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The Photochemistry of Some Binuclear Complexes of Chromium(III)

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Irradiation of the d-d absorption bands of trans-*aquoerythro,* [*I*], *and* trans-*chloroerythro,* [*II*], *chromium (III) leads in both cases to the* cis-*aquoerythro ion with a quantum yield of 0.20, independent of the irradiation wavelength. A second binuclear complex is produced by* NH_3 *photoaquation of* [*II*], *with quantum yields of 0.16 and 0.30 for irradiation of the first* (L_1), *and second* (L_2), *ligand-field bands, respectively.*

The photoreactions are qualitatively different from the thermal paths which involve cleavage of the OH bridge. The reaction modes are those predicted by the chromium(III) photolysis rules and stereomobility is observed in at least one Cr^{III} *center. This behavior conforms to that found in analogous mononuclear species.*

Introduction

Recently, attention has been given to rhodo and erythro complexes of Cr^{III} through X-ray structural determinations[1,2] and absorption[3,4] and emission spectra.[5] While a number of kinetic studies of these binuclear species is reported in the literature,[6] only qualitative observations exist as to their sensitivity to light.[7] The present investigation on OH-bridged chromium(III) complexes was undertaken in order to test whether their photochemistry conforms to the well characterized behavior of the mononuclear ions.[8,9]

The systems chosen were the erythro species *trans*-$[Cr(NH_3)_5(OH)Cr(NH_3)_4(H_2O)](ClO_4)_5$, [I], and *trans*-$[Cr(NH_3)_5(OH)Cr(NH_3)_4Cl](ClO_4)_4$, [II], in acid aqueous solution. The visible absorption spectra of these compounds are similar to those of the mononuclear complexes, and show two bands, indicated as L_1 and L_2,[8] due to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions (in the O_h approximation) within each chromophore. The slow thermal reaction[10] of these ions at room temperature allows accurate photolysis measurements, while the presence of two different types of ligand makes at least two modes of photoreaction possible.

Experimental Section

Materials. Trans-$[Cr(NH_3)_5(OH)Cr(NH_3)_4Cl](ClO_4)_4$, [II], was prepared according to the literature.[7] Its solution absorption spectrum shows maxima at 385 nm ($\varepsilon = 69.5$) and 502 nm ($\varepsilon = 68.8$) in good agreement with literature data.[10] The *trans* configuration was inferred from that of the thermal cleavage products.[10] *Anal.* Calcd for $N_9H_{28}O_{17}Cl_5Cr_2$: Cr, 14.70; bound Cl, 5.02. Found: Cr, 14.6; bound Cl, 5.0.

Trans-$[Cr(NH_3)_5(OH)Cr(NH_3)_4(H_2O)](ClO_4)_5$, [I], was obtained by Hg^{2+} catalyzed aquation of [II] in acid solution.[10] The maxima in the visible absorption spectrum in acid solution are at 375 nm ($\varepsilon = 67.5$) and 498 nm ($\varepsilon = 72.0$). *Anal.* Calcd for $N_9H_{30}O_{22}Cl_5Cr_2$: Cr, 13.17; N, 15.96. Found: Cr, 13.2; N, 15.5.

Cis-$[Cr(NH_3)_5(OH)Cr(NH_3)_4(H_2O)]Cl_5 \cdot H_2O$ was prepared by base hydrolysis of the n-rhodo ion.[7] *Anal.* Calcd for $N_9H_{32}O_3Cl_5Cr_2$: Cr, 21.33; N, 25.85; Cl, 36.33. Found: Cr, 21.2; N, 25.2; Cl, 36.6.

Procedures. 3 ml samples, (0.5–1) × 10^{-2} *M* in complex, in 0.5 *M* $HClO_4$, were irradiated at room temperature using a 500 W high pressure Xenon lamp. Wavelength selection was accomplished using suitable Corning glass filter combinations (see Table I) which gave bands of about 40 nm half-width. Reineckate actinometry was employed.[11] Light intensities were around 1×10^{-6} einst min^{-1} and 10-20 min irradiation periods were used. The energy absorbed was measured under conditions of incomplete absorption, using a method reported earlier.[12] The irradiated sample and an identical "dark" sample kept at the same temperature during photolysis, were ana-

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Table I. Photoaquation quantum yields for *trans*-$Cr(NH_3)_5(OH)Cr(NH_3)_4Cl^{4+}$ in acid aqueous solution at room temperature.

Glass filter combinations	Irradiating wavelength, nm	Φ_{Cl^-} mol einst^{-1}	Φ_{NH_3} mol einst^{-1}	Spectral isosbestic points, nm
CS 3-73 + CS 4-96	530 (L_1)	0.201±0.008	0.16±0.02	372; 455; 561
CS 5-57 + CS 3-72	470	0.205±0.008		
CS 7-51 + CS 4-97	380 (L_2)	0.203±0.005	0.30±0.02	370; 458; 560

lyzed in parallel in order to take into account any possible effect of simultaneous thermal processes.

Free ammonia was determined by a colorimetric procedure, described elsewhere,[13] after separation from the reaction mixture by means of a cation-exchange resin (Permutit Zeo Karb 225 SRC 13). Free chloride was determined by potentiometric titration with silver nitrate using a Radiometer TTT 1c automatic titrator. Spectral measurements were carried out with Beckman DU and Schimadzu MPS 50L spectrophotometers.

Results and Discussion

In 0.5 *M* $HClO_4$ the hydroxo bridges are not affected by acid dissociation ($pK_a \geqslant 7$).[3] The same is true for the more acidic water ligands when they are present: for instance, the *cis*-aquoerythro ion has $pK_a = 2.8$ at 20°C.[3] Thus all possible photolysis products are in their acid form. For both the complexes studied, the only dark reaction is the cleavage of the OH bridge with retention of configuration.[10] However, under the present experimental conditions any thermal process is completely negligible as shown by the fact that the spectra of the "dark" samples do not change during photolysis. Also, extrapolation from literature data[10] yields a rate constant of 1.45×10^{-5} sec^{-1} at 25°C for [II].

Trans-aquoerythro ion [I]. Irradiation of the two ligand field bands with light of 380 nm and 530 nm, respectively, causes an increase in intensity of the L_1 absorption band while L_2 decreases, with very little change in the position of both maxima, as shown in Figure 1. Two isosbestic points are observed at 455 nm and 575 nm. No free ammonia was found in the irradiated solutions. Ion-exchange experiments did not reveal any mononuclear species of Cr^{III} among the photoproducts, and were performed as follows. Photolyzed samples were absorbed in a 5 cm × 1 cm column of the above-mentioned cation exchange resin in the hydrogen form. Complete retention of any complex present occurred upon elution with 3 *M* $HClO_4$, which, in a parallel experiment, was found to move the tripositive $Cr(NH_3)_4(H_2O)_2^{3+}$ and $Cr(NH_3)_5(H_2O)^{3+}$ ions, the species produced by the thermal reaction. The spectra of irradiated solutions can be reproduced by linear combination of those of *trans* and *cis*-aquoerythro ions (see Figure 1). The only photoreaction is thus a *trans*→*cis* isomerization:

$$trans\text{-}Cr(NH_3)_5(OH)Cr(NH_3)_4(H_2O)^{5+} \xrightarrow{h\nu} cis\text{-}Cr(NH_3)_5(OH)Cr(NH_3)_4(H_2O)^{5+} \qquad (1)$$

Fitting the spectra of several independently irradiated solutions gives a quantum yield of 0.20±0.01 moles einst^{-1}, independent of irradiating wavelength.

Trans-chloroerythro ion [II]. Upon irradiation with 380 nm and 530 nm light the intensity of the L_1 absorption band increases and shows a red shift, while the intensity of L_2 decreases and is accompanied by a blue shift, as shown in Figure 2. Three spectral crossing points indicate that also for [II] a single product or constant ratio of products is involved.

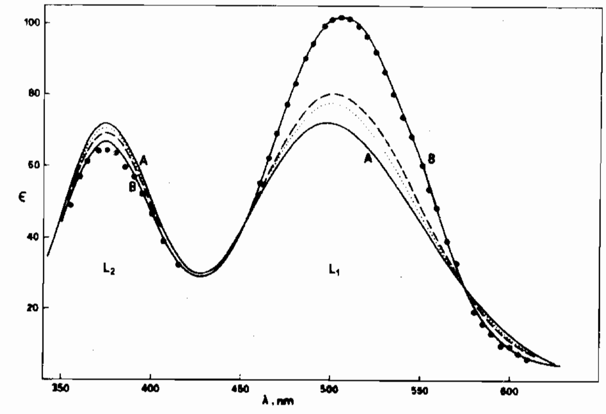

Figure 1. Absorption spectra in 0.5 *M* $HClO_4$. ——— A: *trans*-aquoerythrochromium(III), [I]; ····· and — — —: [I] after 8 and 14 min irradiation; ——— B: *cis*-aquoerythrochromium(III); ●: photoproduct (calculated).

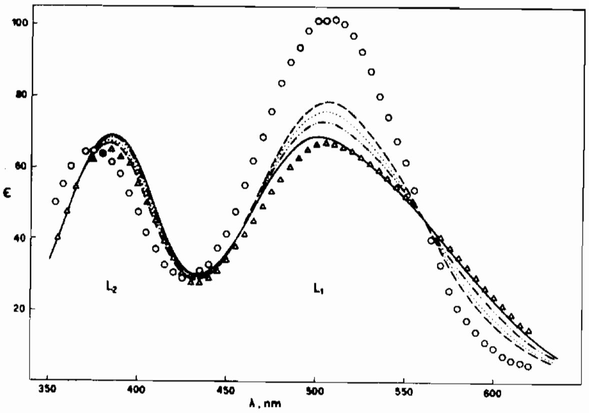

Figure 2. Absorption spectra in 0.5 *M* $HClO_4$. ———: *trans*-chloroerythrochromium(III), [II]; —··—, ······ and — — —: [II] after 6, 12, and 18 min irradiation at 530 nm; ○: Cl^- photoaquation product (calculated); Δ: NH_3 photoaquation product (calculated).

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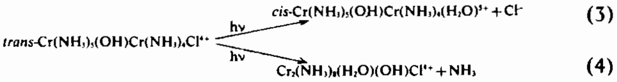
Their position depends on the irradiation wavelength (see Table I). NH_3 and Cl^- are photochemically released. The results of ion-exchange experiments, performed as above, exclude the presence of any mononuclear Cr^{III} ion such as $Cr(NH_3)_4(H_2O)Cl^{2+}$ and $Cr(NH_3)_5(H_2O)^{3+}$. Thus no photochemical cleavage of the OH bridge occurs, as suggested also by the spectral changes. Such a cleavage would cause a drastic decrease in intensity of the L_1 band, contrary to observations.

The average values of NH_3 and Cl^- photoaquation quantum yields, from at least five independent measurements, are shown in Table I. Both Φ_{NH_3} and Φ_{Cl} are of the same order of magnitude as observed when each refers to a main photoaquation path in mononuclear complexes. While the quantum yield for chloride photorelease appears to be wavelength independent, that for NH_3 depends on the irradiation wavelength. Cl^- and NH_3 photoaquation follow zero order kinetics, up to at least 20% reaction, excluding thermal steps and successive photolysis. In the few previously known cases where it was possible to accurately study two modes of photoreaction of a given Cr^{III} complex, they were found to be parallel, i.e. not to simultaneously originate from the same molecule.[14] The same behavior was assumed for the binuclear species, although the photoreactivity of each chromophore may in principle be quite independent from that of the other chromium(III) center. With this hypothesis the absorption features of the two possible photoproducts were deduced from accurate measurement of the spectral differences between irradiated and "dark" samples after photolysis with 530 nm (L_1) and 380 nm (L_2) light. The different ratios of ammonia to chloride quantum yields at the two irradiation wavelengths correspond to different relative amounts of the two photoproducts. At any wavelength, solution of the simultaneous equation

$$\begin{aligned}\Delta A_{530} &= l\{(\varepsilon_{NH_3}-\varepsilon_o)[NH_3]_{530}+(\varepsilon_{Cl}-\varepsilon_o)[Cl^-]_{530}\}\\ \Delta A_{380} &= l\{(\varepsilon_{NH_3}-\varepsilon_o)[NH_3]_{380}+(\varepsilon_{Cl}-\varepsilon_o)[Cl^-]_{380}\}\end{aligned} \quad (2)$$

yields the extinction coefficients ε_{NH_3} and ε_{Cl} for the ammonia and chloride photoaquation products, respectively. ΔA denotes the differences in absorbance mentioned previously, and $[NH_3]$ and $[Cl^-]$ the concentration of free ammonia and chloride, respectively, measured after irradiation at the specified wavelengths. ε_o represents the extinction coefficient of [II] and l the cell path-length. The spectra thus calculated are reported in Figure 2. The agreement of the absorption maxima and of the extinction coefficient of the Cl^- photoaquation product with those of the known *cis*-aquoerythro ion (Figure 1) is unlikely to be due to a coincidence and shows that the above assumption is reasonable.

Identification of the NH_3 photoaquation product appears to be more difficult since the spectra of the possible species are not known. The L_1 band of this product is shifted to the red, with respect to that of [II], consistent with replacement of NH_3 by H_2O. In addition, this band has a broad tail, a feature present only in [II] which contains a chloride ligand. Therefore, this binuclear ion is very likely to still have a coordinated Cl^-, presumably in the original configuration. The above observations are consistent with the following parallel photoreactions:



$$trans\text{-}Cr(NH_3)_5(OH)Cr(NH_3)_4Cl^{4+} \xrightarrow{h\nu} cis\text{-}Cr(NH_3)_5(OH)Cr(NH_3)_4(H_2O)^{5+} + Cl^- \quad (3)$$

$$trans\text{-}Cr(NH_3)_5(OH)Cr(NH_3)_4Cl^{4+} \xrightarrow{h\nu} Cr_2(NH_3)_8(H_2O)(OH)Cl^{4+} + NH_3 \quad (4)$$

Reactions (1) and (3) may be taken as yet a further example of the qualitative difference between the thermal and the photochemical processes in chromium(III). While in the photosubstitution of mononuclear Cr^{III} complexes such as CrA_5X of CrA_4XY, one of the photoreaction modes coincides with the thermally preferred one (even though it is not likely to originate from the same transition state), in the present case the thermal reaction mode (i.e. the cleavage of the hydroxo bridge) is completely absent in the photochemical paths. There is little doubt that the reaction is taking place exclusively from electronically excited states.

Both reactions (1) and (3) give *cis*-aquoerythro ion with the same wavelength-independt quantum yield, suggesting that the photoisomerization of [I] probably occurs through water exchange, with the same mechanism as that leading to chloride aquation of [II].

The behavior of the chloride- or water-containing chromophores conforms to that of the known analogous mononuclear Cr^{III} ions. All *trans*-diacidotetraamminechromium(III) ions investigated to date have given complexes of *cis* configuration as major photoproducts.[15,16] It now appears that these binuclear species fit the general pattern of photochemical stereomobility and thermal retention of configuration recently underlined[16] for chromium(III) aquation reactions.

Furthermore, the Cr^{III} photochemical rules[17] seem able to predict the observed reaction modes in these cases also. In reaction (3) the ligand aquated is that on the axis (OH-Cl) of the octahedron, having the weakest average ligand field strength, and the same would be true for reaction (1) if it occurred *via* water exchange. To the extent that the above rules apply in predicting the type of ligand labilized, the bridging OH group would occupy a lower position than chloride in the spectrochemical series, while the monodentate OH^- ligand is known to have a higher ligand-field strength.

It is not yet possible to establish from which Cr^{III} center the ammonia is labilized. Little information may be derived from the wavelength dependence of Φ_{NH_3} and Φ_{Cl} since it is not known to what extent the absorption relative to the two chromophores overlaps. However, a tentative intepretation may be put forward. Assuming that the two Cr^{III} centers behave

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(14) While this might be difficult to prove with systems such as $Cr(NH_3)_5X^{2+}$, due to the very low aquation quantum yield of the acido group, X, compared with that for NH_3, it has been unambiguosly established from results in our laboratory with *tran*-$Cr(NH_3)_4(NCS)Cl^+$ (Φ_{Cl} = 0.13, Φ_{NCS} = 0.23 moles eist^{-1}). See ref. 15.

(15) P. Riccieri and E. Zinato, Proceedings of the XIV 1.C.C.C. Toronto, 1972. p. 252.

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independently, the empirical rules[17] predict ammonia aquation from the hydroxo-pentaammine chromophore. This assumption is supported by the same order of magnitude for Φ_{NH_3} and Φ_{Cl} which suggest that the two ligands are unlikely to be released from the same Cr^{III} center. It is, in fact, known that when ammonia and an acido group, X, are simultaneously photoaquated from the same Cr^{III} mononuclear ion, Φ_{NH_3} is in the range 0.3-0.4 moles einst^{-1}, while Φ_X is smaller by at least one order of magnitude.[13,18,19]

On the other hand energy transfer between the two bridged Cr^{III} centers may not, in principle, be completely neglected, since it has been found to occur between mononuclear Cr^{III} complexes in solution.[20] Due to overlap of the d-d bands from each center in the spectrum, light absorption excites both simultaneously. After conversion to the lowest quartet (or doublet) excited state within each chromophore the transfer process may depopulate the higher energy one, to a greater, or lesser extent, depending on the energy difference between the levels involved. This might account for the lack of NH_3 in the photoaquation of [I].

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