans	698[c]			$^2E_g \rightarrow {}^4A_{2g}$[d]
			464	$^4B_{1g} \rightarrow {}^4B_{2g}$ ($^4T_{2g}$)
	440 (max)	42.6		
			420	$^4B_{1g} \rightarrow {}^4E_g$ ($^4T_{2g}$)
	385 (min)	12.5		
			339	$^4B_{1g} \rightarrow {}^4E_g$ ($^4T_{1g}$)
	344 (max)	41.5		
			327	$^4B_{1g} \rightarrow {}^4A_{2g}$ ($^4T_{1g}$)
	250 (sh)	155		$^4A_{2g} \rightarrow {}^4T_{2u}$[d]
	240 (sh)	610		
	231 (sh)	1330		
	224 (max)	1610		
	216 (max)	1770		
	209 (sh)	2530		
cis	700[c]			$^2E_g \rightarrow {}^4A_{2g}$[d]
			439	$^4B_1 \rightarrow {}^4E$ ($^4T_{2g}$)
	436 (max)	49.0		
			416	$^4B_1 \rightarrow {}^4B_2$ ($^4T_{2g}$)
	379 (min)	14.0		
	342 (max)	37.6		$^4B_1 \rightarrow {}^4A_2$, ^4E ($^4T_{1g}$)
	252 (sh)	320		$^4A_{2g} \rightarrow {}^4T_{1u}$[d]
	242 (sh)	890		
	233 (sh)	1230		
	225 (sh)	1400		
	217 (sh)	1650		

[a] According to ref 11. [b] Octahedral parent states in parentheses. [c] Transition observed in emission only. [d] In O_h approximation.

$(CN)_2^+$ in the latter. Moreover, *cis*-$Cr(NH_3)_4(CN)_2^+$ could not be detected even upon reaction of stoichiometric amounts of CN^- with the isolated *cis*-$[Cr(NH_3)_4(Me_2SO)(CN)](ClO_4)_2$ intermediate. Evidently, kinetic instability makes these compounds elusive in water. A rationale may be found in the strong trans-labilizing ability of cyanide. In the trans system, after entry of the first CN^-, the trans-Me_2SO ligand is quickly replaced either by another CN^- or by H_2O. Besides the *trans*-dicyano complex, the solutions in fact contain considerable amounts of *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ (in the hydroxo form, as CN^- alkalinizes the medium) that cannot undergo CN^- anation and account for the low product yield. In the cis system, under any condition, the main species of further anation was found to be $Cr(NH_3)_2(CN)_4^-$ (as identified chromatographically by its charge), again consistent with fast, subsequent replacement of trans-NH_3 groups in *cis*-$Cr(NH_3)_4(CN)_2^+$.

Once formed, the *trans*-dicyano isomer is very stable in alkaline solution (as is the cis isomer in the absence of excess CN^-), and its low solubility facilitates accumulation. However, in acidic medium it decomposes faster than the cis complex (vide infra). Rapid loss of the first cyanide may be again explained by a trans effect. These observations are in agreement with the reported impossibility of synthesizing the analogous *trans*-$Cr(en)_2(CN)_2^+$ ion in aqueous HCN[14] and with its obtainment in NaCN (alkaline) solution.[13]

Electronic Absorption Spectra. The LF features of the newly synthesized tetraamminechromium(III) complexes are reported in Tables I and II and in Figures 1 and 2. Two bands are observed in all cases, related to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions in octahedral approximation and in order of increasing energy.

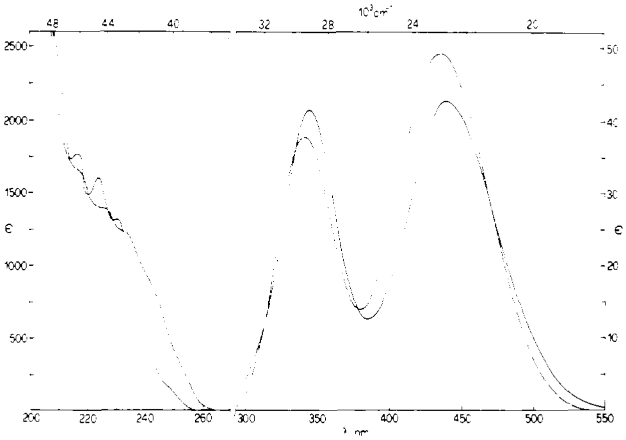

Figure 1. Ligand field (ε on the right) and charge-transfer (ε on the left) absorption spectra of the $Cr(NH_3)_4(CN)_2^+$ complex ions in aqueous solution: solid line, trans isomer; broken line, cis isomer.

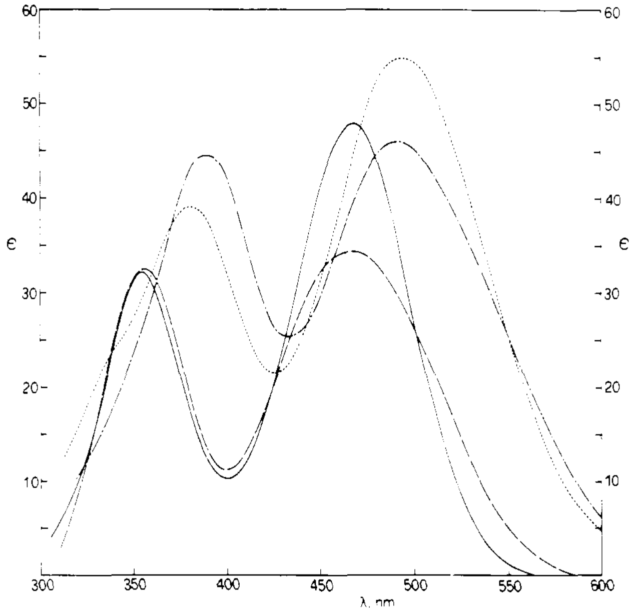

Figure 2. Ligand field absorption spectra of monocyano complexes in aqueous solution: —, *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ at pH 3; - - -, *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ at pH 3; ···, *trans*-$Cr(NH_3)_4(OH)(CN)^+$ at pH 10; -·-, *cis*-$Cr(NH_3)_4(OH)(CN)^+$ at pH 10.

Table II. Ligand Field Absorption Data for Some Monocyanotetraamminechromium(III) Complex Ions in Aqueous Solution

	wavelength, nm (ε, M^{-1} cm^{-1}) $^4A_{2g} \rightarrow {}^4T_{2g}$[c]	min	$^4A_{2g} \rightarrow {}^4T_{1g}$[c]
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$[a]	468 (48)	400 (10)	354 (32)
cis-$Cr(NH_3)_4(H_2O)(CN)^{2+}$[a]	468 (34)	400 (11)	355 (32)
trans-$Cr(NH_3)_4(OH)(CN)^+$[b]	494 (55)	426 (21)	381 (39)
cis-$Cr(NH_3)_4(OH)(CN)^+$[b]	491 (46)	432 (25)	387 (44)
cis-$Cr(NH_3)_4(Me_2SO)(CN)^{2+}$	483 (44)	406 (13)	362 (36)

[a] At pH 3. [b] At pH 10. [c] In O_h approximation.

Focussing attention on the *trans-/cis*-$Cr(NH_3)_4(CN)_2^+$ pair, we see that the positions of the low-energy maxima are congruent with coordination of two CN^- ligands (compared with 462 nm for $Cr(NH_3)_6^{3+}$ and 451 nm for $Cr(NH_3)_5(CN)^{2+}$).[12] The absorption curves of the two isomers are not sufficiently different for being indicative of the actual complex symmetries, as is usually true for other *trans*- and *cis*-$Cr(NH_3)_4X_2^+$ systems.[1,4–6] LF theory predicts that upon lowering the O_h symmetry to either D_{4h} (trans) or C_{2v} (cis), the $^4T_{2g}$ excited state splits into the $^4E + {}^4B_2$ components and the $^4T_{1g}$ state gives rise to the $^4A_2 + {}^4E$ sublevels.[10,11] The splitting of the long-wavelength band is generally observable in trans-disubstituted species but not in the *cis* analogues, the $^4E - {}^4B_2$ energy difference for the former being about twice as great as for the latter.[10,11]

The energies of the four transitions from the $^4B_1$ ground state of the two dicyano complexes have been anticipated in the literature.[11] The corresponding wavelengths are compared with the experimental data in Table I. The relatively small separations between the sublevels (trans, 2250; cis, −1250 cm^{-1}) account for the lack of any spectral splitting, even in the trans compound. However, especially for the latter, a fair agreement may be noticed between the long-wavelength maximum and the average of the predicted components. Such an agreement appears less satisfactory for the shorter wavelength band. Minor spectral details, although not sufficiently diagnostic, vary according to expectations for trans–cis couples. Thus, the low-energy band of *trans*-$Cr(NH_3)_4(CN)_2^+$ is slightly less intense and less symmetric than that of the cis isomer. The ratio between the first and second LF maximum (trans, 1.03; cis, 1.30) proved useful for distinguishing the two forms and for determining the composition of their mixtures.

It should be pointed out that the electronic structures of the dicyanotetraamminechromium(III) ions are unusual with respect to all other known *trans*- and *cis*-$Cr(NH_3)_4X_2^{z+}$ species. While the acido groups other than cyanide are spectrochemically weaker than NH_3, CN^- is a stronger field ligand. As a consequence, the splittings of the O_h energy levels are opposite to the usual occurrence and give rise to different excited-state sequences. Since the lowest quartet excited state is quite important in the photochemistry of chromium(III),[3] the dicyanotetraammine ions are expected, and found,[24] to exhibit atypical photolabilization patterns. Thus, the lowest spin-allowed excited state of *trans*-$Cr(NH_3)_4(CN)_2^+$ is $^4B_{2g}$ instead of ^4E_g, and its antibonding character is equatorial ($d_{x^2-y^2}$) rather than axial (d_{z^2}). Likewise, for *cis*-$Cr(NH_3)_4(CN)_2^+$ such a state is ^4E instead of $^4B_2$.

As far as the monocyano complexes are concerned (Table II), they may be regarded as virtually octahedral, on the basis of the average ligand environment. The splittings of the O_h states should be very small as the two heteroligands exert higher and lower spectrochemical strengths, respectively, than NH_3.

All the cyanoammine species, like $Cr(NH_3)_5(CN)^{2+}$,[12] are characterized by a high-intensity UV band, with onset at ca. 260 nm. This absorption is interpreted as a metal-to-ligand, $d(t_{2g}) \rightarrow \pi^*,CN^-(t_{1u})$ charge-transfer (CT) transition ($^4A_{2g} \rightarrow {}^4T_{2u}$ in O_h approximation), on the grounds of the π-acceptor character of CN^- and by analogy with spectral assignments for $Cr(CN)_6^{3-}$ and other hexacyano complexes.[25] An interesting property, supporting this attribution, is the neat, organic-type series of shoulders (Table I). The constancy and the magnitude (ca. 1600 cm^{-1}) of the energy differences are consistent with a vibrational progression associated with the C–N stretch.[25] Promotion of an electron into a π*(CN) orbital is expected to lower the C–N stretching frequency (the observed decrement is about 25%) with respect to the ground electronic state. A theoretical analysis of this aspect has been recently presented for some hexacarbonyl complexes,[26] the CT transitions of which are of the same type as the present ones. The above succession is not observed in all other acidoammines possessing π-donor acido groups which give rise to ligand-to-metal, CT excitations.

When one of the CN^- ligands of the $Cr(NH_3)_4(CN)_2^+$ ions is replaced by H_2O, the CT bands drop to about half of their initial intensities, whereas the positions of the shoulders remain unaltered. Upon complete cyanide aquation, these absorptions disappear.

Luminescence Spectra. While the low-energy, spin-forbidden transitions of the dicyano species are barely seen in absorption, the reverse process, $^2E_g \rightarrow {}^4A_{2g}$ (in O_h approximation) emission, takes place in oxygen-free aqueous solution, even at room temperature. The phosphorescence is of medium intensity for both complexes. The emission maxima are given in Table I.

Infrared Spectra. *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ exhibit a sharp band near 2130 cm^{-1}, attributed to the C–N stretching. For both isomers the peak intensity is rather weak, as already noticed for $Cr(NH_3)_5(CN)^{2+}$ [12] and *trans*-[13] and *cis*-$Cr(en)_2(CN)_2^+$.[13,14] Higher resolution reveals a small splitting (2128 and 2134 cm^{-1}) in the trans complex and no splitting in the cis one. This is apparently inconsistent with the stated geometries since a splitting, if any, is expected to occur in the case of the cis configuration. Yet, all the experimental evidence other than the IR spectra (especially the isomerism of the aquation products; vide infra) unequivocally supports the assigned structures. To account for this discrepancy, one may invoke solid-state effects. However, we believe these faint IR absorptions to be inadequate for isomeric identification, as the predicted splitting may well be hidden. It is significant in this respect that no splitting at all was observed in the C–N stretching band of the analogous *cis*-$Cr(en)_2(CN)_2^+$ complex, the geometry of which was confirmed by resolution into optical antipodes.[14] The other IR features of the two dicyano compounds do not allow distinction between the two stereochemistries as is possible with diacidobis(ethylenediamine) complexes.[13,14,27]

In addition to the C–N vibration at 2139 cm^{-1}, the IR spectrum of *cis*-$Cr(NH_3)_4(Me_2SO)(CN)^{2+}$ shows the S–O stretching at 958 cm^{-1}. The frequency is lower than in free Me_2SO and denotes oxygen (rather than sulfur) coordination.[28]

Solution Behavior. The charges of the various chromium(III) cations are confirmed by the ion-exchange tests (see Experimental Section) and by electrical conductance. The monopositive dicyano complexes are selectively eluted by 0.02 M $NaClO_4$, and the dipositive monocyano compounds are displaced by 0.05 M $NaClO_4$. In parallel tests these solutions move 1+ and 2+ ions, respectively, as *trans*-$Cr(NH_3)_4Cl_2^+$ and $Cr(NH_3)_5Cl^{2+}$ but not the tripositive $Cr(NH_3)_6^{3+}$ ion. Molar conductivity determinations were performed on the species that could be isolated as solid salts. At 20 °C, 1×10^{-3} M aqueous solutions of the perchlorates gave 92, 95, and 195 Ω^{-1} cm^2 for *trans*-$Cr(NH_3)_4(CN)_2^+$, *cis*-$Cr(NH_3)_4(CN)_2^+$, and *cis*-$Cr(NH_3)_4(Me_2SO)(CN)^{2+}$, respectively. The values are in the usual ranges for 1:1 and 1:2 electrolytes.

Besides being the only satisfactory means of separation of the two dicyano complexes, chromatography provides additional stereochemical evidence. According to expectation, the same eluant displaces the nonpolar trans isomer more rapidly than the polar cis analogue. Also the solubilities of the perchlorates in water differ as expected on the basis of general experience with *trans*- and *cis*-$Cr(NH_3)_4X_2^+$ cations,[4-6] the trans isomer being far less soluble than the cis one.

Thermal Aquation. Both dicyanotetraammine ions are considerably inert in neutral or alkaline solutions at room temperature, as shown by the invariance of the respective absorption spectra for at least 12 h. By contrast, acidification ($HClO_4$) induces rapid cyanide aquation. Ligand replacement is indicated by a red shift of the LF maxima, paralleled by a drop of the characteristic CT band. The spectral modifications indicate substitution to occur in two successive steps, and the evolution of the low-energy band is peculiar to each isomer.

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In the case of the trans species, first such a feature becomes progressively more intense, and three isosbestic points persist at 449 (ϵ 41), 387 (ϵ 13), and 357 nm (ϵ 31 M^{-1} cm^{-1}), up to at least 95% loss of one CN^- group. During the subsequent, slower solvation stage, the absorbance decreases and new crossing points, appearing at 511 (ϵ 20), 412 (ϵ 11), and 361 nm (ϵ 29 M^{-1} cm^{-1}), are maintained until cyanide is totally released.

For the cis complex the absorption changes are opposite to those described above, i.e., the optical density first increases and then decreases. The lack of isosbestic behavior suggests that in this case the two CN^- ligands are displaced at comparable rates. Isosbestic points are observed at 479 (ϵ 33), 405 (ϵ 10), and 367 nm (ϵ 27 M^{-1} cm^{-1}) when the isolated *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ intermediate undergoes further CN^- aquation.

The absorption curves of the ultimate aquation products remain constant for at least 24 h at room temperature and at any pH between 0 and 3. Also the spectra of independently synthesized *trans*- and *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$ ions do not vary under the same conditions, consistent with literature data.[1,2,4] Unlike the LF bands of *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$, those of the corresponding diaquo compounds are very different, both in shape and in intensity.[4] Particularly significant for isomeric discrimination are the ratios between the first and the second maximum: 0.71 and 1.36 for trans and cis, respectively. Comparison of the aquated species with authentic samples of the diaquotetraammine complexes indicates that (within instrumental uncertainty of 3%) cyanide substitution is completely stereoretentive. The finding is in line with the known stereorigidity of chromium(III) in water.[1,23] The aquation processes may be thus summarized by eq 1–4.

$$trans\text{-}Cr(NH_3)_4(CN)_2^+ + H_2O \rightarrow trans\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+} + CN^- \quad (1)$$

$$trans\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+} + H_2O \rightarrow trans\text{-}Cr(NH_3)_4(H_2O)_2^{3+} + CN^- \quad (2)$$

$$cis\text{-}Cr(NH_3)_4(CN)_2^+ + H_2O \rightarrow cis\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+} + CN^- \quad (3)$$

$$cis\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+} + H_2O \rightarrow cis\text{-}Cr(NH_3)_4(H_2O)_2^{3+} + CN^- \quad (4)$$

The large basicity of cyanide is clearly responsible for the stability of the $Cr-CN^-$ bond at high pH values (enhanced by π back-bonding) as well as for efficient protonation of the departing ligands that favors labilization at low pH. The reactions appear to proceed mainly through acid-assisted pathways, and the catalysis is fairly strong. The behavior is quite similar to that of $Cr(NH_3)_5(CN)^{2+}$.[12]

The *trans*-dicyano complex is more reactive than the *cis*- by 1 order of magnitude. While a systematic kinetic study is in progress and will be reported elsewhere, preliminary measurements show that for acidities lower than 10^{-1} M, the dependence on $[H^+]$ of the observed rates for reactions 1–4 is linear. Approximate values for second-order rate constants at 25 °C are $k_1 \approx 8 \times 10^{-2}$, $k_2 \approx 10^{-4}$, and $k_3 \approx k_4 \approx 5 \times 10^{-3}$ M^{-1} s^{-1}.

As already mentioned, the trans-labilizing effect of CN^-, related to its π-acceptor character,[29,30] may provide a rationalization for the difference between k_1 and k_3. The relative reactivity is opposite to the usual findings, as trans-disubstituted complexes with π-donor ligands generally aquate more slowly than the cis ones.[1,2,6,29,30] Furthermore, such an effect may explain the large factor separating k_1 from k_2, as opposed to the similarity between k_3 and k_4.

Also *cis*-$Cr(NH_3)_4(Me_2SO)(CN)^{2+}$ was examined qualitatively and was found to release cyanide in acid solution. Successive loss of Me_2SO leads to *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$.

Cyanoaquo Complexes. Stereoretention during aquation of both dicyano complexes up to complete CN^- loss warrants the configurations of the respective cyanoaquo intermediates.

In the trans system, the large factor separating the rates of the first and the second solvation stage allows accumulation of large amounts (>98%) of *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$. Because of the less favorable kinetic conditions of the cis system, only mixtures of the three species participating in eq 3 and 4 can be obtained, containing at the most ca. 40% of *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$.

The two cyanoaquo isomers were isolated by ion-exchange chromatography and, although precipitation as solid salts was not possible, they were characterized in solution. The CN^-:Cr ratio resulted to be unity in each case. The LF maxima, reported in Table II and in Figure 2, confirm replacement of one cyanide by the spectrochemically weaker H_2O ligand. The absorption bands are very similar for the two forms and do not present any splitting, as already mentioned. In contrast to the parent compounds, the low-energy band of the *trans*-cyanoaquo ion is more intense than that of the cis counterpart. In addition, both complexes still exhibit the typical chromium-to-cyanide CT absorption.

Acid–Base Properties. Upon alkalinization, the color of these species turns instantaneously from yellow to orange-red as the LF maxima are displaced to longer wavelengths. The change is reversible and denotes deprotonation of the water ligand, consistently with the lower LF strength of OH^- relative to H_2O. The absorption spectra of the two cyanohydroxo cations are included in Table II and in Figure 2.

The acid strength of both $Cr(NH_3)_4(H_2O)(CN)^{2+}$ complexes was estimated by spectral analysis at various pH between 3 and 10 (at a constant ionic strength of 0.1 M). The concentration pK_a's were found to be 5.5 ± 0.1 for the trans and 5.6 ± 0.1 for the cis isomer. Although these values cannot be regarded as truly thermodynamic, a comparison appears possible with the acidity of other acidoaquotetraammine, trans/cis pairs. The available literature data[1,31,32] show a general trend: (1) the higher the σ- and π-donor abilities of the acido group, the lower the acid strength and (2) trans complexes are more sensitive to these factors than their cis analogues. The cyanoaquo ions are less acidic than the corresponding $Cr(NH_3)_4(H_2O)_2^{3+}$ ions (trans, $pK_a = 4.38$; cis, $pK_a = 4.96$),[31] in accordance with a stronger σ bonding for CN^- than for H_2O. However, there appears to be no significant difference between the acidities of the two forms, and, furthermore, the acid dissociation constants are very close to that of $Cr(NH_3)_5(H_2O)^{3+}$.[1] Both these facts may be accounted for by a balancing of the σ (strong donor) and π (acceptor) properties of CN^- that would result in an effect comparable to that induced by the (weaker σ-donor only) NH_3 ligand in the aquopentaammine complex.

Acknowledgment. Financial support of the National Research Council of Italy (CNR) is gratefully acknowledged.

Registry No. A, 72402-58-5; B, 62728-50-1; *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$, 77904-36-0; *cis*-$[Cr(NH_3)_4(CN)_2]ClO_4$, 77981-99-8; *trans*-$[Cr(NH_3)_4(CN)_2]CN$, 77904-37-1; *cis*-$[Cr(NH_3)_4(Me_2SO)(CN)](ClO_4)_2$, 77904-39-3; *trans*-$[Cr(NH_3)_4(H_2O)(CN)]^{2+}$, 74523-68-5; *cis*-$[Cr(NH_3)_4(H_2O)(CN)]^{2+}$, 74482-64-7; *trans*-$[Cr(NH_3)_4(OH)(CN)]^+$, 77904-40-6; *cis*-$[Cr(NH_3)_4(OH)(CN)]^+$, 77982-00-4; *trans*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$, 36834-73-8; *cis*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$, 42402-01-7.

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