

Preliminary Investigations of the Reactions of the Hexaquo Chromium(III) Ion with α,α' -Dipyridyl and with *o*-Phenanthroline

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The investigation of the reactions of the α,α' -dipyridyl-hexaquo chromium(III) system and the *o*-phenanthroline-hexaquo chromium(III) system in acid solution has been initiated. In the case of the phenanthroline system, spectral studies indicate the initial reaction to be first order in chromium and first order in phenanthroline. The dipyridyl system is analogous. In each of the two systems, a diaquobis(diamine)chromium(III) nitrate is isolated and indirect evidence indicates that this salt is the *trans*-diaquo compound. A second product, probably the *cis*-diaquo compound, remained in the solution. There was no indication of tris(diamine)chromium(III) formation.

Complexes of α,α' -dipyridyl and of *o*-phenanthroline and metal(III) ions are not usually prepared by the direct addition of the bases to the aqueous metal(III) salt solution because of the possibility of hydroxide precipitation (*e.g.* chromium¹) or of the formation of some basic salt (*e.g.* iron²). The usual path of preparation is the reaction of the base with a lower oxidation state metal ion and oxidation of this complex to the desired (III)-oxidation state (*e.g.* chromium^{3,4}).

We find in the case of the hexaquo chromium(III) ion that if rather than using the free base, the acid salt of the base is used, no hydroxide precipitation occurs and complex formation takes place. Solutions of various concentrations of dipyridylum nitrate and hexaquo chromium(III) nitrate when mixed in the pH range 1.5—3.0 slowly change colour from the characteristic hexaquo chromium(III) ion colour to wine red. The change in light absorption was followed with a Cary recording spectrophotometer. Fig. 1 gives the spectrum at various times of a sample containing dipyridylum nitrate and hexaquo chromium(III) nitrate maintained at 60°C.

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THE REACTION OF *o*-PHENANTHROLINE WITH HEXAQUO CHROMIUM(III) ION IN ACID SOLUTION

The *o*-phenanthroline-hexaquo chromium(III) system exhibits similar behaviour as shown in Fig. 1 for the dipyriddy system. The phenanthroline system was extensively investigated by following the change in visible absorption of samples of various reactant concentrations in constant salt medium of 1.0 M sodium nitrate maintained at 60°C. The short wavelength band of hexaquo chromium(III) ion is obscured by the nitrate and the phenanthroline absorptions, but the long wavelength band at 574 m μ with an $\epsilon_{\max.}$ of 15.5 was free of these interferences. The band envelope of the reactant band, intermediate band and the products bands changed with time and the maximum asymptotically approached 505 m μ with an apparent $\epsilon_{\max.}$ of 54.

An orange-red salt separated from this reaction mixture. It had an absorption band with a maximum at 495 m μ and an $\epsilon_{\max.}$ of 40.7 in a solution 1.0 M in sodium nitrate indicating the presence of a second, more strongly absorbing product, which was not isolated. The absorbance of the liquid remaining from the crystallization indicated that this product had an approximate maximum at 510 m μ and an approximate $\epsilon_{\max.}$ of 60. Examination of the family of curves obtained from the time study of a single sample indicates that these envelopes could be explained by four bands: the reactant chromium band, an intermediate band at 525–530 m μ and two product bands, one at 495 m μ and another at 510 m μ .

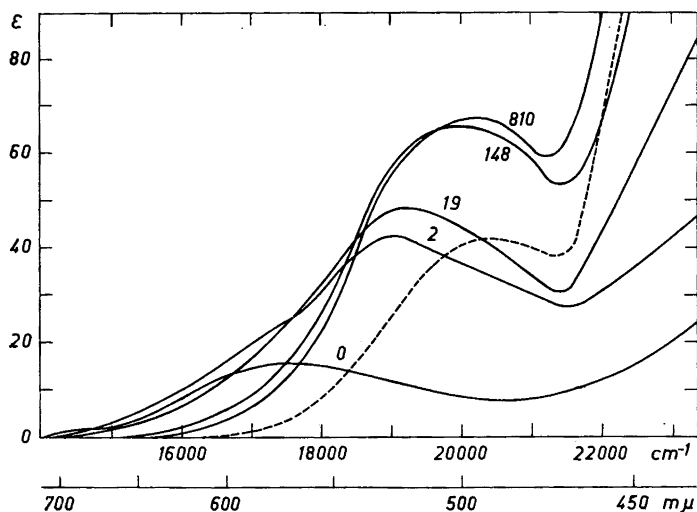


Fig. 1. Spectra of a mixture 0.0214 M in $\text{Cr}(\text{H}_2\text{O})_6(\text{NO}_3)_3$, 0.171 M in dipy \cdot HNO_3 , 1.0 M in NaNO_3 and 0.01 M in HNO_3 followed in time at 60°C. The numbers on the solid line spectra indicate the time in hours that the mixture had been maintained at 60°C before samples were taken and measured at 25°C. The dashed line spectrum is that of $[\text{Cr}(\text{dipy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$ isolated from the mixture.

Abseissae: Wave number in cm^{-1} , and wavelength in m μ .

Ordinate: The molar decadic extinction coefficient ϵ .

Table 1. Initial rate dependence of chromium ion concentration, phenanthroline ion concentration, and hydrogen ion concentration.

$[\text{Cr}(\text{H}_2\text{O})_6^{3+}]$	$[\text{phenH}^+]$	$[\text{H}_3\text{O}^+]$	$[\text{Cr}^{3+}]$ reacted in 100 h at 60°C.*
0.0214	0.0288	0.12	0.00026
0.0214	0.0576	0.12	0.00056
0.0214	0.0864	0.12	0.00075
0.0214	0.0288	0.040	0.00086
0.0214	0.0576	0.040	0.00162
0.0214	0.0864	0.040	0.00259
0.0214	0.0288	0.020	0.00186
0.0214	0.0576	0.020	0.00308
0.0214	0.0864	0.020	0.00458
0.0117	0.0390	0.013	0.00457
0.0234	0.0390	0.013	0.00633
0.0351	0.0390	0.013	0.00842

The initial rate of change of the band envelope varied directly with chromium ion concentration and with phenanthroline ion concentration. In the pH range (1.0—3.0) this initial rate is inhibited by the hydrogen ion concentration approximately inversely first order (see Table 1). These experiments lead to an initial rate law:

$$\frac{+d[\text{H}^+]}{dt} = k \frac{[\text{phenH}^+][\text{Cr}(\text{H}_2\text{O})_6^{3+}]}{[\text{H}^+]} \quad (1)$$

A series of experiments was tried where the release of hydrogen ions was followed at 60°C by a Radiometer Titrator maintaining pH = 2.2 by the controlled addition of standard sodium hydroxide. These experiments met with but limited success; one moderately successful run with the concentrations: $[\text{Cr}(\text{H}_2\text{O})_6^{3+}] = 0.0214 \text{ M}$, $[\text{phenH}^+] = 0.0856 \text{ M}$, and pH = 2.20 gave an initial proton release of 0.149 mM per hour. Inserting in (1) this run gives a rate constant of $k = 0.513 \times 10^{-3} \text{ h}^{-1}$.

Since the acid salt of the base is also in equilibrium with the free base and the hydrogen ions ($pK_a = 4.96$ at 25°C⁵ and ~ 4.3 at 60°C)

$$[\text{phen}] = 10^{-4.3} \frac{[\text{phenH}^+]}{[\text{H}^+]} \quad (2)$$

Substitution of (2) into (1) gives:

$$\frac{+[\text{H}^+]}{dt} = 10.3 \cdot [\text{phen}] [\text{Cr}(\text{H}_2\text{O})_6^{3+}] \quad (3)$$

This rate expression with $k_1 = 10.3 \text{ M}^{-1}\text{h}^{-1}$ (or $2.85 \times 10^{-3} \text{ M}^{-1} \cdot \text{sec}^{-1}$) confirms that a mono(diamine) complex corresponding to the intermediate band at 525—530 μm is the first reaction product.

* Estimated from the optical density at 505 μm of the samples at the end of 100 h compared to the optical density of the samples at this wavelength after a very long time (as much as 1 500 h).

PREPARATION OF SALT ISOLATED FROM REACTION MIXTURE

The first samples of the salt obtained were a by-product of the spectral-kinetic studies. A more direct preparation is by refluxing 100 ml of a mixture of 0.1 M $\text{Cr}(\text{H}_2\text{O})_6(\text{NO}_3)_3$ and 0.4 M phen HNO_3 in water for a period of 8 h. Four aliquots of sodium hydroxide were added to the reflux mixture to neutralize the hydrogen ions released at the end of 1, 3, 5, and 7 h. At the end of this period sufficient nitric acid was added to lower the pH to 1; approximately one half of the water was evaporated and upon cooling the salt crystallized out. The salt was recrystallized from 0.1 M nitric acid, washed with 0.1 M nitric acid and dried in a desiccator over sulfuric acid. The approximate yield under these conditions based on the total chromium was 60 %.

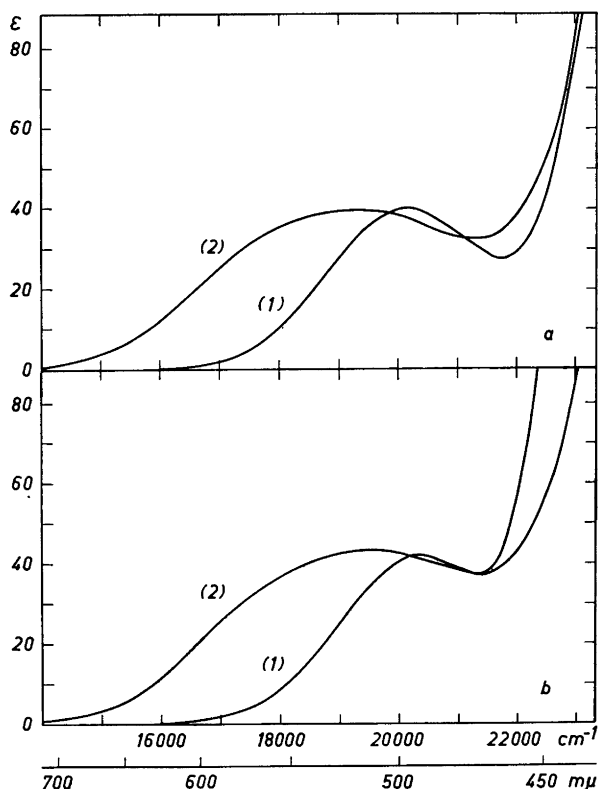
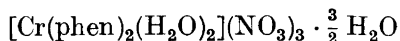


Fig. 2. Spectra of the bis(diamine)chromium(III) complexes in 1 M NaNO_3 . a: Spectra of the $[\text{Cr}(\text{phen})_2(\text{H}_2\text{O})_2]^{3+}$ (1) and $[\text{Cr}(\text{phen})_2(\text{OH})_2]^+$ (2). b: Spectra of the $[\text{Cr}(\text{dipy})_2(\text{H}_2\text{O})_2]^{3+}$ (1) $[\text{Cr}(\text{dipy})_2(\text{OH})_2]^+$ (2). Abscissae and ordinate: Same as Fig. 1.

A carbon hydrogen nitrogen analysis * of the isolated salt indicated a C:H:N ratio of 24:23:7 and a possible formula of:



and a formula weight of 661. (Found: C 43.30; H 3.40; N 14.71; Cr 7.60. Calc. for $\text{CrC}_{24}\text{H}_{23}\text{N}_7\text{O}_{12\frac{1}{2}}$: C 43.65; H 3.48; N 14.81; Cr 7.85).

S. E. Rasmussen of this laboratory determined the dimensions of the unit cell and found the crystal to be orthorhombic and probably of the space group $Pba2, C^8_{2v}$ No. 32.

The axes are:

$$a = 9.49 \text{ \AA} \quad b = 32.2 \text{ \AA} \quad c = 9.03 \text{ \AA}$$

This combined with the density of 1.57 g/cm^3 gives a formula weight of 4×652 . A general position of the space group is fourfold.

The absorption spectrum of this salt varied with the pH. Fig 2a gives the spectrum of the diaquo salt in 0.1 M nitric acid and also the spectrum of the corresponding dihydroxo complex in 0.1 M sodium hydroxide. The potentiometric titration, using glass and calomel electrodes, of the salt in 1 M sodium nitrate solution gives a curve typical of a dibasic acid with approximate $\text{p}K_1 = 3.4$ and $\text{p}K_2 = 6.0$ and a formula weight of 666. The approximate solubility of the salt in water is 0.05 moles per liter.

A solution of the purified salt dissolved in an aqueous solution of 1 M sodium nitrate and 0.16 M phenanthroline nitrate and placed in a thermostated oven at 60°C for a period of six weeks showed no shift in the wavelength of absorption but underwent a decrease in absorbance, a behaviour that cannot be explained by the formation of a tris(phenanthroline)chromium(III) ion with its lower wavelength of absorption nor by interconversion of the salt to the more strongly coloured form that we have as yet been unable to obtain from the reaction mixture. Such a behaviour could be explained by postulating that the equilibrium is at a position intermediate between the mono(phenanthroline)chromium(III) ion and the bis(diamine) ion for these concentrations.

THE α, α' -DIPYRIDYL-CHROMIUM(III) REACTION

The case of the reaction of α, α' -dipyridylum nitrate with hexaquo chromium(III) nitrate in a 1.0 M aqueous sodium nitrate solution of initial $\text{pH} = 2.0$ is very similar to the more extensively studied phenanthroline case. The main differences are: (1) the initial rate of reaction is nearly tenfold greater for the same initial concentrations; (2) the mono(dipyridyl) chromium band is distinctly resolved from the reactant band and product bands; and, (3) the bis(diamine) salt isolated was formed to a lesser extent, more soluble and more difficult to crystallize.

Fig. 1 illustrates the dipyridyl case. The solution was 0.0214 M in hexaquo chromium(III) nitrate, 0.171 M in dipyridylum nitrate, 1.0 M in sodium

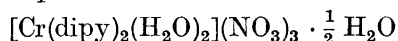
* We are indebted to Mr. Preben Hansen who carried out the C, H, and N determinations in Prof. K. A. Jensen's laboratory.

nitrate and initial pH = 2.0. The band envelopes of the reactant band, intermediate band and the products bands changed with time and asymptotically approached 495 $m\mu$ and an apparent $\epsilon_{\max.} = 68$. An orange salt isolated from this mixture had an absorption band with a maximum at 490 $m\mu$ and an $\epsilon_{\max.} = 42.8$. Again, a more strongly absorbing second product with a somewhat different wavelength of absorption is indicated but not isolated.

PREPARATION OF DIAQUOBIS(DIPYRIDYL)CHROMIUM(III) NITRATE

A direct preparation of this salt is effected by the refluxing of 100 ml of an aqueous mixture 0.1 M in $\text{Cr}(\text{H}_2\text{O})_6(\text{NO}_3)_3$ and 0.4 M in dipy HNO_3 for a period of 4 h periodically neutralizing the hydrogen ions released with sodium hydroxide. At the end of this period the unreacted dipyridyl was precipitated from the solution with sodium hydroxide and the solution filtered. The pH of the filtrate is lowered to 1 with nitric acid and it is evaporated to approximately 20 ml. The solution is allowed to stand for several hours and crystals form. These are recrystallized from 0.1 HNO_3 , washed with 0.1 M HNO_3 and dried over sulfuric acid. Approximate yield based on the chromium is 35 %.

A carbon-hydrogen nitrogen analysis of this orange salt indicated a C:H:N ratio of 20:21:7 and a possible formula of:



and a formula weight of 595. (Found: C 40.70; H 3.57; N 16.55. Calc. for $\text{CrC}_{20}\text{H}_{21}\text{N}_7\text{O}_{11\frac{1}{2}}$: C 40.35; H 3.53; N 16.45).

The absorption spectrum varied with pH. Fig. 2b gives the spectrum of the diaquo salt in 0.1 M nitric acid and also the spectrum of the dihydroxo complex in 0.1 M sodium hydroxide. The potentiometric titration of the salt in 0.1 M sodium nitrate solution also gives a curve typical of a dibasic acid with approximate $\text{p}K_1 = 3.5$ and $\text{p}K_2 = 6.1$ and a formula weight of 586. The approximate solubility of the salt in water is 0.6 moles per liter.

DISCUSSION

Diamines such as α, α' -dipyridyl and *o*-phenanthroline will react directly with hexaquo chromium(III) in aqueous solution in the pH range 1.5—3.0. A mono complex is first formed and the reaction continues to form a bis(diamine) ion. There is no direct evidence as to whether the diaquobis(diamine) ions formed are the *cis*- or the *trans*-diaquo ions. In complex ions of this type the *trans* forms are the lesser soluble entities. In the case of the *cis*- and the *trans*-diaquobis(ethylenediamine)chromium(III) ions, Woldbye⁶ reports that the long wavelength chromium band has an $\epsilon_{\max.}$ of approximately 30 in the case of the *trans* compound but an $\epsilon_{\max.}$ of over 60 for the *cis* compound. Therefore, we believe the salt isolated to be the *trans*-diaquo compound and that the more soluble, more strongly light absorbing *cis*-diaquo compound remains in solution. The rates of formation are slow but the rates of *cis-trans* interconversion and decomposition are very slow, even at 100°C; thus indicating a large stability constant.

No evidence of a tris(diamine) complex ion formation was detected. The principal *trans*-diaquo product is extremely stable and cannot add a third diamine molecule without rearrangement and the less abundant *cis*-diaquo compound must react with the excess amine exceedingly slowly.

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REFERENCES

1. Pfeiffer, P. and Werdelmann, B. *Z. anorg. Chem.* **263** (1950) 31.
2. Blau, F. *Monatsh.* **19** (1898) 647.
3. Hammett, L. P., Walden, G. H. and Edmonds, S. M. *J. Am. Chem. Soc.* **56** (1934) 1092.
4. Barbieri, G. A. and Tettamanzi, A. *Atti reale accad.nazl. Lincei* **15** (1932) 877.
5. Lee, T. S., Kolthoff, I. M. and Leussing, D. L. *J. Am. Chem. Soc.* **70** (1948) 2348.
6. Woldbye, F. *Acta Chem. Scand.* **12** (1958) 1079.

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