Pergamon

PII: S0277-5387(97)00091-0

Polyhedron Vol. 16, No. 19, pp. 3371–3378, 1997
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0277-5387/97 $17.00+0.00

Ternary complex formation by diaquanitrilotriacetatochromium(III) with 2,2′-bipyridine and 1,10-phenanthroline in aqueous media: a kinetic investigation

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(Received 23 October 1996; accepted 28 February 1997)

Abstract—In solution the complexes $[Cr(nta)(H_2O)_2]$ (**1**) and $[Cr(Hnta)(H_2O)_3]^+$ (**1H**) co-exist in a protonic equilibrium. **1** and **1H** react with 1,10-phenanthroline to form [Cr(nta)(phen)] (**1p**) and $[Cr(Hnta)(H_2O)(phen)]^+$ (**1HP**) respectively. 2,2′-bipyridine (bipy) reacts similarly and forms [Cr(nta)(bipy)] (**1b**) and $[Cr(Hnta)(H_2O)(bipy)]^+$ (**1Hb**). The relative proportions of **1p** and **1b** in solution increases with increased pH. **1Hp** and **1Hb** have been isolated and characterized in solution. Rate constants for the formation of **1Hp** and **1Hb** are more than 10^3 times larger than the corresponding rate constants for the formation of **1p** and **1b**. This observation is probably the first direct demonstration of an anchimeric effect exhibited by the flanging carboxylate arm of a tridentate nta. Aquation of **1p, 1b, 1Hp** and **1Hb** are acid independent in the pH range 3.85–5.4. © 1997 Elsevier Science Ltd

Keywords: kinetics; chromium(III); 2,2′-bipyridine; 1,10-phenanthroline; ternary complex; nitrilotriacetate.

The nitrilotriacetate ion, nta^{3-} is an important member of the aminopolycarboxylate class of ligands. Thermodynamics and kinetics of formation and dissociation of several ternary complexes of bivalent metal ions of first transition series have been investigated with nta^{3-} as the primary ligand [1–5]. But relatively less attention has been devoted to the complexes of nta^{3-} with the trivalent metal ions [6–9], for which the Cr^{III}-nta system [7–9] is an example. The framework has been selected to work out the principles of metal complex interaction with proteins [10,11], a class of reactions where ternary complex formation might have an important role. But this framework has rarely been the subject for investigation of kinetics of ternary complex formation.

Recently, we have for the first time synthesised the solid complex $[Cr(nta)(H_2O)_2]$ **1**, and investigated the kinetics of the formation and dissociation of the ternary complex $[Cr(nta)(pd)]^-$ (pd = pentane-2,4-dione). Interesting mechanistic conclusions emerged thereby [9].

We report here on the kinetics of reaction of **1** with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) in weakly acidic aqueous media to see the effect of coordinated nta on the substitution pattern of Cr^{III}.

EXPERIMENTAL

Materials

The solid crystalline complex $[Cr(nta)(H_2O)_2]$ (**1**) was prepared as described earlier [9] by heating an aqueous suspension of freshly prepared $Cr(OH)_3$ with H_3nta (Koch light, England) on a water bath for 5 h. The solution after suitable work up yielded 1.1 g (yield 20%) of bluish-black crystals of **1** from a MeOH–H_2O media. (Found: C, 26.2; H, 3.9; N, 5.2; Cr, 18.8. Calc.: C, 26.1; H, 3.6; N, 5.1; Cr, 18.8% for $C_6H_{10}NCrO_8$).

An aqueous solution of **1** exhibits two visible bands at 405 and 556 nm with respective $\varepsilon = 99.5$ and 93.0 $mol^{-1}\ dm^3\ cm^{-1}$ respectively in the pH range 1.5–2.5. Crystalline solid complexes [Cr(nta)(bipy)] (**1b**) and

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$[Cr(nta)(phen)]\cdot4H_2O$ (**1p**) were prepared by literature methods [12] with minor modifications: Complex **1** and the ligand (bipy or phen) were mixed in a 1 : 1.2 molar proportion in 20 cm^3 of water and heated until a clear solution was formed. On cooling, reddish-brown crystals of **1b** or **1p** (as the case may be) were formed. Yield after recrystallisation from hot water, 40% for **1b**, 30% for **1p**. Chromium content of the complexes were estimated spectrophotometrically at 372 nm by alkali–H_2O_2 oxidation method as described earlier [13]. [Cr(nta)(bipy)]: Calc: Cr, 13.1; C, 48.5; H, 3.6; N, 10.6. Found: Cr, 13.1; C, 48.3; H, 3.5; N, 10.7%. $[Cr(nta)(phen)\cdot4H_2O]$: Calc. Cr, 10.2; C, 42.3; H, 4.3; N, 8.2. Found: Cr, 10.3; C, 42.2; H, 4.4; N, 8.1%.

UV–vis spectra and ε_{max} values of the complexes **1b** and **1p** agree fairly well with the literature report [12]. **1b**: Reported: $\varepsilon^{530} = 86$, Found: $\varepsilon^{530} = 85$ mol^{-1} dm^3 cm^{-1}, **1p**: Reported: $\varepsilon^{537} = 82$, Found: $\varepsilon^{535} = 88$ mol^{-1} dm^3 cm^{-1}.

The amount of bipy and phen in the complexes **1Hp** and **1Hb** in solution were determined by boiling them with 0.1 mol dm^{-3} KOH solution on a water bath. The $Cr(OH)_3$ thus precipitated was filtered off. The filtrate was concentrated, and pH adjusted to ~10 with HCl. The solution was extracted with n-heptane by vigorous shaking. Then [bipy] and [phen] were estimated spectrophotometrically in the organic solvent at 282 nm and 264 nm respectively using absorbance calibration plots [14,15].

Melting points of the supplied ligands 2,2′-bipyridine (E. Merck) and 1,10-phenanthroline (E. Merck) agreed within ±1°C of the literature value, and were used as received. Ionic strength was maintained at 0.1 mol dm^{-3} using KNO_3. Solutions of KNO_3 (BDH) were standardised using a cation exchanger (Dowex 50W X8) in the H^+-form. HNO_3 solutions were standardised with standard NaOH solution. All other materials used were of analytical grade. Doubly distilled water was used all through.

Physical measurements and kinetics

UV–vis spectra and solution absorbances in a 5 cm quartz cell were recorded with a Shimadzu (UV 1601 PC) spectrophotometer. Kinetics were measured by a sample quenching technique at 45.0°, 55.0° and 65.0° for bipy and at 50.0°, 60.0° and 70.0°C for phen. Kinetics were followed at 405 nm, which is one of the spectral peaks of **1**, and where the rise in absorbance is high but the ligands, bipy and phen, absorb negligibly.

All the pH measurements were made using an Orion (Model 710 A) pH meter, equipped with a micro glass-combination electrode (9802 BN). The linearity of the electrode was established using pH 4, 7 and 9 buffers. The electrode was calibrated to read $[H^+]$ directly using a series of acid solutions at ionic strength used for kinetic measurements. The $[H^+]$ in these solutions were measured by titration against standard NaOH solutions.

The observed first-order rate constants (k_0) were determined as usual from the slopes of the $\ln(A_e - A_t)$ *vs* time (t) data, using a standard least squares program. The reported k_0 are mean values from 2–3 kinetic runs. The uncertainties of the reported kinetic and equilibrium parameters are standard deviations [16a].

The nitrate media were used instead of perchlorate because of the low solubility of $Hbipy^+ClO_4^-$ and $Hphen^+ClO_4^-$ in the experimental pH range, 3.8–5.4.

RESULTS AND DISCUSSION

Spectral changes and reaction products

Figure 1 shows the spectra of the complexes $[Cr(nta)(H_2O)_2]$ (**1**) and $[Cr(nta)(phen)]\cdot4H_2O$ (**1p**) at different pH. The reversible pH-dependence of the spectra of **1** is well known to be due to deprotonation of its coordinated water. But pH-dependence of the spectra of **1p** have never been reported before.

Spectral changes during the reaction of **1** with excess phen at pH 4.0 and at pH 4.95 have been shown in Figs 2 and 3 respectively. It is noticeable that the equilibrium spectra of a mixture of **1** and phen closely resemble that for **1p**, when the pH of the solution is relatively high (4.95). But the spectra differ sig-

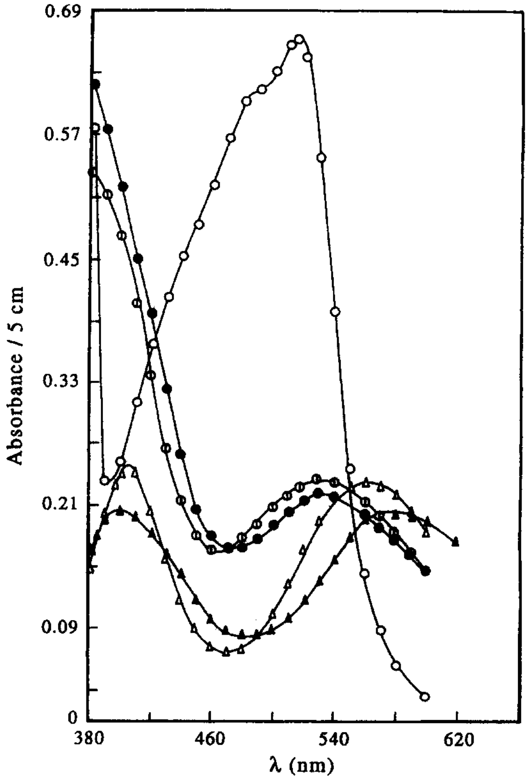

Fig. 1. UV–vis spectra of complexes: (△) 1 at pH 4.01; (▲) 1 at pH 6.05; (◐) 1p at pH 3.8; (●) 1p at pH 6.1; (○) 1Hp at pH 3.5. [complex], 0.5 mmol dm^{-3}.

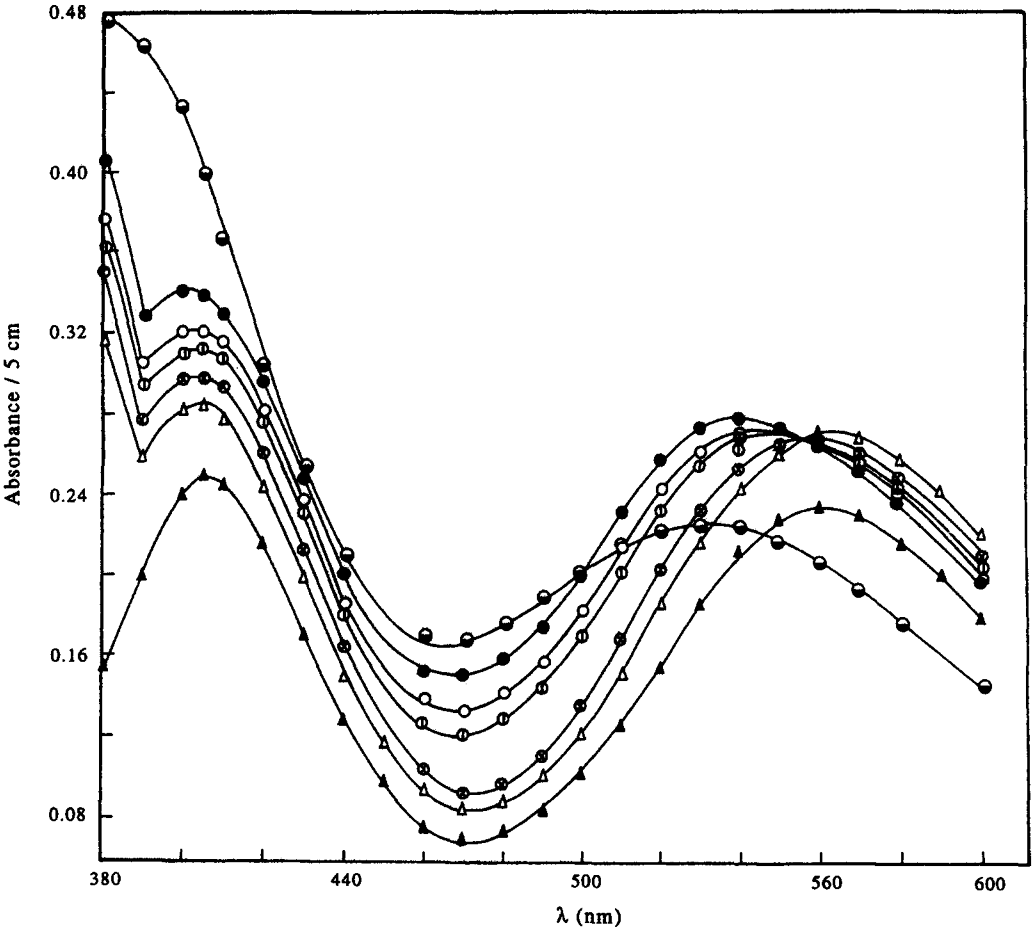

Fig. 2. Spectra of 1+phen: (▲) immediately after mixing; (△) 20 min.; (⊗) 110 min.; (⦶) 260 min.; (○) 500 min.; (●) 750 min. Temp., 60°C. pH, 4.01; C_{phen}, 5.0 mmol dm^{-3}.

nificantly from that of **1p** at lower pH (4.0). Evidently, the reaction products at lower pH contain some absorbing material(s) other than **1** and **1p**. To identify this 'other product(s)', we charged a reaction mixture of **1** and phen at pH 4.0 on a Sephadex SPC-25 cation exchanger column in the Na^+ form. When washed with water, a diffuse orange–yellow band was retained on the resin bed, while a purple–red solution passed unabsorbed. This purple–red colour is typical for a mixture of **1** and **1p**.

The orange–yellow band could be eluted with a 0.05 mol dm^{-3} $NaNO_3$ solution indicating a unipositive species **1HP** (say). Chromium and phen content of the eluted solution, was found to be in the ratio 1 : 1. The UV–vis spectra for **1Hp** are displayed in Figure 1 along with the spectra of **1** and **1p** for comparison. In all probability, **1Hp** is $[Cr(Hnta)(phen)(H_2O)]^+$ which has a less symmetrical structure than either **1** or **1p** and therefore has a higher ε_{max} (265 mol^{-1} dm^3 cm^{-1}) at 515 nm.

Further observations on the spectral changes in the course of reaction between **1** and phen revealed that the final spectra not only depend on pH but also on C_{phen}. A plot of A_e *vs* C_{phen} at 405 nm (Fig. 4) clearly indicates the equilibrium nature of the reaction of **1** with phen. Closely similar observations were made in the reaction of **1** with bipy. We isolated and characterised $[Cr(Hnta)(bipy)(H_2O)]^+$ (**1Hb**) in solution as in the case of **1Hp**. For **1Hb**, $\lambda_{max} = 522$ nm ($\varepsilon = 250$ mol^{-1} dm^3 cm^{-1}).

For an equilibrated mixture of **1** and phen at a given pH, one obtains for the total chromium concentration,

$$C_{Cr} = [\mathbf{1}] + [\mathbf{1p}] + [\mathbf{1Hp}] \qquad (1)$$

and for the absorbance at equilibrium,

$$A_e = \varepsilon_1[\mathbf{1}] + \varepsilon_{1p}[\mathbf{1p}] + \varepsilon_{1Hp}[\mathbf{1Hp}] \qquad (2)$$

C_{Cr}, A_e, ε_1, ε_{1p} and ε_{1Hp} are known. Further [**1Hp**] could be measured from the resin-bed experiments. One could thus obtain [**1**] and [**1p**] using eqs (1) and (2) [16b]. Hence the ratio [**1Hp**] : [**1p**] could be obtained. This ratio at different experimental pH is given in Table 1. It is evident that [**1Hp**] decreases while [**1p**] increases with increasing pH, until at and

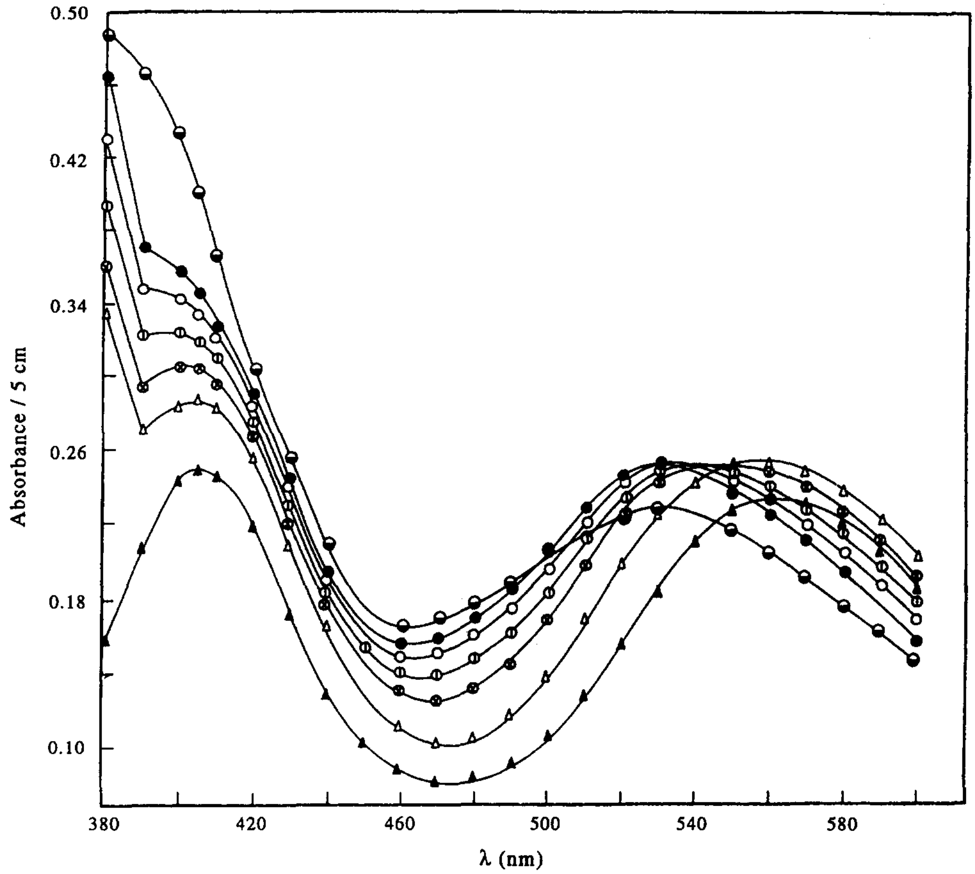

Fig. 3. Spectra of 1 + phen; (▲) immediately after mixing; (△) 25 min.; (⊗) 100 min., (⦶) 300 min.; (○) 480 min.; (●) 720 min.; Temp., 60°C; pH, 4.95; C_{phen}, 5.0 mmol dm^{-3}.

above pH 5, **1p** is nearly the exclusive product. One can thus conclude that **1** reacts with phen to produce only **1p** at higher pH, but a mixture of **1p** and **1Hp** is obtained when the pH is low. Very similar results were obtained in the reactions of **1** with bipy (Table 1)

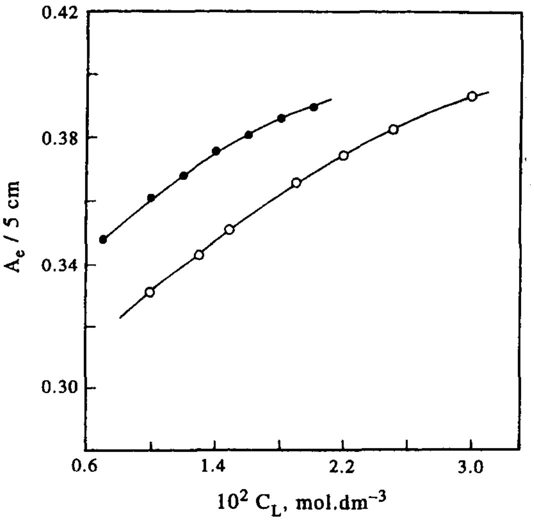

Fig. 4. Plots of A_e *vs* C_L: (●) L = phen; Temp., 60°C; (○) L = bipy; Temp., 45°C.

Kinetics

For the reactions of **1** with both phen and bipy, $\ln(A_e - A_t)$ *vs* time (t) data gave excellent fit to a straight line relation for at least 90% attainment of the equilibrium. The observed rate constants (k_0) have been collected in Table 2. k_0 increases linearly with increasing C_L (L = phen or bipy). k_0 *vs* C_L plots at different fixed pH values are excellent straight lines with finite intercept and the dependence may be very well represented by eq. (3) where L = phen or bipy.

$$k_0 = k_f^L C_L + k_d^L \quad (3)$$

k_f^L and k_d^L at different temperatures were evaluated from the slopes and intercepts of the approximate k_0 *vs* C_L plots and are given in Table 2.

k_f^L values decrease with increasing $[H^+]$ but k_d^L remains unchanged. The experimental scatter in k_d^{bipy} (intercept of k_0 *vs* C_{bipy} plots) is more than that in k_d^{phen} but no trend in k_d^{bipy} as a function of $[H^+]$ is apparent. Most probably the experimental data indi-

Table 1. Equilibrium species distribution in the reaction of $[Cr(nta)(H_2O)_2]$ with 1,10-phenanthroline and 2,2′-bipyridine[a]

	Conc. (mmol dm^{-3}) for			
pH	**1**	**1p**	**1HP**	Product ratio
				[1 Hp]/[1p]
4.0	0.45	1.31	0.2	0.153 (0.150)[b]
4.5	0.10	1.80	0.088	0.049 (0.047)[b]
4.7	0.05	1.88	0.06	0.032 (0.030)[b]
	Conc. (mmol dm^{-3}) for			
	1	**1b**	**1Hb**	**[1 Hb]/[1b]**
4.0	0.73	1.01	0.240	0.238 (0.247)[b]
4.5	0.30	1.50	0.145	0.097 (0.098)[b]
4.7	0.15	1.75	0.080	0.046 (0.049)[b]

[a] $\varepsilon(\lambda)$ (mol^{-1} dm^3 cm^{-1}) for different species: **1,** 63(515); **1p,** 84(515); **1Hp,** 265(515); **1,** 66(522); **1b,** 85(522); **1Hb,** 250(522).

[b] Parenthetical values are obtained kinetically. See text.

cate that k_d^{phen} and k_d^{bipy} both are independent of $[H^+]$ as found earlier [14,15,17–19].

A scheme, which explains most simply our analyses of products and the kinetic observations, is given below:

Scheme

$$\mathrm{H\,phen^+} \overset{K_a}{\rightleftharpoons} \mathrm{phen} + \mathrm{H^+} \tag{4}$$

$$\mathrm{H\,bipy^+} \overset{K'_a}{\rightleftharpoons} \mathrm{bipy} + \mathrm{H^+} \tag{5}$$

$$\underset{\mathbf{1}}{[Cr(nta)(H_2O)_2]} + H^+ \overset{K_{1H}}{\rightleftharpoons} \underset{\mathbf{1H}}{[Cr(Hnta)(H_2O)_3]^+} \tag{6}$$

$$\mathbf{1} + \mathrm{phen} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{1p} \tag{7}$$

$$\mathbf{1H} + \mathrm{phen} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{1Hp} \tag{8}$$

$$\mathbf{1} + \mathrm{bipy} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \mathbf{1b} \tag{9}$$

$$\mathbf{1H} + \mathrm{bipy} \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} \mathbf{1Hb} \tag{10}$$

From the above scheme k_0, for phen may be represented by eq. (11)

$$k_0 = \frac{(k_1K_a + k_2K_aK_{1H}[H^+])C_{\text{phen}}}{(K_a + [H^+])(1 + K_{1H}[H^+])} + (k_{-1} + k_{-2}) \tag{11}$$

Since, it is known [9] that $K_{1H}[H^+] \ll 1$, we have,

$$k_0 = (k_a + [H^+])^{-1}(k_1K_a + k_2K_aK_{1H}[H^+]) \, . \, C_{\text{phen}} + (k_{-1} + k_{-2}) \tag{12}$$

Thus eq. (12) is equivalent to eq. (3), with

$$k_f^{\text{phen}} = (K_a + [H^+])^{-1}(k_1K_a + k_2K_aK_{1H}[H^+])$$

and

$$k_d^{\text{phen}} = k_{-1} + k_{-2}$$

Therefore, a plot of $k_f^{\text{phen}}(K_a + [H^+])$ *vs* $[H^+]$ would give slope $= k_2K_aK_{1H}$ and intercept $= k_1K_a$, from which k_2 and k_1 can be calculated using the known values [20,9] for K_a and K_{1H}. Analogous treatment would give for bipy k'_2 and k'_1. The rate constants k_1, k'_1, k_2, k'_2, $(k_{-1}+k_{-2})$, and $(k'_{-1}+k'_{-2})$ are given in Table 3 along with activation parameters.

According to the scheme, the species ratio **[1Hp]** : **[1p]** should be [21]

$$[\mathbf{1Hp}]/[\mathbf{1p}] = k_2K_{1H}[H^+]/k_1 \tag{13}$$

The ratio **[1Hb]** : **[1b]** can be evaluated using an analogous eq. (14)

$$[\mathbf{1Hb}]/[\mathbf{1b}] = k'_2K_{1H}[H^+]/k'_1 \tag{14}$$

Species concentration ratios thus calculated from kinetic data are found to be in excellent agreement with those obtained from equilibrium experiments (see Table 1). This agreement is a strong support for the proposed scheme.

Water exchange rate [22,23] (k_{ex}) of $[Cr(H_2O)_6]^{3+}$ at 55°C is 1.48×10^{-4} s^{-1}. The much higher values for k_1 and k'_1 compared to k_{ex} indicate strong labilization of the Cr^{III}—OH_2 bonds in $[Cr(nta)(H_2O)_2]$. This labilization is expected due to the strong σ-donor character of nta which lowers the Lewis acidity of the Cr^{III} center. $\Delta H^{\#}$ value for the k_1 or k'_1 path are much lower than that for water exchange at $[Cr(H_2O)_6]^{+3}$ (108.6 kJ mol^{-1}) [23]. $\Delta S^{\#}$ for water exchange, on the other hand, is much less negative than the corresponding value for k_1 or k'_1 paths. It might be noted that complex **1** has a lesser number of replaceable water molecules than there are in $[Cr(H_2O)_6]^{3+}$. Therefore, substitution of water molecules should be statistically more probable in $[Cr(H_2O)_6]^{3+}$ than it is in **1**, and $\Delta S^{\#}$ for k_{ex} should be more positive.

Some representative rate constants for ternary complex formation by the complex **1** are given in Table 4 along with data from present work. The 5–10 times slower rate of formation of the bipy and phen complexes is typical and was observed earlier, e.g. for the Cu^{II}–nta system [3]. The explanation given for Cu^{II}–nta system is applicable in our system as well. The observation is consistent with a mechanism in which the rate determining step is the sterically controlled ring closure.

Table 2. Representative first-order rate constants for the reaction of $[Cr(nta)(H_2O)_2]$ (0.5 mmol dm^{-3}) with 1,10-phenanthroline and 2,2′-bipyridine, I = 0.1 mol dm^{-3} (KNO_3)

$10^2[H^+]$ mmol dm^{-3}	C_L mmol dm^{-3}	10^5k_0 s^{-1}	$10^2[H^+]$ mmol dm^{-3}	C_L mmol dm^{-3}	10^5k_0 s^{-1}
		50.0°C ; L = phen			
12.02	7.0	1.07	1.99	7.0	2.00
	10.0	1.32		10.0	2.58
	12.0	1.43		12.0	3.05
	14.0	1.57		14.0	3.43
	16.0	1.75		16.0	3.80
	18.0	1.84		18.0	4.28
	20.0	2.00		20.0	4.65
	$10^4k_f = 7.0\pm0.2^a$			$10^4k_f = 20.5\pm0.88^a$	
	$10^6k_d = 5.92\pm0.12^b$			$10^6k_d = 5.57\pm0.23^b$	
7.08	7.0	1.33	0.98	7.0	2.40
	10.0	1.60		10.0	3.25
	12.0	1.75		12.0	3.77
	14.0	2.03		14.0	4.25
	16.0	2.15		16.0	4.85
	18.0	2.40		18.0	5.34
	20.0	2.62		20.0	5.92
	$10^4k_f = 9.9\pm0.32^a$			$10^4k_f = 26.8\pm0.9^a$	
	$10^6k_d = 6.01\pm0.16^b$			$10^6k_d = 5.37\pm0.24^b$	
3.39	7.0	1.65	0.40	7.0	2.85
	10.0	2.13		10.0	3.75
	12.0	2.50		12.0	4.44
	14.0	2.85		14.0	5.13
	16.0	3.10		16.0	5.70
	18.0	3.40		18.0	6.42
	20.0	3.77		20.0	7.06
	$10^4k_f = 16.1\pm0.64^a$			$10^4k_f = 32.5\pm0.92^a$	
	$10^6k_d = 5.38\pm0.22^b$			$10^6k_d = 5.37\pm0.22^b$	
		55.0°C ; L = bipy			
12.59	10.0	4.13	2.40	10.0	5.60
	13.0	4.65		13.0	6.65
	16.0	5.40		16.0	7.90
	20.0	6.22		20.0	9.32
	23.0	6.70		23.0	10.30
	26.0	7.37		26.0	11.47
	30.0	8.40		30.0	13.05
	$10^3k_f = 2.10\pm0.04^a$			$10^3k_f = 3.7\pm0.08^a$	
	$10^5k_d = 1.47\pm0.03^b$			$10^5k_f = 1.89\pm0.03^b$	
7.08	10.0	4.53	1.17	10.0	6.03
	13.0	5.35		13.0	7.40
	16.0	6.35		16.0	8.62
	20.0	7.26		20.0	10.40
	23.0	8.17		23.0	11.76
	26.0	8.77		26.0	12.88
	30.0	9.93		30.0	14.55
	$10^3k_f = 2.67\pm0.05^a$			$10^3k_f = 4.26\pm0.09^a$	
	$10^5k_d = 1.93\pm0.04^b$			$10^5k_d = 1.83\pm0.03^b$	

Table 2. *Continued*

$10^2[H^+]$ mmol dm^{-3}	C_L mmol dm^{-3}	10^5k_0 s^{-1}	$10^2[H^+]$ mmol dm^{-3}	C_L mmol dm^{-3}	10^5k_0 s^{-1}
3.55	10.0	5.13	0.48	10.0	6.30
	13.0	6.15		13.0	7.75
	16.0	7.27		16.0	9.35
	20.0	8.70		20.0	11.05
	23.0	9.38		23.0	12.55
	26.0	10.57		26.0	13.70
	30.0	11.90		30.0	15.75
	$10^3k_f = 3.36 \pm 0.05$[a] $10^5k_d = 1.81 \pm 0.03$[b]			$10^3k_f = 4.67 \pm 0.10$[a] $10^5k_d = 1.71 \pm 0.03$[b]	

[a] mol^{-1} dm^3 s^{-1}.
[b] s^{-1}.

Table 3. Kinetic parameters for the reactions of $[Cr(nta)(H_2O)_2]$ with 1,10-phenanthroline and 2,2′-bipyridine[a]

Temp (°C)	10^3k_1	$10^3k'_1$	k_2	k'_2	k_2K_{1H}	k'_2K_{1H}	$10^5(k_{-1}+k_{-2})$	$10^5(k'_{-1}+k'_{-2})$
45.0		2.6±0.08				6.9±0.35		0.6±0.04
50.0	3.8±0.18		3.16±0.13		5.7±0.27		0.56±0.03	
55.0		4.9±0.22		7.03		12.8±0.5		1.8±0.08
60.0	7.0±0.27				11.50±0.57		1.5±0.06	
65.0		8.95±0.44				19.9±1.0		5.0±0.24
70.0	12.5±0.44				22.4±1.2		3.8±0.15	
$\Delta H^{\neq}$ kJ mol^{-1}	51±4.7	51±4.6			60±5.0	44±4.3	86±7	88±7.3
$\Delta S^{\neq}$ JK^{-1} mol^{-1}	−135±12	−134±11.8			−44±4.5	−90±9.2	−81±9	−68±8.5

[a] Unit for k_1, k'_1, k_2 and k'_2 is mol^{-1} dm^3 s^{-1}, for k_2K_{1H} and k'_2 K_{1H} mol^{-2} dm^6 s^{-1}, for $(k_{-1}+k_{-2})$ and $(k'_{-1}+k'_{-2})$ is s^{-1}.

Table 4. Representative rate constants for the reaction of $[Cr(nta)(H_2O)_2]$ with some ligands

Ligands	10^3 Rate constant (mol^{-1} dm^3 s^{-1})	Temp. (°C)	Ref.
Pentane-2,4-dione	33.9	50	9
SCN^-	9.1	35	8
Eriochrome black-T	95.0	30	8
Solochrome yellow-2G	23.0[a]	40	7
1,10-phenanthroline	3.8	50	This work
2,2′-bipyridine	2.68	45	This work

[a] s^{-1}.

The k_2 values reported in this paper are interesting. They are more than 10^3 times larger than k_1. It is likely that the flanging carboxylate end of **1H** greatly labilizes the water molecules. Similar labilizations are known in the ligand substitution reactions of Cr(III) complexes with edta and related aminopolycarboxylate ligands [24–28] due to transient coordination of the pendant groups of the aminopolycarboxylates. Such anchimeric effect has profound physiological significance and has attracted continuing attention for two decades.

The k_d^{phen} and k_d^{bipy} values are usual for aquation of various Cr^{III} complexes. However, as implied in the proposed scheme both k_d^{bipy} and k_d^{phen} are composite constants and further discussions on k_d values may not be rewarding. But it might be mentioned that according to earlier workers [17–19] the dissociation of bipy and phen ligands from $[Cr(L)_3]^{+3}$ are acid independent in the pH interval 0–10.7. For the corresponding Fe^{II} complexes $[Fe(L)_3]^{2+}$, the pH independence is observed in the range 0–5. Above pH 5 base hydrolysis path becomes important [29,30].

In our proposed scheme we have not included the HL^+ species since it is well known that HL^+ is about 10^3 times less reactive due to the shielding effect on the reaction site of phen and bipy by a proton [31].

The first hydrolysis constant for complex **1** is 5.13×10^{-6} at 50°C [9]. It is expected that the concentration of $[Cr(nta)(OH)(H_2O)]^-$ (**1h**) should be appreciable, at least at the higher pH range. But we have not considered **1h** as a reactive species though it is well known that the hydroxoaqua species of Cr^{III} are kinetically more active towards replacement by monodentate ligands. But high structural rigidity [32] of H $phen^+$ and H $bipy^+$ compared to monodentate ligands requires the presence of two H_2O molecules *cis* to each other for substitution; **1h** has only one replaceable H_2O molecule and hence cannot react with H $phen^+$ and H $bipy^+$ unless a strong Cr^{III}—OH bond can be broken. Such a possibility is very unlikely and has not been considered.

Acknowledgement—Award of a teacher fellowship to SKB by the University Grants Commission (New Delhi) is gratefully acknowledged.

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