

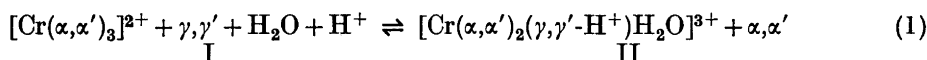
The Formation and the Thermodynamic Parameters of a Mixed α,α' - and γ,γ' -Bipyridyl Complex of Chromium(II)

JENS ULSTRUP

*Chemistry Department A, The Technical University of Denmark,
Building 207, DK-2800 Lyngby, Denmark*

From the spectral changes in aqueous solutions containing $[\text{Cr}(\text{bipy})_3]^{2+}$ and varying amounts of α,α' - and γ,γ' -bipyridyl, a mixed α,α' - and γ,γ' -bipyridyl complex has been identified in rapid equilibrium with $[\text{Cr}(\text{bipy})_3]^{2+}$. The data are consistent with the composition $[\text{Cr}(\alpha,\alpha')_2(\gamma,\gamma'\text{-H}^+)\text{H}_2\text{O}]^{3+}$ of the complex, indicating the coordination of a monoprotonated γ,γ' -bipyridyl. The thermodynamic parameters of the equilibrium as well as the spectral characteristics of the mixed complex are reported.

The influence of γ,γ' -bipyridyl on the kinetics of redox reactions between $[\text{Cr}(\text{bipy})_3]^{2+}$ and some cobalt(III) complexes has been studied recently.¹ The work was prompted by a desire to investigate the possibility of outer-sphere remote-attack mechanisms^{2,3} in electron-transfer reactions, and the nature of the activated complex of such reactions. In order to obtain reasonably accurate values of the rate constants, it was necessary to know the identity and the equilibrium constants at various temperatures of a mixed α,α' - and γ,γ' -bipyridyl complex of chromium(II), formed by the addition of γ,γ' -bipyridyl to aqueous solutions of $[\text{Cr}(\text{bipy})_3]^{2+}$. The present work describes spectrophotometric evidence that the mixed complex is formed in the following overall equilibrium, which is rapidly established



The equilibrium thus implies the coordination of a protonated γ,γ' -bipy.*

EXPERIMENTAL

Materials. Doubly distilled water was used throughout. $[\text{Cr}(\text{bipy})_3](\text{ClO}_4)_2$ was prepared by adding α,α' -bipyridyl to a solution of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion and precipitating by perchloric acid.⁴ The solutions of $[\text{Cr}(\text{bipy})_3]^{2+}$ were obtained either by direct dissolution of

* For α,α' -bipyridyl the symbols α,α' or bipy are used. For γ,γ' -bipyridyl the symbol γ,γ' .

the solid perchlorate in deoxygenated aqueous NaCl, or by mixing deoxygenated solutions of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (from dissolution of electrolytic chromium in HCl) and excess α, α' -bipyridyl. In the first case some oxidation took place during the dissolution process, as also noted previously,⁵ but the resulting chromium(III) complex was shown not to interfere with the equilibrium. The concentration of $[\text{Cr}(\text{bipy})_3]^{3+}$ was determined by measuring the absorbance at 562.5 nm, where $\epsilon = 4.34 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. HCl, NaCl, and α, α' -bipyridyl were AnalaR grade and used without further purification, while γ, γ' -bipyridyl was reagent grade and recrystallized from water several times before use. The purity of both α, α' - and γ, γ' -bipyridyl was checked spectrophotometrically.

Equilibrium constants. Due to the low solubility of $[\text{Cr}(\text{bipy})_3](\text{ClO}_4)_3$ in perchlorate media, the equilibrium measurements were carried out in 0.1 M NaCl as a constant salt medium, instead of NaClO_4 . As $[\text{Cr}(\text{bipy})_3]^{3+}$ is oxygen sensitive, all experiments involving this ion were performed using syringe techniques and in an atmosphere of nitrogen, scrubbed by solutions of chromium(II) chloride. Solutions of $[\text{Cr}(\text{bipy})_3]^{3+}$ were mixed with deoxygenated solutions of the appropriate concentrations of α, α' - and γ, γ' -bipyridyl, and pH adjusted to the required value with deoxygenated HCl. The spectra were then measured on a Beckman DU spectrophotometer using 5 cm quartz cells. No redox reaction between chromium(II) and γ, γ' -bipyridyl was observed. As the total concentrations of the bipyridyls were always much higher than the concentration of chromium(II), no corrections in the concentration values of the bipyridyls were made for the amounts coordinated to chromium(II).

The pK values of α, α' - and γ, γ' -bipyridyl were obtained by potentiometric titration of solutions of the pure bases in 0.1 M NaCl by 0.1 M HCl. A Radiometer pH meter 4 equipped with glass and calomel electrodes was used.

RESULTS

The addition of γ, γ' -bipyridyl to solutions of $[\text{Cr}(\text{bipy})_3]^{3+}$ causes a change in the colour of the solution from wine-red to blue-violet. Fig. 1 shows the

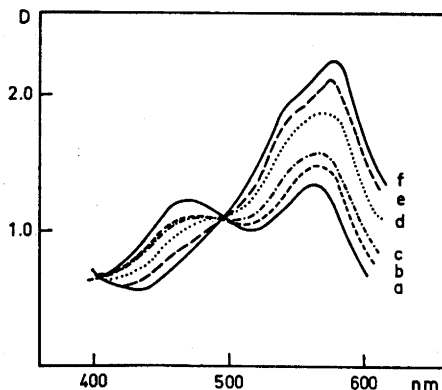
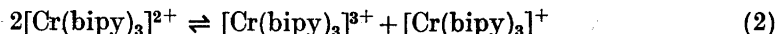


Fig. 1. Effect of increasing C_{γ}^0 on the visible absorption spectrum of $[\text{Cr}(\text{bipy})_3]^{3+}$. pH = 3.25. $t = 25^\circ\text{C}$. $C_{\alpha}^0 = 2.0 \times 10^{-4} \text{ M}$. Total $[\text{Cr}(\text{II})]$ corrected to $6.18 \times 10^{-5} \text{ M}$. a: $C_{\gamma}^0 = 0$. b: $C_{\gamma}^0 = 2.50 \times 10^{-4} \text{ M}$. c: $C_{\gamma}^0 = 5.00 \times 10^{-4} \text{ M}$. d: $C_{\gamma}^0 = 7.20 \times 10^{-4} \text{ M}$. e: $C_{\gamma}^0 = 1.30 \times 10^{-3} \text{ M}$. f: $C_{\gamma}^0 = 1.84 \times 10^{-3} \text{ M}$.

absorption spectrum of $[\text{Cr}(\text{bipy})_3]^{2+}$ in the range 400–600 nm, and the effect of adding increasing amounts of γ, γ' -bipyridyl at a constant pH. The new species produced also had low-intensity shoulders at 650 and 720 nm.

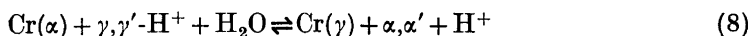
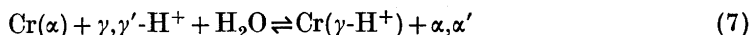
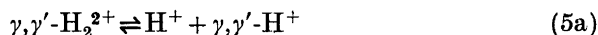
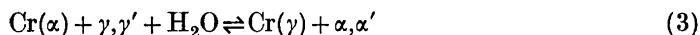
$[\text{Cr}(\text{bipy})_3]^{2+}$ is known to participate in a rapid equilibrium in solutions of certain proton acceptors^{7,8}



and the colour of $[\text{Cr}(\text{bipy})_3]^+$ is deep blue, which could give rise to the colour change observed. However, several lines of evidence show that this is not the new species being formed, when γ, γ' -bipyridyl is added. Firstly, the isobestic point at 496 nm is evidence of a 1:1 correspondence between $[\text{Cr}(\text{bipy})_3]^{2+}$ and the new species. As $[\text{Cr}(\text{bipy})_3]^{3+}$ has a very small extinction coefficient at this wave-length, an equilibrium such as (2) is very unlikely. Secondly, although the proton acceptor properties of γ, γ' -bipyridyl might be expected to shift equilibrium (2) to the right, this assumption is ruled out by the fact, that the spectral changes are smaller, when pH is increased, and that, in the absence of γ, γ' -bipyridyl, increasing amounts of α, α' -bipyridyl (which has roughly the same pK value as γ, γ' -bipyridyl) has no effect at all. Finally, a strict first-order dependence in $[\text{Cr}(\text{II})]_{\text{tot}}$ was always observed in the kinetic runs of the reaction between the equilibrium mixtures containing chromium(II) and cobalt(III);¹ this would not have been the case if a disproportionation equilibrium had been involved.

Together with the observation, that for a given concentration of γ, γ' -bipyridyl, increasing concentrations of α, α' -bipyridyl result in decreasing spectral changes of the solutions, all this strongly suggests a competition between α, α' - and γ, γ' -bipyridyl for the coordination sites of chromium(II). It was concluded that the new species must be a γ, γ' -bipyridyl complex in a rapid equilibrium with $[\text{Cr}(\text{bipy})_3]^{2+}$. This conclusion is supported by the treatment below, which shows that the data are consistent with a replacement of one coordinated α, α' -bipyridyl by one (protonated) γ, γ' -bipyridyl. Presumably one water molecule occupies the sixth coordination site of chromium(II), as γ, γ' -bipyridyl, although bidentate, for steric reasons can coordinate through one nitrogen atom only.

If α, α' -bipyridyl is monocoordinated in an intermediate state of the replacement by γ, γ' -bipyridyl, it is reasonable to assume that it is not protonated, as the proton would then be very close to the Cr^{2+} nucleus and subject to a strong electrostatic repulsion. In the γ, γ' -bipyridyl ligand, however, the non-coordinating nitrogen is located at a considerable distance from the metal center, and the possible protonation of this nitrogen atom should be taken into account. The following equilibria are therefore considered to account for the spectral changes observed



where $\text{Cr}(\alpha)$ and $\text{Cr}(\gamma\text{-H}^+)$ are abbreviated symbols of species I and II of eqn. (1), and $\text{Cr}(\gamma)$ the complex in which unprotonated γ, γ' -bipyridyl is coordinated.

The spectral difference in the visible range between $\text{Cr}(\gamma)$ and $\text{Cr}(\gamma\text{-H}^+)$ is probably small; therefore the existence of the isobestic point at 496 nm is not sufficient evidence for the presence of one of these species only. However, from the values of the dissociation constants of the bipyridyls, it is easy to show, by calculations analogous to the ones below, that equilibria (3) and (8) both imply the formation of increasing amounts of $\text{Cr}(\gamma)$ (increasing κ) with decreasing $[\text{H}^+]$, which is contrary to the observed results. Therefore, the unprotonated $\text{Cr}(\gamma)$ cannot be present in significant amounts, and the dominant new species must be the protonated complex $\text{Cr}(\gamma\text{-H}^+)$.

It is thus relevant to consider the overall equilibrium (7), which is the sum of the equilibria (3)–(5), as the main representative of the overall process in the solution. To calculate the equilibrium constant K we have

$$[\text{Cr}(\gamma\text{-H}^+)][\alpha, \alpha'] / [\text{Cr}(\alpha)][\gamma, \gamma'\text{-H}^+] = K$$

Replacing, at a given pH, $[\alpha, \alpha']$ and $[\gamma, \gamma'\text{-H}^+]$ by the total concentrations C_α° and $C_{\gamma'}^\circ$ of the bipyridyls, we get

$$[\text{Cr}(\gamma\text{-H}^+)]C_\alpha^\circ / [\text{Cr}(\alpha)]C_{\gamma'}^\circ = \kappa, \text{ or } [\text{Cr}(\gamma\text{-H}^+)] / [\text{Cr}(\alpha)] = \kappa' C_{\gamma'}^\circ$$

where $\kappa' = \kappa / C_\alpha^\circ$. At a given wave-length, it is also found by straight-forward calculations that

$$1/(D/c_0l - \epsilon_0) = 1/(\epsilon_1 - \epsilon_0) + 1/\kappa' (\epsilon_1 - \epsilon_0) \times 1/C_{\gamma'}^\circ \quad (9)$$

where ϵ_0 and ϵ_1 are the molar extinction coefficients of species I and II, D the total measured absorbance, l the light path length, and c_0 the total concentration of chromium(II). ϵ_1 and κ' can thus be obtained by plotting eqn. (9), and from κ' , κ can be obtained by multiplication by C_α° .

The relation between κ and K can be found when the dissociation constants of the bipyridyls are known. α, α' -Bipyridyl can associate one proton only in the media used here ($3 < \text{pH} < 5$), while both singly and doubly protonated γ, γ' -bipyridyl are present in significant amounts.⁹

Denoting the acid dissociation constants of the conjugate acids by K_1^α for α, α' -, and by $K_1^{\gamma'}$ and $K_2^{\gamma'}$ for γ, γ' -bipyridyl, it is found that

$$\kappa(1 + K_1^{\gamma'}/[\text{H}^+] + [\text{H}^+]/K_2^{\gamma'}) = K(1 + [\text{H}^+]/K_1^\alpha) \quad (10)$$

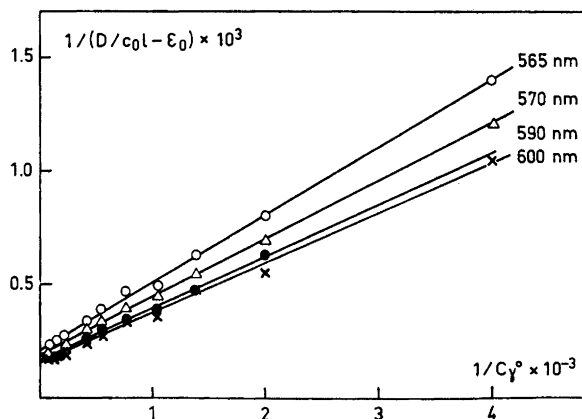


Fig. 2. Plots of eqn. (9). pH = 3.25. $t = 25^\circ\text{C}$. $C_\alpha^\circ = 2.0 \times 10^{-4}$ M. Variable total $[\text{Cr}(\text{II})]$.

Fig. 2 shows typical experimental plots of eqn. (9). In all cases straight lines were obtained, at a number of different wavelengths, giving constant values of ϵ_1 and κ for different C_α° . The ϵ_1 values are plotted against the wave-length in Fig. 3, showing the isobestic point at 496 nm ($\epsilon = 3.53 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$).

Table 1. $\text{p}K$ values and heats of dissociation for protonated bipyridyls. ΔH° in kcal mol $^{-1}$.

$t^\circ\text{C}$	$\text{p}K_1^\alpha$	$\text{p}K_1^\gamma$	$\text{p}K_2^\gamma$
18.8	4.564	4.830	2.730
25.0	4.523	4.770	2.690
31.5	4.436	4.699	2.618
40.0	4.385	4.602	2.568
ΔH°	3.7	4.7	4.2

Table 2. Corresponding values of measured κ - and $[\text{H}^+]$ -values, and K -values calculated from eqn. 10.

$t^\circ\text{C}$	$[\text{H}^+]$	κ	K	$t^\circ\text{C}$	$[\text{H}^+]$	κ	K
25.0	5.9×10^{-4}	0.159	0.0101	13.5	5.9×10^{-4}	0.086	0.0047
25.0	4.0×10^{-4}	0.126	0.0109	13.5	1.4×10^{-4}	0.027	0.0047
25.0	2.5×10^{-4}	0.117	0.0148	18.0	5.9×10^{-4}	0.112	0.0069
25.0	2.5×10^{-4}	0.112	0.0143	18.0	5.9×10^{-4}	0.118	0.0072
25.0	1.26×10^{-4}	0.060	0.0138	18.0	2.24×10^{-4}	0.057	0.0072
25.0	1.00×10^{-4}	0.044	0.0124	18.0	1.12×10^{-4}	0.028	0.0064
25.0	0.63×10^{-4}	0.032	0.0134	31.5	5.9×10^{-4}	0.198	0.0154
				31.5	3.55×10^{-4}	0.152	0.0168
				31.5	1.41×10^{-4}	0.049	0.0150

The dissociation constants of the bipyridyls at different temperatures are given in Table 1; the values are found to be in good agreement with literature values.^{9,10} Table 2 reports corresponding values of κ , $[\text{H}^+]$, and K , at different temperatures, calculated by means of the dissociation constants of Table 1. The average values of K found are: 13.5°C, $K = 0.0047$; 18.0°C, $K = 0.0071$; 25°C, $K = 0.0128$; 31.5°C, $K = 0.0157$. From a plot of the $\log K$ values thus obtained, against the reciprocal temperature, ΔH° and ΔS° are calculated to be 12 kcal mol $^{-1}$ and 33 cal K $^{-1}$ mol $^{-1}$, respectively.

DISCUSSION

It is shown that the new species formed is predominantly a protonated γ, γ' -bipyridyl complex in the pH-range investigated, but due to the hydrolysis and disproportionation of $[\text{Cr}(\text{bipy})_3]^{2+}$ outside a fairly narrow pH-range,⁶⁻⁸ it has not been possible to investigate the protonation equilibrium separately.

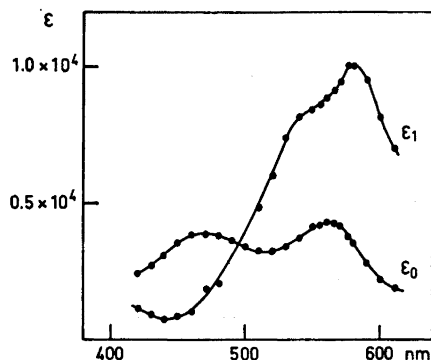


Fig. 3. Molar extinction coefficients of $[\text{Cr}(\alpha, \alpha')_2(\gamma, \gamma'\text{-H}^+)\text{H}_2\text{O}]^{3+}$.

Thermodynamic parameters. The value of ΔH° is higher than the values of the step-wise enthalpies of aquation of the LFSE-stabilized $[\text{M}(\text{bipy})_3]^{2+}$ complexes, where M is Fe, Ni, and Cu.¹¹⁻¹³ The relatively high value can be explained by the dechelation and by the loss of LFSE, when γ, γ' -bipyridyl and water replace α, α' -bipyridyl. Thus, π -bonding between Cr^{2+} and α, α' -bipyridyl in the low-spin d^4 $[\text{Cr}(\text{bipy})_3]^{2+}$ increases the bond strength of this complex¹⁴ and forms a five-membered ring of a high degree of electron delocalization. The bonding of the monocoordinating γ, γ' -bipyridyl does not compensate for the energy spent in breaking this ring system. The additional increase in ΔH° as compared to the hydration enthalpies of the $[\text{M}(\text{bipy})_3]^{2+}$ complexes might be due to a withdrawal of the mobile π -electron system of γ, γ' -bipyridyl towards the proton at the remote end of the ligand, thus resulting in a weakening of the metal-ligand bond.

The high positive value of ΔS° is probably due to a considerable gain in configurational entropy, partly arising from the factors mentioned above. However, as the coordination of a water molecule would give rise to a considerable loss in translational entropy, it is necessary, to account for the overall big positive effect, to assume a more "loose" bonding of at least one of the two hetero-ligands. This assumption is reasonable in view of the tetragonally distorted octahedral structure of the bis-ethylene chromium(II) complex¹⁵ and of the distorted octahedral or even pentacoordinated structures of many bis-complexes of chelate N -coordinating complexes of the electronically similar Cu^{2+} ion.¹⁶

Spectral data. Previous observations^{7,8,11} and a qualitative MO diagram suggest that the two peaks of $[\text{Cr}(\text{bipy})_3]^{2+}$ on Fig. 1 are metal-to-ligand $t_{2g} - \pi^*$ and $t_{2g} - \pi^{**}$ transitions. This is also supported by agreement between the transition energy difference and the $\pi^* - \pi^{**}$ energy difference of bipy calculated by the simple Hückel approximation, assuming a value of $50 \text{ kcal}^{-1} \text{ mol}^{-1}$ for the exchange integral.¹⁸

Three Gaussian peaks, at 505 nm ($\epsilon = 2.37 \times 10^3$), 545 nm ($\epsilon = 5.47 \times 10^3$), and 591 nm ($\epsilon = 6.48 \times 10^3$), are required to reproduce the experimental absorbances of the γ, γ' -bipyridyl complex satisfactorily in the range $400 - 600 \text{ nm}$; The intensity of the bands suggests them to be of charge-transfer nature, but as such bands are usually asymmetric,¹⁹ the analysis can only be tentative.

Also, no immediate possibility exists of stating whether the complex is *cis*- or *trans*-. The chromium(III) product of oxidation by molecular oxygen or cobalt(III) is mainly *trans*-,^{1,20,21} but as this is not the primary product, its configuration is not necessarily identical with that of the γ,γ' -bipyridyl complex.

Only a very slight shift of the peaks, if any, was observed when the solvent was changed from water to 50 % or 96 % methanol. This shows that in the

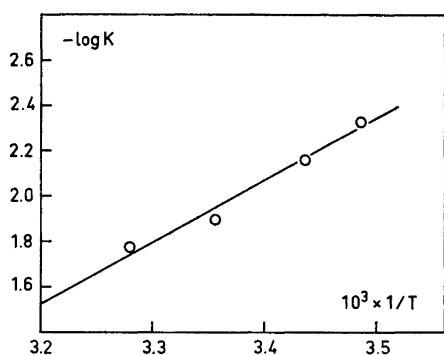


Fig. 4. Plot of $-\log K$ against $1/T$.

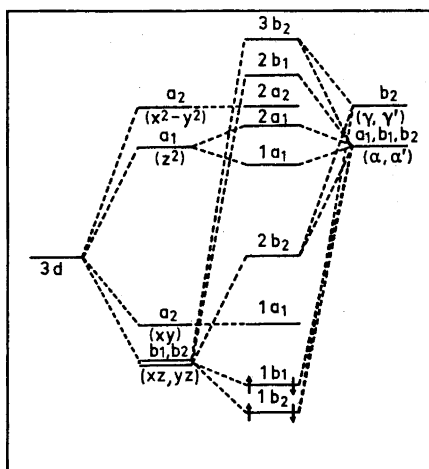


Fig. 5. Simplified π -MO diagram of the γ,γ' -bipyridyl complex. Interaction with metal d -orbitals only.

excited state the electron must be symmetrically delocalized, preferentially on the α,α' -bipyridyl ligands. Otherwise a shift towards smaller wave-lengths would be expected because of the smaller solvation of a polar excited state in methanol.²²

Assuming a *trans*-configuration, and considering only π -overlap between metal d orbitals and π -orbitals of the coordinated bipyridyls, a simple MO diagram of the C_{2v} complex can be constructed (Fig. 6²¹). The second column shows the crystal field splitting of the metal d orbitals, and the third column the MO's arising from interaction with the a_1 , a_2 , and b_2 π -orbitals of the ligands. As all transitions except $b_2 \leftrightarrow b_1$ and $a_2 \leftrightarrow a_1$ are symmetry allowed, the two low-intensity shoulders at 650 and 720 nm could then be $1b_1 \leftrightarrow 1a_2$ and $1b_2 \leftrightarrow 1a_2$, which are in fact internal metal transitions. The high peak at 591 nm represents a transition from an orbital which is predominantly metal yz to the non-bonding $2b_2$, formed by contribution from both α,α' - and γ,γ' -bipyridyl, and the 505 and 545 nm peaks can finally most conveniently be described as metal-to-ligand transitions.

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