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Characterization of *cis*-Chloroaquobis(2,2'-dipyridyl)chromium(III) Cation, and Kinetics of Primary and Secondary Aquation of *cis*-Dichlorobis(2,2'-dipyridyl)chromium(III) Cation[1a,1b]

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Aquation of cis-$Cr(dipy)_2Cl_2^+$ *in 0.1-0.5* F *HCl* ($\mu=$ *0.1-0.5* M, *NaCl*) *has been studied spectrophotometrically at 50-70°. At 70°* ($\mu=0.5$ M) *the first-order rate constant is* $(5.4\pm0.5)\times10^{-5}$ sec^{-1}, *independent of the acid concentration;* $E_a=23.4\pm0.8$ *kcal* $mole^{-1}$ *and* log PZ(sec^{-1})$=10.62\pm0.55$. *The product is the previously not fully characterized* cis-$Cr(dipy)_2(OH_2)Cl^{2+}$, *with no evidence for concurrent aquation* via *Cr–N bond rupture. At 70° in 0.13* F *HCl or* HNO_3 ($\mu=$ *0.13* M) cis-$Cr(dipy)_2(OH_2)^{2+}$ *appears to aquate concurrently to* cis-$Cr(dipy)_2(OH_2)_2^{3+}$ *and to an unidentified species of charge* $\geqslant 4+$, *perhaps* $Cr(dipy)(dipyH)(OH_2)_3^{4+}$ (via *the intermediate* $Cr(dipy)(dipyH)(OH_2)_2Cl^{3+}$), *with a total first-order rate constant of* $(6.9\pm0.8)\times10^{-5}$ sec^{-1}. *The* cis-*chloroaquo species has been fully characterized, and its visible absorption spectrum is reported. The new pink complex* $Cr(dipy)(OH_2)_4^{3+}$ *has been chromatographically isolated from a 0.1* F *HCl solution of* cis-$Cr(dipy)_2Cl_2^+$ *which had been aged at 70° for 50 days.*

Introduction

No kinetic investigations of aquation, base hydrolysis, anation, isomerization, or redox reactions of bis(2,2'–dipyridyl) complexes of chromium(III) appear to have been reported, except for the isotope exchange reaction[2] between solvent water and fully ^{18}O-labeled oxalatobis(2,2'–dipyridyl)chromium(III) cation, $Cr(dipy)_2ox^+$,[3] the substitution of a 2,2'dipyridyl ligand of *cis*-dichlorobis(2,2'-dipyridyl)chromium(III) cation, *cis*-$Cr(dipy)_2Cl_2^+$, by solvent dimethylsulfoxide,[4] and two qualitative observations[4,5] on aquation of *cis*-$Cr(dipy)_2Cl_2^+$. Identification of the product of the *cis*-$Cr(dipy)_2Cl_2^+$ aquation was not reported, and indeed one possible aquation product, namely, *cis*-chloroaquobis(2,2'-dipyridyl)chromium(III) cation, *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$, has not been previously fully characterized.

Accordingly, we report here a quantitative kinetic investigation of the aquation of *cis*-$Cr(dipy)_2Cl_2^+$ and a qualitative study of the aquation of *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$, in order to compare the aquation kinetic parameters for these complexes having aromatic heterocyclic diamine ligands with those for the more familiar bis(ethylenediamine) and related aliphatic bis(diamine) and tetraamine complexes of chromium(III). An additional motivation has been to learn if aquation with Cr–N bond rupture competes with aquation *via* Cr–Cl bond rupture, as has been found to be the case for certain diacidobis(diamine)chromium(III) complexes.[6] A complete characterization of *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$, including its visible absorption spectrum, is also reported. Isolation of the new pink complex $Cr(dipy)(OH_2)_4^{3+}$ is also described.

There has been much confusion in the literature regarding the existence of *cis* and *trans* configurations of $Cr(dipy)_2Cl_2^+$, $Co(dipy)_2Cl_2^+$, and $Co(phen)_2Cl_2^+$, and the composition of the cobalt complexes.[7] A single-crystal X-ray structure analysis of violet $[Co(phen)_2Cl_2]Cl\,.\,3H_2O$ has shown[8] that the two chloro ligands are *cis* to each other. Gibson and McKenzie[4] have shown by the X-ray powder diffraction patterns that this compound and $[Cr(phen)_2Cl_2]Cl\,.\,4H_2O$ (their α polymorph) are isomorphous, and have also found red-brown $[Cr(dipy)_2Cl_2]Cl\,.\,2H_2O$ and violet $[Co(dipy)_2Cl_2]Cl\,.\,2H_2O$ as commonly prepared[9,10] to be isomorphous. They concluded from the d–d reflectance spectra of these solids that each has the *cis*-dichloro configuration. Andersen *et al.*[11] also concluded that $M(AA)_2Cl_2^+$ ($M=Cr^{III}$, Co^{III}, Rh^{III}, Ir^{III}; AA

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(2) J.A. Broomhead, I. Lauda, and P. Nimmo, *Chem. Commun.*, 652 (1969).

(3) Abbreviations used: en=ethylenediamine, $H_2N(CH_2)_2NH_2$; pn=propylenediamine, $CH_3CH(NH_2)CH_2NH_2$; ibn=isobutylenediamine, $H_2NCH_2C(CH_3)_2NH_2$; dien = diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$; trien = triethylenetetraamine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; dipy = 2,2'-dipyridyl, $(C_5H_4N)_2$; phen = 1,10-phenanthroline, $C_{12}H_8N_2$; ox = oxalate dianion, $C_2O_4^{2-}$.

(4) J. G. Gibson and E. D. McKenzie, *J. Chem. Soc., A*, 2637 (1969).

(5) J. Josephsen and C. E. Schäffer, *Chem. Comm.*, 61 (1970)

(6) C. S. Garner and D. A. House, « Transition Metal Chemistry,» Vol. 6, R. L. Carlin, editor, Marcel Dekker, Inc., New York, 1970, p. 192-198.

(7) The literature is too voluminous to cite here. Ref. 4 gives a survey of many of the claims and counter-claims, with references. See also, D. M Palade, *Zh. Neorg. Khim.*, *10*, 2772, 2776 (1969); *Russ. J. Inorg. Chem.* (*Engl. Transl.*), *10*, 1459, 1461 (1969).

(8) A. V. Ablov, A. Yu. Kon, and T. I. Malinovskii, *Dokl. Akad. Nauk SSSR*, *167*, 1051 (1966); *Proc. Acad. Sci* (*U.S.S.R.*), *167*, 410 (1966).

(9) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(10) F. M. Jaeger and J. A. van Dijk, *Z. Anorg. Allgem. Chem.*, *227*, 273 (1936).

(11) P. Andersen, J. Josephsen, G. Nord (Waind), C. E. Schäffer, and R. L. Tranter, *Chem. Commun.*, 408 (1969).

= dipy, phen) and related diacido complexes have the *cis* configuration, based upon synthesis by cleavage of the corresponding di-μ-hydroxo-bis(AA) complexes and interconversion of $Cr(AA)_2ox^+$ and the difluoro, dichloro, and diaquo analogues (such evidence assumes no isomerization in these conversions, but it is unlikely that isomerization would have occurred in every case). Palade[12] has concluded from structure computations using bond distances from *cis*-$[Co(phen)_2Cl_2]Cl \cdot 3H_2O$[8] that the *trans* isomer is incapable of existence. He has inferred that *trans*-$Co(dipy)_2Cl_2^+$ is also too unstable to exist; the same should be true of the Cr^{III} analogues in view of the similarity of Cr—N and Co—N bond distances. Thus, there now seems little doubt of the *cis* configuration and the probable nonexistence of the *trans* forms of all these complexes, a point relevant to the stereochemistry of the systems we discuss below.

Experimental Section

Cis-*Dichlorobis(2,2'dipyridyl)chromium(III) Chloride Dihydrate.* This compound was prepared as described earlier.[9] *Anal.* Calcd for $[Cr(dipy)_2Cl_2]Cl \cdot 2H_2O$: C, 47.50; H, 3.98; N, 11.05; Cl, 20.98; Cr, 10.31. Found: C, 47.66; H, 3.93; N, 10.68; Cl, 20.76; Cr, 10.40. The visible absorption band (in 1:1 MeOH–H_2O) was at 555 nm (ε 45.5), in agreement with the value 555 nm (no ε) reported earlier[13] in the same solvent. The compound was shown to be a dichloro (rather than a chloroaquo) complex by dissolution in 0.01 *F* HNO_3, absorption on a H^+ DowexAG50W-X4 cation-exchange resin, and elution of the complex with 4 *F* HNO_3 (after first washing out and discarding the free Cl^-); the Cl:Cr atom ratio of the eluted complex was 2.00.

cis-*Chloroaquobis(2,2'-dipyridyl)chromium(III) Cation.* This complex was isolated in solution by cation exchange chromatography of aged *cis*-$Cr(dipy)_2Cl_2^+$ solutions. Typically, 0.38 g (0.75 mfwt) of *cis*-$[Cr(dipy)_2Cl_2]Cl \cdot 2H_2O$ in 200 ml of 0.1 *F* HCl was aged at 70° for 2 hr, then charged onto a 15-cm × 1-cm diameter column of H^+ Dowex AG50W-X2 (200-400 mesh) resin at *ca.* 20°. Free Cl^- was washed out with 1000 ml of 0.001 *F* HNO_3 and discarded. *Ca.* 3000 ml of 0.3 *F* HNO_3 was used to separate the adsorbed species into three bands: a bottom brown band of unreacted dichloro complex, a middle red band of the chloroaquo complex, and an upper weak yellow of diaquo complex. The latter was physically removed and discarded. The red band was then physically removed, put on top of a fresh 1-cm column of resin, and eluted with 40 ml of 4 *F* HNO_3, giving a solution *ca.* 0.9 m*M* in *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$, free of other chromium species. Eluent flow rate was 2 ml/min, and typical separations required 4-6 days.

cis-*Diaquobis(2,2'dipyridyl)chromium(III) Cation.* Attempts were made to prepare *cis*-$[Cr(dipy)_2(OH_2)_2](NO_3)_3 \cdot 0.5H_2O$ by the method of Inskeep and Bjerrum,[14,15] but even with additional recrystallization and other modifications, the product was grossly impure, as shown by Cr analysis (2.96% *vs.* 8.73% calcd) and visible absorption spectrum (band at 493 nm (ε 14.4) *vs.* 490 nm (ε 42.8) given in Ref. 14).

A sample of *cis*-$[Cr(dipy)_2(OH_2)OH](ClO_4)_2$[16] was dried for 2 hr at 60°; portions dissolved in HCl or HNO_3, which rapidly converts the hydroxoaquo complex to the diaquo complex, gave absorption bands at 448 (ε 92.4) and 492 nm (ε 43.7), in satisfactory agreement with the values 448 (ε 94.2) and 492 nm (ε 44.8) reported by Schäffer.[16]

Tetraaquo-2,2'-dipyridylchromium(III) Cation. The pink complex $Cr(dipy)(OH_2)_4^{3+}$ was isolated as follows from a 0.1 *F* HCl solution of *cis*-$[Cr(dipy)_2Cl_2]Cl \cdot 2H_2O$ aged at 70° for 50 days, then charged onto a 21-cm × 1cm diameter column of H^+ Dowex AG50W-X2 (200-400 mesh) resin at *ca.* 20°. Free Cl^- was washed out with 500 ml of 0.01 *F* HNO_3 and discarded, then 2000 ml of 0.4 *F* HNO_3, followed by 2000 ml of 0.6 *F* HNO_3, was used at 2 ml/min to bring a red band (Cl:Cr atom ratio of 0.96, and absorption band at 516 nm (ε 40.2), similar to the band of *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$) to the bottom of the column, leaving a separate pink band in the middle of the column, leaving a separate pink band in the middle of the column, and at the top a separate yellow-orange band (*cis*-$Cr(dipy)_2(OH_2)_2^{3+}$). The top band was physically removed, then the pink central band was physically removed, placed on a fresh 1-cm resin column, and the pink complex eluted with 100 ml of 4 *F* HNO_3. See Results section for characterization of the pink species.

Other Complexes. Together with *cis*-$[Cr(dipy)_2Cl_2]Cl \cdot 2H_2O$, the complexes $[Cr(dipy)_2ox]Cl \cdot 4H_2O$,[17] $[Cr(en)_2ox]Cl \cdot 3H_2O$,[18] and *cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$[19] were used to study cation-exchange elution behavior of bis(dipy) and bis(en) analogues. Purity was checked by agreement of the visible absorption maxima with published values.

Other Chemicals. These were as described previously.[20]

Chemical Analyses. Analyses for Cr, Cl, C, and H were performed as described earlier.[20] Analyses for N were made by a micro Kjeldahl method.

Kinetic Runs. Procedures were similar to those described previously,[20] except that reaction solutions were torch-sealed in Pyrex ampoules because of the

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[12] D. M Palade, *Zh. Neorg. Khim. 14*, 763 (1969); *Russ. J. Inorg. Chem. (Engl. Transl.)*, *14*, 399 (1969).

[13] W. A. Baker, Jr., and M. G. Phillips, *Inorg. Chem.*, *4*, 915 (1965).

[14] R. G. Inskeep and J. Bjerrum, *Acta Chem. Scand.*, *15*, 62 (1961)

[15] The claim in Ref. 14 that a *trans* isomer of the diaquo complex was also prepared was later retracted in R. G. Inskeep and M. Benson, *J. Inorg. Nucl. Chem.*, *20*, 290 (1961).

[16] Obtained through the kindness of Prof. C. E. Schäffer of the H. C. Orsted Institute, Copenhagen, Denmark. The compound had been prepared as described in Ref. 11; analyses were reported by Prof. Schäffer as C, 39.8; H, 3.20; N, 9.24; Cl, 11.91 - in good agreement with calcd values of C, 40.0; H, 3.20; N, 9.35; Cl, 11.90.

[17] J. A. Broomhead, M. Dwyer, and N. Kane-Maguire, *Inorg. Chem.*, *7*, 1388 (1968).

[18] F. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939).

[19] D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, *83*, 4152 (1961).

[20] C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta*, *1*, 17 (1967)

higher reaction temperatures. The ampoules were wrapped with Al foil to exclude light as a routine precaution.

Results

Characterization of cis-*Cr(dipy)$_2$(OH$_2$)Cl^{2+}*. A compound described as [Cr(dipy)$_2$(OH$_2$)Cl](ClO$_4$)$_2$. 2H$_2$O has been reported by Tucker *et al.*,[21] who made it by a complicated electrolytic reduction procedure. Analyses for C, H, N, Cr, and total Cl were in good agreement with values calculated for the assumed formula, and the compound probably is the chloroaquo complex since a positive test for free Cl$^-$ was obtained only after the salt was heated. No geometric configuration was assigned and no spectral data were reported.

Bayazitova, Zelentsov, and Spitsyn[22] claimed that use of the method of Burstall and Nyholm,[9] or the modification of Baker and Phillips,[13] for the preparation of [Cr(dipy)$_2$Cl$_2$]2H$_2$O gave [Cr(dipy)$_2$(OH$_2$)Cl]Cl$_2$. nH$_2$O instead. Bayazitova *et al.* reported they could also prepare the chloroaquo compound by a simpler method in which CrCl$_3$. 6H$_2$O was used instead of anhydrous CrCl$_3$. No geometric configuration was assigned and no spectral data were given. Analyses for Cr, N, and H$_2$O were in good agreement with values calculated for the assumed formula. However, [Cr(dipy)$_2$Cl$_2$]Cl . 2H$_2$O and [Cr(dipy)$_2$(OH$_2$)Cl]Cl$_2$. H$_2$O have the same elemental composition, and one cannot be certain which of these compounds was made by Bayazitova *et al.*, although analyses for «2Cl» and «3Cl» suggest the compound may have been the chloroaquo compound. On the other hand, the methods of Burstall and Nyholm and of Baker and Phillips, as well as the simpler method of Bayazitova *et al.*, have given only *cis*-[Cr(dipy)$_2$Cl$_2$]Cl . 2H$_2$O in our hands.[23]

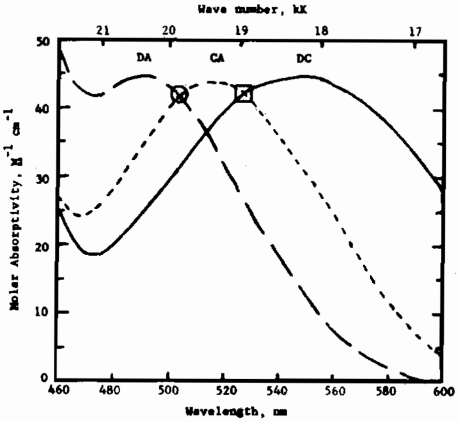

Figure 1. Visible absorption spectra of diacidobis(2,2'-dipyridyl)-chromium(III) complexes in 4 *F* HCl at 20-25°: DC, *cis*-Cr(dipy)$_2$Cl$_2$$^+$; CA, *cis*-Cr(dipy)$_2$(OH$_2$)Cl^{2+}; DA, *cis*-Cr-(dipy)$_2$(OH$_2$)$_2$$^{3+}$.

We have synthesized *cis*-Cr(dipy)$_2$(OH$_2$)Cl^{2+} by aquation of *cis*-Cr(dipy)$_2$Cl$_2$$^+$ and isolated the chloroaquo complex in aqueous solution, free of other chromium species (see Experimental Section). The visible absorption spectrum is given in Figure 1. The complex was characterized as follows.

As shown by the proper isosbestic points (see below) the chloroaquo complex is essentially the sole direct product of aquation of *cis*-Cr(dipy)$_2$Cl$_2$$^+$, and aquates partly to *cis*-Cr(dipy)$_2$(OH$_2$)$_2$$^{3+}$. This not only indicates the intermediate is the chloroaquo complex, but also suggests it has the *cis* configuration, since in the aquation of all Cr^{III} substrates of the type *cis*-Cr-(AA)$_2$XY^{n+} (AA= en and other diamines) studied so far there is 100% stereoretention within experimental error.[24] Moreover, the work of Palade and others cited in the Introduction sugests that *trans*-diacidobis-(2,2'-dipyridyl)chromium(III) complexes are probably too unstable to exist.

Table I. High-Wavelength d-d Absorption Maximum for Cr(dipy)$_2$XY^{n+} and Cr(dipy)(OH$_2$)$_4$$^{3+}$ and Their Cr^{III} Aliphatic Amine Analogues at 20—25° ^{a}

Complex	λ_{max}, nm
cis- Cr(dipy)$_2$Cl$_2$$^+$ ^{b}	550 (44.2)
cis-α-Cr(trien)Cl$_2$$^+$ ^{c}	535 (95.5)
cis-Cr(pn)$_2$Cl$_2$$^+$ ^{d}	530 (80.6)
cis-Cr(en)$_2$Cl$_2$$^+$ ^{e}	528 (70.6)
trans-Cr(pn)$_2$Cl$_2$$^+$ ^{f}	577 (27.9)
trans-Cr(en)$_2$Cl$_2$$^+$ ^{e}	578 (24.5)
cis-Cr(dipy)$_2$(OH$_2$)Cl^{2+} ^{b}	517 (43.5)
cis-β-Cr(trien)(OH$_2$)Cl^{2+} ^{c}	515 (83.5)
cis-Cr(pn)$_2$(OH$_2$)Cl^{2+} ^{d}	511 (74.7)
cis-Cr(en)$_2$(OH$_2$)Cl^{2+} ^{e}	510 (71.4)
trans-Cr(en)$_2$(OH$_2$)Cl^{2+} ^{e}	546 (20.5)
cis-Cr(dipy)$_2$(OH$_2$)$_2$$^{3+}$ ^{b}	492 (44.5)
cis-Cr(pn)$_2$(OH$_2$)$_2$$^{3+}$ ^{d}	487 (76.0)
cis-Cr(en)$_2$(OH$_2$)$_2$$^{3+}$ ^{g}	484 (67.0)
trans-Cr(en)$_2$(OH$_2$)$_2$$^{3+}$ ^{g}	508 (sh, 23)
Cr(dipy)(OH$_2$)$_4$$^{3+}$ ^{b}	528 (29.5)
Cr(trienH$_2$)(OH$_2$)$_4$$^{5+}$ ^{h}	522 (48.7)
Cr(dienH)(OH$_2$)$_4$$^{4+}$ ^{i}	520 (48.9)
Cr(ibn)(OH$_2$)$_4$$^{3+}$ ^{j}	518 (29.0)
Cr(pn)(OH$_2$)$_4$$^{3+}$ ^{j}	515 (36.0)
Cr(en)(OH$_2$(OH$_2$)$_4$$^{3+}$ ^{k}	512 (41.7)

^{a} Acid aqueous solution, usually 0.1—4 *F* HCl or HClO$_4$; values inside parentheses in the λ_{max} column are molar extinction coefficients ε in M^{-1}cm^{-1}. ^{b} This research. ^{c} Ref. 20. ^{d} Ref. 25. ^{e} Ref. 19. ^{f} Ref. 26. ^{g} Ref. 27. ^{h} Reg. 28. ^{i} Ref. 29. ^{j} Ref. 30. ^{k} Ref. 31.

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(21) B. V. Tucker, AEC Accession No. 33196, Report No. TID-20587; abstracted in *Chem. Abstr.*, *62*, 7387h (1965); B. V. Tucker, J. M. Fitzgerald, L. G. Hargis, and L. B Rogers, *J. Electroanal. Chem.*, *13*, 400 (1967).

(22) E. A. Bayazitova, V. V. Zelentsov, and V. I. Spitsyn, *Zh. Neorg. Khim.*, *13*, 479 (1968); *Russ. J. Inorg. Chem.* (*Engl. Transl.*), *13*, 249 (1968).

(23) Reaction times and concentrations (other than a 2:1 mole ratio of dipy to CrCl$_3$. 6H$_2$O) were not given for the Bayazitova *et al* method. We tried varying the reaction time from 4 to 180 hr (at 65°) and the amount of CrCl$_3$. 6H$_2$O per 80 ml of MeOH from 1.5 to 6 g, but in every case the product was *cis*-[Cr(dipy)$_2$Cl$_2$]Cl . 2H$_2$O, as shown by its visible absorption spectrum.

(24) Ref. 6, Table 23 and 25.

(25) M. Esparza and C. S. Garner, *J. Inorg. Nucl. Chem.*, *29*, 2377 (1969); *30*, 1984 (1968).

(26) J. A. McLean, Jr., and R. R. Barona, *Inorg. Nucl. Chem. Lett.*, *5*, 385 (1969).

(27) F. Woldbye, *Acta Chem. Scand.*, *12*, 1079 (1958).

(28) R L. Wilder, D. A. Kamp, and C. S. Garner,(*Inorg. Chem.*, in press.

(29) D. K. Lin and C. S. Garner, *J. Am. Chem. Soc.*, *91*, 6637 (1969).

(30) D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, *6*, 1077 (1967).

(31) R F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, *7*, 749 (1968); *7*, 2678 (1968).

The Cl:Cr atom ratio of 1.02 and the N:Cr atom ratio of 3.82 found experimentally for the isolated chloroaquo complex are in satisfactory agreement with the proposed formulation.

As seen in Figure 1, the d–d absorption maximum of the complex in 4 *F* HCl is at a wavelength intermediate to that of *cis*-$Cr(dipy)_2Cl_2^+$ and *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$, as would be expected from the relative ligand field strengths of the chloro and aquo ligands. Table I, which gives the high-wavelength d–d absorption-maximum wavelengths for these complexes and analogues with the same type of chromophores, further supports the assignment of the *cis* configuration to the bis(2,2′-dipyridyl) complexes (the lower-wavelength maxima are not given because they are generally obscured in the bis(2,2′-dipyridyl) complexes by high-intensity charge-transfer bands).

In cation-exchange chromatography of a mixture of *cis*-$Cr(dipy)_2Cl_2^+$, *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$, and *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$, the bottom (brown) band and the top (yellow-orange) band have been shown to be the dichloro 1+ and diaquo 3+ complexes, respectively, with the red band of the 2+ chloroaquo complex found in the middle of the resin column as expected for the species of intermediate charge.

When chromatography of *cis*-$Cr(dipy)_2Cl_2^+$ was first undertaken we noted that it eluted much more difficultly than expected by analogy with *cis*-$Cr(en)_2Cl_2^+$. Accordingly, we compared the elution behavior of 0.12 mfwt each of the singlycharged cations of *cis*-$[Cr(dipy)_2Cl_2]Cl \cdot 2H_2O$, *cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$, $[Cr(dipy)_2ox]Cl \cdot 4H_2O$, and $[Cr(en)_2ox]Cl \cdot 3H_2O$ in 0.1 *F* HNO_3 charged onto separate 8-cm × 1cm diameter columns of H^+ Dowex AG50W-X4 (200-400 mesh) resin at *ca.* 20°. Only 88% of *cis*-$Cr(dipy)_2Cl_2^+$ was aluted with 150 ml of 3 *F* HNO_3 *vs.* >95% elution of *cis*-$Cr(en)_2Cl_2^+$ with 85 ml of 1 *F* HNO_3; earlier work[20] has shown >95% of *cis*-α-$Cr(trien)Cl_2^+$ is eluted with 200 ml of 0.6 *F* $HClO_4$. For the oxalato complexes, only 86% of *cis*-$Cr(dipy)_2ox^+$ was eluted with 250 ml of 0.4 *F* HNO_3, followed by 100 ml of 0.6 *F* HNO_3, 100 ml of 1 *F* HNO_3, and finally 100 ml of 4 *F* HNO_3 *vs.* 92% elution of *cis*-$Cr(en)_2ox^+$ with only 100 ml of 0.4 *F* HNO_3. The presence of the aromatic heterocyclic ligands greatly increases the affinity for the resin, perhaps because of a similarity with the aromatic styrene-divinylbenzene polymer lattice of the resin. This is probably why the pink species characterized as $Cr(dipy)(OH_2)_4^{3+}$ (see below) elutes more readily than *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$ of the same charge but twice as many 2,2′-dipyridyl ligands. This behavior could also explain why *bis*(2,2′dipyridyl) species of charge ≥4+, such as $Cr(dipy)(dipyH)(OH_2)_3^{4+}$, $Cr(dipyH)_2(OH_2)_4^{5+}$, and $Cr(dipyH)_2(OH_2)_3Cl^{4+}$, one or more of which appears to be produced (see below) in aquation of *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ and of *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$, have been observed as orange-red bands which we have been unable to elute, even with 250 ml of 4 *F* HNO_3 followed by 100 ml of 6 *F* HNO_3 or with 100 ml of 12 *F* HCl.

Characterization of $Cr(dipy)(OH_2)_4^{3+}$. *Ca.* 56% of the total Cr in a 0.1 *F* HCl solution of *cis*-$Cr(dipy)_2Cl_2^+$ which had been aged at 70° for 50 days was isolated chromatographically (see Experimental Section) in the form of a pink complex believed to be the previously unreported $Cr(dipy)(OH_2)_4^{3+}$. The characterization is based on the following evidence.

Such a tetraaquo complex is expected, from work[28-31] with related diaquobis(diamine)chromium(III) complexes, to exist as an isolable intermediate in the aquation of *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$ to $Cr(OH_2)_6^{3+}$. Because of the very long reaction times involved and the lengthy chromatographic separations, as well as our inability to elute species of charge ≥4+ from the cation-exchange resins, we have not shown that the pink complex is generated from the hypothetical $Cr(dipy)(dipyH)(OH_2)_3^{4+}$ (it is generated, however, by aging *cis*-$(dipy)_2(OH_2)_2^{3+}$ in 0.12 *F* HNO_3 at 100° for 46 hr) or that the pink complex aquates to the hypothetical $Cr(dipyH)(OH_2)_5^{4+}$ or the known $Cr(OH_2)_6^{3+}$.

The Cl:Cr atom ratio of 0.05 and N:Cr atom ratio of 2.12 found for the pink complex are in satisfactory accord with the proposed formulation.

As seen in Table I, the d–d absorption maximum of the pink complex in 4 *F* HNO_3 has the wavelength expected for $Cr(dipy)(OH_2)_4^{3+}$ by analogy with the band wavelengths for the other $Cr(AA)(OH_2)_4^{n+}$ complexes of essentially the same chromophores and symmetry given in Table I (even the trend evident with decreasing number of C atoms of the diamine ligand is preserved). The only other nonchloro complex with one 2,2′dipyridyl ligand which would be a possible intermediate in the aquation of *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$ to $Cr(OH_2)_6^{3+}$ is the hypotetical $Cr(dipyH)(OH_2)_5^{4+}$, with a protonated unidentate 2,2′-dipyridyl ligand. The pink complex cannot be this pentaaquo complex, however, because the latter would be expected from analogy with $Cr(trienH_3)(OH_2)_5^{6+}$,[28] $Cr(dienH_2)(OH_2)_5^{5+}$,[29] $Cr(enH)(OH_2)_5^{4+}$,[31] and $Cr(NH_3)(OH_2)_5^{3+}$[32] to have its low-energy d–d absorption maximum at or slightly greater than the upper end of the range 545-552 nm observed for these analogues, whereas the pink complex has its band at 525 nm.

Finally, the chromatographic behavior is compatible with the $Cr(dipy)(OH_2)_4^{3+}$ formulation, in that the pink complex is eluted somewhat more readily than *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$ of the presumed same charge. As discussed above, the presence of one less 2,2′-dipyridyl ligand in $Cr(dipy)(OH_2)_4^{3+}$ would result in easier elution.

Aquation of cis-$Cr(dipy)_2Cl_2^+$. Because of the low solubility of the perchlorate salt of *cis*-$Cr(dipy)_2Cl_2^+$, the aquation could not be studied in $HClO_4$ medium. The kinetic behavior in 0.1-0.5 *F* HCl at 50-70° was analyzed spectrophotometrically. Values of the first-order rate constant k_1 could be evaluated for each run by the relation

$$2.30 \log [(A_o - A_\infty)/A - A_\infty)] = k_1 t \qquad (1)$$

where A_o, A, and A_∞ are the optical absorbances (at a given wavelength) at reaction time zero, time t, and at 100% aquation of one chloro ligand, respectively. With A_∞ calculated from the spectrum of *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$, plots of equation 1 at 550 and 570 nm

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(32) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

gave excellent straight lines up to *ca.* 20% reaction, then curvature became apparent from the secondary aquation. Since the secondary reactions appear to be complicated (see below), possibly involving a Cl^- anation back reaction from *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$, treatment of the data by consecutive first-order equations was not feasible. However, by analyzing the kinetics at 620 and 504 nm (where the chloroaquo and diaquo complexes have zero absorbance and the same, nonzero, absorbance, respectively), the effect of the secondary reactions was minimized; such rate plots were linear to at least 25% reaction and gave values of k_1 agreeing within 5-10% with the values from the 550- and 570 nm data. Further justification for this procedure, and evidence of negligible contribution from a *cis*-$Cr(dipy)_2Cl_2^+$ aquation path involving Cr—N bond rupture, is given by the existence of a well-defined isosbestic point at 526±4 nm (ε 42.8±0.5) up to *ca.* 20% reaction, in good agreement with the values 527±4 nm (ε 42.5±0.6) predicted from Figure 1 for the reaction

$$cis\text{-}Cr(dipy)_2Cl_2^+ + H_2O \xrightarrow{k_1} cis\text{-}Cr(dipy)_2(OH_2)Cl^{2+} + Cl^- \quad (2)$$

Table II presents the k_1 values. These are seen to be independent of hydrogen ion concentration in the range 0.1-0.5 *F* HCl and of ionic strength in the same range, within experimental error.

Table II. First-Order Rate Constant for Aquation of *cis*-Cr $(dipy)_2Cl_2^+$ in the Dark

Temp.,[a] °C	[HCl], *F*	C_o,[d] m*M*	μ,[c] *M*	sec^{-1} 10^5k_1,[d]
70.25	0.10	2.74	0.10	4.98 ±0.50
70.25	0.11	2.67	0.11	5.29 ±0.53
70.25	0.11	2.78	0.11	5.25 ±0.53
70.25	0.12	1.68	0.12	5.40 ±0.54
70.25	0.10	2.74	0.51	5.37 ±0.54
70.25	0.10	2.61	0.51	5.34 ±0.53
70.25	0.51	2.75	0.51	5.37 ±0.54
60.15	0.10	2.74	0.51	2.05 ±0.21
60.15	0.10	2.81	0.51	1.99 ±0.13
50.15	0.10	2.78	0.51	0.654±0.060
50.15	0.10	2.80	0.51	0.654±0.060
50.15	0.51	2.83	0.51	0.654±0.060

[a] ±0.10° at 70°; ±0.05° at 60° and 50°. [b] Initial concentration of dichloro complex. [c] Ionic strength, controlled with NaCl. [d] Error is combined least-squares statistical standard deviation (±2%) and standard deviation in A_∞.

An excellent Arrhenius plot was obtained with the 0.10 *F* HCl (μ=0.51 *M*, NaCl) values of k_1. The activation parameters are: $E_a = 23.4 \pm 0.8$ kcal mole^{-1}, log *PZ* (sec^{-1}) = 10.62±0.55, and $\Delta S_{298}^* = -11.9 \pm 2.5$ cal °K^{-1} mole^{-1}. By extrapolation, $k_1 = (2.9 \pm 0.5) \times 10^{-7}$ sec^{-1} ($t_{1/2}$=670 hr) at 25°.

Aquation of *cis*-$Cr(dipy)_2Cl_2^+$ is not complicated by a back reaction from Cl^- anation of *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ (reverse of reaction 2) in 0.1 *F* HCl at 70° even by 38 hr (10 half-times for *cis*-$Cr(dipy)_2Cl_2^+$ aquation) inasmuch as chromatography of the reaction solution showed no *cis*-$Cr(dipy)_2Cl_2^+$ was present.

Aquation of cis-*$Cr(dipy)_2(OH_2)Cl^{2+}$*. This reaction was not studied in detail because of the tedious synthesis of the complex in a pure state, because of our inability to elute species of charge ⩾4+ which are produced, and because preliminary observations indicated the system was complicated.

Some information on this aquation can be obtained from data on the *cis*-$Cr(dipy)_2Cl_2^+$ reaction in 0.1 *F* HCl at 70°. Beyond *ca.* 20% reaction the original isosbestic point was found to shift with successive spectral scans, and after *ca.* 30% reaction a new isosbestic point appeared at 518±2 nm (ε 38.4±0.4). Chromatography of a 120-min (32% reaction) solution gave the expected amount of *cis*-$Cr(dipy)_2Cl_2^+$, further substantiating the spectral determination of k_1; *ca.* 20% and 8% of the Cr (separations not fully quantitative) appeared to be present as *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ and *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$, respectively. However, an isosbestic point would not be expected from Figure 1 for the consecutive reactions consisting of reaction 2 followed by the secondary aquation

$$cis\text{-}Cr(dipy)_2(OH_2)Cl^{2+} + H_2O \xrightarrow{k_2} cis\text{-}Cr(dipy)_2(OH_2)_2^{3+} + Cl^- \quad (3)$$

Trial-and-error calculations showed that a pseudo isosbestic point in the range 516-520 nm (ε 38.8-39.5) could arise if the chloroaquo and diaquo complexes were produced in a ratio of anywhere from 1:3 to 2:1 as a result of reactions 2 and 3 plus a backreaction from Cl^- anation of *cis*-$Cr(dipy)_2(OH_2)_3^{3+}$. Attempts to study such a back reaction in 0.1 *F* HCl and in 0.13 *F* HCl-0.12 *F* HNO_3 at 70° (starting with *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$) did indicate the apparent occurrence of the reverse of reaction 4 with rates very roughly comparable to that of reaction 3, but a third species was forming (chromatography of a 200-min sample indicated *ca.* 15% nonelutable species) and the nature and rate of the reactions could not be determined.

However, the *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ aquation has additional complications. Starting with chromatographically isolated *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ (readjusted to a lower acidity and ionic strength by rechromatography, and in some cases by the OH^- Dowex AG2-X8 resin technique[33]), the rate of Cl^- release and of spectral change in 0.12 *F* HNO_3 and of spectral change in 0.13 *F* HCl was followed at 70°. First-order rate behavior was found up to 40% reaction (120 min), with a rate constant of $(6.9 \pm 0.8) \times 10^{-5}$ sec^{-1} in each case (spectral runs analyzed at 540 or 550 nm, with A_∞ calculated from the spectrum of *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$). In each case an isosbestic point (not fully sharp) was observed at 505-508 nm (ε 41.2-41.8), which agrees approximately with the 504 nm (ε 42.1) isosbestic point expected if *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ aquates only to *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$. However, such first-order behavior would not be expected for the run in HCl if the product were solely the *cis*-diaquo complex and if the latter Cl^- anates as fast as suggested by the rough experiment above. Moreover, chromatographic separations on a 180-min sample from the HCl run showed *ca.* 48% of the chloroaquo complex unreacted (in agreement with the 48% predicted from the above

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(33) D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, *1*, 20 (1962).

6.9×10^{-5} sec^{-1} rate constant), but only 28% of the Cr as *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$, the remaining 24% being found as a nonelutable band of species of charge $\geqslant4+$ (see above). In HNO_3 medium the respective amounts (only semi-quantitative) were 43% chloroaquo, 38% diaquo, and 19% nonelutable band, suggesting that more aquation occurred to the diaquo complex in the absence of sufficient Cl^- to create a back reaction. Since the diaquo complex is known not to generate a nonelutable species under these conditions (see below), these observations indicate that *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ aquates in 0.13 *F* HCl at 70° *ca.* 45% *via* Cr–N bond rupture and *ca.* 55% *via* Cr–Cl bond rupture (in 0.12 *F* HNO_3 the net amounts would be 33% and 67%, respectively). The simplest explanation of the data is that the Cr–N bond rupture leads in a largely rate-controlling step to $Cr(dipy)(dipyH)(OH_2)_2Cl^{3+}$, which then more rapidly aquates with Cl^- release to $Cr(dipy)(dipyH)(OH_2)_3^{4+}$. The latter would be expected to be nonelutable, and in solution could have[34] a spectrum much like that of *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$, thus possibly acounting for the isosbestic point observed and being compatible with the observed rate of Cl^- release and spectral change.

Clearly, however, the situation is too complex to be sure of the reaction scheme, and the above rate constant is merely a total rate constant for the disappearance of *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ by all paths.

Aquation of cis-*$Cr(dipy)_2(OH_2)_2^{3+}$*. A single observation was made of the aquation of *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$ in 0.12 *F* HNO_3 at 70° and 100°. At times up to 78 hr at 70° the d–d absorption band changed from 492 (ε 44.5) to 494 nm (ε 40.5). Chromatography of the 78-hr solution showed the presence of *ca.* 12% of a nonelutable species, probably 1,2,6-$Cr(dipy)(dipyH)(OH_2)_3^{4+}$. As indicated in footnote 34, the 1,2,6-triaquo complex would be expected to have its low-energy d–d absorption band at *ca.* 493-495 nm, and the small change in wavelength observed in the aquation could be accounted for. If one calculates the aquation rate from the 88% of unreacted *cis*-diaquo substrate, the first-order rate constant would be 5×10^{-7} sec^{-1} ($t_{1/2}\sim400$ hr), which is qualitatively in accord with the *ca.* 20% *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$ found chromatographically in a 0.1 *F* HCl solution of *cis*-$Cr(dipy)_2Cl_2^+$ which had been aged at 70° for 1200 hr.

In this latter solution, *ca.* 56% of the Cr was chromatographically isolated as $Cr(dipy)(OH_2)_4^{3+}$. This is a possible product of the aquation of the hypothesized 1,2,6-$Cr(dipy)(dipyH)(OH_2)_3^{4+}$, and this supposition is supported by the fact that *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$ aged for 46 hr in 0.12 *F* HNO_3 at 100° gave a pink solution with a d–d spectrum essentially the same as that of $Cr(dipy)(OH_2)_4^{3+}$.

Discussion

Table III compares the kinetic parameters for aquation of *cis*-$Cr(dipy)_2Cl_2^+$ with those for aquation of some related dichloro complexes with aliphatic diamine ligands. The presence of the aromatic heterocyclic ligands appears to dramatically reduce the aquation rate relative to the *cis*-dichlorobis(aliphatic diamine)-chromium(III) analogues, the rate reduction arising partly from the greater activation energy and partly from the more negative entropy of activation. Since aquation of octahedral Cr^{III} substrates is generally thought to proceed *via* a dissociative activation (either S_N1 dissociation, or I_d dissociative interchange),[44] this rate reduction may arise primarily from decreased tendency for solvation in the presence of the heteroaromatic ligands. Since in a dissociative aquation mechanism the transition state is making greater demands on solvation, the heteroaromatic ligands should result in a rate reduction. If the activation entropy argument of Tobe[40] regarding chloro aquation of a wide variety of chloroacidobis(diamine)cobalt(III) complexes is applicable to Cr^{III} analogues, the negative entropy of activation for aquation of *cis*-$Cr(dipy_2$-Cl_2^+ suggests a dissociative activation *via* an incipient tetragonal pyramid.

Table III. Comparison of Aquation Rates of *cis*-$Cr(dipy)_2Cl_2^+$ with some Cr^{III} and Co^{III} Aliphatic Amine Analogues at 25° [a]

Complex	10^5k, sec^{-1}	E_a, kcal mole^{-1}	ΔS^*, cal°K^{-1} mole^{-1}
cis-$Cr(dipy)_2Cl_2^+$ [b]	0.029	23.4	−12
cis-α-$Cr(trien)Cl_2^+$ [c]	19.2	21.2	−6
cis-$Cr(pn)_2Cl_2^+$ [d]	35	—	—
cis-$Cr(en)_2Cl_2^+$ [e]	33	21.1	−6
trans-$Cr(en)_2Cl_2^+$ [f]	2.25	23.2	−3
cis-$Co(dipy)_2Cl_2^+$ [g]	~6 [h]	—	—
cis-α-$Co(trien)Cl_2^+$ [i]	16	21.6	−6
cis-β-$Co(trien)Cl_2^+$ [i]	150	20.9	−3
cis-$Co(en)_2Cl_2^+$ [j]	24.4	22.2	−5
trans-$Co(trien)Cl_2^+$ [i]	350	26.1	+16
trans-$Co(pn)_2Cl_2^+$ [k]	6.2	—	—
trans-$Co(en)_2Cl_2^+$ [l]	3.53	26.8	+14

[a] Acidic aqueous solution, usually 0.1—4*F* HCl, $HClO_4$, or HNO_3. [b] This research; *k* extrapolated from 50—70°. [c] Ref. 20. [d] Ref. 25. [e] Ref. 36. [f] Ref. 37; Cl^- release path only. [g] Ref. 4. [h] In 1:1 $MeOH$—H_2O at 20°; in view of Ref. 11, catalysis by traces of Co^{II} may be very important and the true *k* value much smaller. [i] Rfs. 38-40. [j] Refs. 40-42. [k] Ref. 43. [l] Refs. 40, 43.

The apparently greater rate of aquation of *cis*-$Cr(dipy)_2(OH_2)Cl^{2+}$ than of *cis*-$Cr(dipy)_2Cl_2^+$ is unexpected, since if the mechanism is dissociative the second chloro ligand would be expected on electrostatic grounds to be more slowly released than the first and

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(34) The hypothesized $Cr(dipy)(dipyH)(OH_2)_3^{4+}$, if it were the 1,2,6-triaquo isomer, should have its low-energy d-d absorption band at essentially the same wavelength as does 1,2,6-$Cr(dien)(OH_2)_3^{3+}$, namely, 495 nm, [35] and 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$, namely 493 nm; [28] the *cis*-$Cr(dipy)_2(OH_2)_2^{3+}$ band is at 492 nm.

(35) S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, *31*, 811 (1969).

(36) J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, *79*, 4285 (1957).

(37) D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, *18*, 219 (1961).

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(39) A. H. Sargeson and G. H. Searle, *Inorg. Chem.*, *6*, 2172 (1967).

(40) M. L. Tobe, *Inorg. Chem.*, *7*, 1260 (1968).

(41) J. P. Mathieu, *Bull. Soc. Chim. Fr.*, *3*, 2152 (1936).

(42) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

(43) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, *78*, 709 (1956).

(44) Ref. 6, p 204-208.

this is generally found to be the case with dichlorobis-(aliphatic diamine) complexes. However, the competitive aquation *via* Cr–N bond rupture may play a role. Not enough is known yet about the factors responsible for such competition between aquation *via* loss of a unidentate acido group and aquation *via* rupture of one bond to a bidentate (or multidentate) amine ligand.

It is desirable to examine the aquation rates of other Cr^{III} bis(2,2′-dipyridyl) complexes to see if the behavior of the *cis*-dichloro complex is representative of this class of substrate.