Ligand Dissociation Rate Constants of Tris(4,4′-dimethyl-2,2′-bipyridine)chromium(II) and Tris(5,5′-dimethyl-2,2′-bipyridine)chromium(II) Complexes

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Synopsis. Ligand dissociations of tris(4,4′-Me_2bpy)- and tris(5,5′-Me_2bpy)chromium(II) complexes** have been studied by scavenging the ligand with zinc ion according to a stopped-flow method.

The ligand dissociation of $[Cr(bpy)_3]^{2+}$ was first studied by a redox reaction between $[Cr(bpy)_3]^{2+}$ and $[Co(PO_4)(NH_3)_5]$ using a stopped-flow method[1] and subsequently by d.c. polarography,[2,3] while that for a heterogeneous system was studied cyclic voltammetrically.[4,5] Reports were given on the ligand dissociation rate constants obtained from the studies of the oxidation of $[Cr(bpy)_3]^{2+}$ or $[Cr(phen)_3]^{2+}$ with $[Co(NH_3)_6]^{3+}$ by the stopped-flow method.[6,7] Since all the results were obtained by indirect methods, attempts were made to obtain the ligand dissociation rate constants of $[Cr(bpy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ directly by the stopped-flow method.[8] Although the ligand dissociation rate constants for a few complexes of 1,10-phenanthroline derivatives ($[Cr(5\text{-Me(phen)})_3]^{2+}$, $[Cr(5\text{-Cl(phen)})_3]^{2+}$ and $[Cr(5\text{-Br(phen)})_3]^{2+}$)*** were measured cyclic voltammetrically,[5] no paper has appeared so far on chromium(II) complexes of 2,2′-bipyridine derivatives. We have studied the ligand dissociations of $[Cr(4,4'\text{-}Me_2bpy)_3]^{2+}$ and $[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$, and obtained their kinetic and activation parameters.

Experimental

Apparatus. The stopped-flow apparatus for kinetic measurements was the same as reported.[7] Ultraviolet and visible absorption spectra were measured with a Hitachi recording spectrophotometer Type EPS-3T using a quartz cell of 1.0 mm optical path.

Reagents. 4,4′-Me_2bpy and 5,5′-Me_2bpy were synthesized according to the procedure of Sasse and Whittle.[9] The synthesized ligands 4,4′-Me_2bpy and 5,5′-Me_2bpy were checked spectrophotometrically. High purity nitrogen was used after further purification with activated copper columns. All other chemicals were of GR grade and used without purification.

Measurements of Absorption Spectra. The absorption spectra of *ca.* 2 mmol dm^{-3} aqueous solutions of $[Cr(4,4'\text{-}Me_2bpy)_3]^{2+}$ and $[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$ were measured. Preparation of the sample solution using a vacuum line was carried out as reported previously.[7] Since 4,4′-Me_2bpy and 5,5′-Me_2bpy were hardly soluble in water, not being able to give solutions of the desired concentration, suspensions of these ligands were used. Chromium (II) complex solutions were obtained by mixing anhydrous chromium(II) chloride with their respective suspensions. Absorption spectra of these complexes were measured and found to agree with those reported.[10]

Kinetic Measurements. A solution of $[Cr(4,4'\text{-}Me_2bpy)_3]^{2+}$ or $[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$ and a zinc chloride solution were mixed with the stopped-flow apparatus, the concentrations of chromium(II) complexes and zinc ion being 2.0 mmol dm^{-3} and 50 mmol dm^{-3}, respectively. The ionic strength for each solution was adjusted to 0.20 mol dm^{-3} by addition of sodium chloride, the pH being adjusted to 5.3 with an acetic acid–sodium acetate buffer solution. Kinetic measurements were performed by observing the absorbance change of the starting chromium(II) complex with time after mixing the solution of the chromium(II) complex with excess zinc ion used as a scavenger. The wavelengths were fixed at 571 nm for $[Cr(4,4'\text{-}Me_2bpy)_3]^{2+}$ and 565 nm for $[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$. The temperatures for the kinetic measurements were in the range 20—45 °C, the respective temperature being kept constant within ±0.1 °C.

Reaction Analysis. Reaction curves, absorbance *vs.* time, were analyzed by means of

$$\ln[(A_t-A_\infty)/(A_0-A_\infty)] = k_{obsd}\,t, \qquad (1)$$

where A_0, A_t, and A_∞ denote the absorbance of the solution at time $t=0$, t and ∞, respectively, and k_{obsd} is the apparent first-order rate constant.

Results and Discussion

Plots of log (A_t-A_∞) *vs.* t show linearity over the whole range of the reaction curves, indicating that the reaction is of first-order type.

The following succesive equilibria seem to hold for both the complex of 4,4′-Me_2bpy and that of 5,5′-Me_2bpy:

Table 1. Rate constants for the ligand dissociation of Cr(II) complexes[a]

Complex	Temp/°C	k_{obsd}/s^{-1}[b]
$[Cr(4,4'\text{-}Me_2bpy)_3]^{2+}$	20.0	0.644±0.005 (7)
	25.0	1.17 ±0.02 (6)
	30.0	2.05 ±0.03 (6)
	35.0	3.60 ±0.04 (8)
	40.0	5.93 ±0.06 (7)
	45.0	9.68 ±0.12 (5)
$[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$	20.0	0.338±0.002 (6)
	25.0	0.663±0.002 (6)
	30.0	1.22 ±0.01 (6)
	35.0	2.14 ±0.04 (7)
	40.0	3.91 ±0.04 (7)

a) At pH 5.3. b) Number of measurements given in parentheses.

** Ligands, 4,4′-Me_2bpy and 5,5′-Me_2bpy, represent 4,4′-dimethyl-2,2′-bipyridine and 5,5′-dimethyl-2,2′-bipyridine, respectively.

*** The abbreviations "5-Me(phen)," "5-Cl(phen)," and "5-Br(phen)" represent 5-methyl-, 5-chloro-, and 5-bromo-1,10-phenanthroline, respectively.

Table 2. Kinetic and activation parameters of the ligand dissociation for chromium(II) complexes at pH 5.3

Complex	k_{diss}/s^{-1} a)	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	Ref.
$[Cr(bpy)_3]^{2+}$	0.390 ±0.003	84.4±1.5	30.6±4.8	8
$[Cr(phen)_3]^{2+}$	0.0643±0.0014	89.0±1.9	30.3±6.3	8
$[Cr(4,4'\text{-}Me_2bpy)_3]^{2+}$	1.17 ±0.02	81.5±1.5	30.1±4.5	b)
$[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$	0.663±0.002	89.9±1.0	53.5±4.0	b)

a) Values at 25.0 °C. b) This work.

$$[Cr(LL)_3]^{2+}+2H_2O \rightleftharpoons [Cr(H_2O)_2(LL)_2]^{2+}+LL, \quad (2)$$

$$[Cr(H_2O)_2(LL)_2]^{2+}+2H_2O \rightleftharpoons [Cr(H_2O)_4(LL)]^{2+}+LL, \quad (3)$$

$$[Cr(H_2O)_4(LL)]^{2+}+2H_2O \rightleftharpoons [Cr(H_2O)_6]^{2+}+LL, \quad (4)$$

where LL denotes 4,4'-Me_2bpy and 5,5'-Me_2bpy. Since zinc ion rapidly scavenges the free ligand,[11] no reverse reactions need be considered for the equilibria under excess zinc ion. Thus, the ligand dissociation of this system could be observed. The kinetic measurements of the present experiment satisfy the above conditions. Since the molar extinction coefficient of the bis complex is considered to be small, in analogy to $[Cr(bpy)_3]^{2+}$,† the dissociation of the tris to the bis complex can be determined. A first-order reaction was observed over the whole range of each reaction curve, and thus the determination of the first step (Eq. 2) is considered to be rate-determining. It is evident that the observed rate constant k_{obst} represents the rate constant for the ligand dissociation of the tris to bis complex.

The rate constants obtained under various temperatures are given in Table 1, and kinetic and activation parameters in Table 2, along with the previous data.[8] The ligand dissociation rate constants of $[Cr(4,4'\text{-}Me_2bpy)_3]^{2+}$ and $[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$ are greater than those of $[Cr(bpy)_3]^{2+}$. This seems to correspond to greater rates of $[Cr(5\text{-}Me(phen))_3]^{2+}$, $[Cr(5\text{-}Cl(phen))_3]^{2+}$ and $[Cr(5\text{-}Br(phen))_3]^{2+}$ as compared with $[Cr(phen)_3]^{2+}$.[5] The values of activation entropy $\Delta S^{\ddagger}$ for $[Cr(bpy)_3]^{2+}$, $[Cr(phen)_3]^{2+}$, and $[Cr(4,4'\text{-}Me_2bpy)_3]^{2+}$ are *ca.* 30 J K^{-1} mol^{-1}, whereas that for $[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$ is far greater. The positive activation entropy suggests that the ligand dissociation of the present system proceeds *via* the dissociative mechanism,[12] while the greater value of $\Delta S^{\ddagger}$ for $[Cr(5,5'\text{-}Me_2bpy)_3]^{2+}$ suggests the possibility of a different dissociative mechanism.

† In the case of $[Cr(bpy)_3]^{2+}$,[8] the absorbance at the starting point of the reaction is estimated to be 0.833 (concentration, 0.96 mmol dm^{-3}; molar extinction coefficient, 4340 dm^3 mol^{-1} cm^{-1}; cell length, 2 mm). If most of the tris complex was consumed for the formation of the bis complex during the dead-time, the initial absorbance observed would be less than 0.154, since the molar extinction coefficient of the bis complex is 803 dm^3 mol^{-1} cm^{-1}.[8] However, in a typical case, the absorbance for the first observable reaction signal was 0.624, the reaction curve approaching zero. The first-order plot fell on a straight line over the whole range observed. The reaction seems to correspond to the dissociation of the tris to the bis complex, and this step is regarded to be rate-determining.

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