

Given the limits of Hückel MO calculations and the complexity of the compounds compared here, it is not surprising that the observed correlation between  $K_c$  and the LUMO charge densities is not clearly linear or exponential. Although the question of thermodynamic stability of mixed-valence systems is certainly complex<sup>2-5,17</sup> and requires thorough MO treatments, this study of mixed-valence complexes that exist at rather positive potentials does provide some guidelines for the design of novel conjugated bridging ligands<sup>15</sup> particularly capable of stabilizing mixed-valence oxidation states. In such ligands, the combined LUMO charge densities of all coordination centers should be as large as possible

(pyrazine of the Creutz-Taube ion<sup>1</sup> has  $\sum c_N^2 = 0.55^{16}$ ) while other factors such as metal-metal distance seem to be of less importance.

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## High-Pressure Kinetic Study of Formation and Dissociation of First- and Second-Row $d^{10}$ Divalent Metal Ion Complexes with Bipyridine in Aqueous Solution: A Cation Size Dependent Reaction Mechanism<sup>1</sup>

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The rate constants for the formation and dissociation of  $Zn(H_2O)_4bpy^{2+}$  and  $Cd(H_2O)_4bpy^{2+}$  as well as the stability constants of these two complexes have been studied as a function of temperature in aqueous solution. The kinetic and equilibrium parameters obtained are  $k_f^{298}/M^{-1} s^{-1} = (2.3 \pm 0.2) \times 10^6$ ,  $k_r^{298}/s^{-1} = 13 \pm 5$ ,  $\log(K^{298}/M^{-1}) = 5.23 \pm 0.05$ ,  $\Delta H_f^\ddagger/kJ mol^{-1} = 35.4 \pm 0.6$ ,  $\Delta H_r^\ddagger/kJ mol^{-1} = 62.8 \pm 0.9$ , and  $\Delta H^\circ/kJ mol^{-1} = -27.4 \pm 0.9$  for  $Zn^{2+}$  and  $k_f^{298}/M^{-1} s^{-1} = (3.3 \pm 0.3) \times 10^6$ ,  $k_r^{298}/s^{-1} = 160 \pm 20$ ,  $\log(K^{298}/M^{-1}) = 4.33 \pm 0.06$ ,  $\Delta H_f^\ddagger/kJ mol^{-1} = 24.0 \pm 2.3$ ,  $\Delta H_r^\ddagger/kJ mol^{-1} = 46.1 \pm 2.8$ , and  $\Delta H^\circ/kJ mol^{-1} = -22.1 \pm 2.4$  for  $Cd^{2+}$ . The influence of pressure on the rate constants for formation of the complexes has also been studied. For  $Cd^{2+}$ , determination of the rate constant for the dissociation of the mono complex at variable pressure could be made by adding  $Cu^{2+}$  to form the  $Cu(H_2O)_4bpy^{2+}$  complex quantitatively and measuring the rate-limiting dissociation of the  $Cd^{2+}$  complex. For the analogue  $Zn^{2+}$  system, the activation volume for the dissociation process had to be calculated as the difference between the reaction volume obtained from a variable-pressure equilibrium study and the activation volume for the formation step. For  $Zn^{2+}$ , the small negative activation entropies ( $\Delta S_f^\ddagger/J K^{-1} mol^{-1} = -4 \pm 2$  and  $\Delta S_r^\ddagger/J K^{-1} mol^{-1} = -12 \pm 3$ ) and positive activation volumes ( $\Delta V_f^\ddagger/cm^3 mol^{-1} = +7.1 \pm 0.4$  and  $\Delta V_r^\ddagger/cm^3 mol^{-1} = +3.6$ ) are interpreted in terms of a dissociative interchange mechanism. The negative values found for  $Cd^{2+}$  ( $\Delta S_f^\ddagger/J K^{-1} mol^{-1} = -39.7 \pm 8.2$ ,  $\Delta S_r^\ddagger/J K^{-1} mol^{-1} = -48.4 \pm 9.7$ ,  $\Delta V_f^\ddagger/cm^3 mol^{-1} = -5.5 \pm 1.0$ , and  $\Delta V_r^\ddagger/cm^3 mol^{-1} = -6.9 \pm 1.2$ ) show that an associative interchange mechanism operates. This change in activation mode on going from the first to the second row is attributed to the large difference in ionic radius between the two cations.

### Introduction

The interest in kinetic studies of simple substitution reactions on metal ions has been revived since variable-pressure techniques have become productive investigation tools to complement the traditional mechanistic criteria. The number of inorganic reactions for which volumes of activation have been measured is thus in constant progression, and confidence in the ability of this parameter to help in characterizing the mechanism of simple coordination reactions is also increasing regularly.<sup>2</sup> Some information has been collected for most first-row octahedral transition-metal cations, and it is now clear that the mechanisms are similar for solvent exchange and ligand substitution. It has also been learned that these mechanisms gradually change along the series from associative to dissociative activation mode, at least for the 2+ and 3+ oxidation states in water, methanol, and acetonitrile media.<sup>3</sup> Kinetics of solvent exchange and complex formation on second-row octahedral cations has received much

less interest, however, probably because of the more complex chemistry involved with these ions. Our study of  $Mo(H_2O)_5NCS^{2+}$  formation from  $Mo(H_2O)_6^{3+}$  seems in fact to be the only variable-pressure work in water reported to date.<sup>4</sup> In the present account, we extend our investigations to a later member on this row, the  $d^{10}$  divalent cadmium ion, and, for the sake of comparison, to its first-row parent  $Zn^{2+}$ . The rates for water exchange of these two cations are too fast to be measured at the present stage of NMR instrumentation, and one is forced to turn toward complex formation reactions that can be studied by other experimental techniques. In this context, we have chosen to study the formation, dissociation, and equilibrium of the mono complexes of  $Zn^{2+}$  and  $Cd^{2+}$  with the uncharged bidentate bipyridine ligand in aqueous solution, using stopped-flow and UV-visible spectroscopic techniques at variable temperature and pressure.

### Experimental Section

**Chemicals and Solutions.** Hydrated  $Zn(ClO_4)_2$  was prepared from  $ZnO$  (Merck, p.a.) dissolved in concentrated  $HClO_4$  (Merck, p.a.), and it was recrystallized from water.  $Cd(ClO_4)_2 \cdot 6H_2O$  (Ventron, p.a.),  $Cu(ClO_4)_2 \cdot 6H_2O$  (Fluka, purum), and 2,2'-bipyridine (bpy, Fluka, p.a.) were used as supplied. Stock solutions were prepared volumetrically at room temperature with doubly distilled water. The pH of all sample solutions was set between 5.8 and 6.0 and measured with a combined

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**Table I.** Activation and Thermodynamic Parameters for Formation, Dissociation, and Equilibrium of  $\text{Cd}(\text{H}_2\text{O})_4(\text{bpy})^{2+}$  and  $\text{Zn}(\text{H}_2\text{O})_4(\text{bpy})^{2+}$ 

	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$
$k_f^{298}/\text{M}^{-1}\text{s}^{-1}$	$(2.3 \pm 0.2) \times 10^6$ <sup>a</sup>	$(3.3 \pm 0.3) \times 10^6$
$k_r^{298}/\text{s}^{-1}$	$13 \pm 5$ <sup>b</sup>	$160 \pm 20$
$\log(K^{298}/\text{M}^{-1})$	$5.23 \pm 0.05$ <sup>c</sup>	$4.33 \pm 0.06$ <sup>d</sup>
$\Delta S_f^\ddagger/\text{J K}^{-1}\text{mol}^{-1}$	$-4 \pm 2$	$-40 \pm 8$
$\Delta S_r^\ddagger/\text{J K}^{-1}\text{mol}^{-1}$	$-12 \pm 3$	$-48 \pm 10$
$\Delta S^\circ/\text{J K}^{-1}\text{mol}^{-1}$	$+8 \pm 3$ <sup>e</sup>	$+9 \pm 8$ <sup>f</sup>
$\Delta H_f^\ddagger/\text{kJ mol}^{-1}$	$35.4 \pm 0.6$	$24.0 \pm 2.3$
$\Delta H_r^\ddagger/\text{kJ mol}^{-1}$	$62.8 \pm 0.9$	$46.1 \pm 2.8$
$\Delta H^\circ/\text{kJ mol}^{-1}$	$-27.4 \pm 0.9$ <sup>g</sup>	$-22.1 \pm 2.4$ <sup>h</sup>
$\Delta V_f^\ddagger/\text{cm}^3\text{mol}^{-1}$	$+7.1 \pm 0.4$ <sup>i</sup>	$-5.5 \pm 1.0$ <sup>i</sup>
$\Delta V_r^\ddagger/\text{cm}^3\text{mol}^{-1}$	$+3.6$ <sup>j</sup>	$-6.9 \pm 1.2$ <sup>i</sup>
$\Delta V^\circ/\text{cm}^3\text{mol}^{-1}$	$+3.5 \pm 0.4$ <sup>k</sup>	$+1.4$ <sup>i</sup>

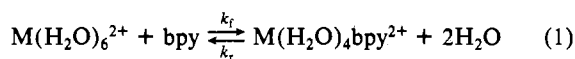
<sup>a-d</sup> Literature values<sup>9,12</sup> (same units as above): (a)  $10^6$ ; (b) 16; (c) 5.2, 5.3; (d) 4.30, 4.18. <sup>e-h</sup> Literature values<sup>12,25</sup> (same units as above): (e) 0 to +20; (f) +8.3 to +10.6; (g) -22 to -30; (h) -21, -21.2. <sup>i</sup> At 273 K. <sup>j</sup> Obtained by difference. <sup>k</sup> At 298 K.

glass electrode containing saturated NaCl as reference electrolyte. Under the concentration and pH conditions of the experiments, protonation of bpy ( $\text{p}K_a = 4.30$ ) amounted to a maximum of 3% and hydrolysis of  $\text{Cd}^{2+}$  ( $\text{p}K_a \approx 9.0$ ) and  $\text{Zn}^{2+}$  ( $\text{p}K_a \approx 10.0$ ) was always negligible.<sup>5</sup> In the study of  $\text{Cd}(\text{H}_2\text{O})_4\text{bpy}^{2+}$  dissociation, the added  $\text{Cu}^{2+}$  was always in at least 15-fold excess of which a minimum of 90% was in the nonhydrolyzed form.<sup>6</sup> In all cases, concentrations were expressed in molarities at 0.1 MPa<sup>7</sup> and the ionic strength was fixed at 0.01 M with  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (Merck, p.a.).

**Kinetic and Equilibrium Measurements.** The experimental setups for kinetic and equilibrium experiments were as described previously.<sup>4,8</sup> The observation wavelength was 304 nm for  $\text{Cd}(\text{H}_2\text{O})_4\text{bpy}^{2+}$  and 305.5 nm for  $\text{Zn}(\text{H}_2\text{O})_4\text{bpy}^{2+}$  complex formation. The temperature dependence of the kinetics at ambient pressure was studied from 273.2 to 293.2 K for  $\text{Cd}^{2+}$  and from 273.2 to 303.2 K for  $\text{Zn}^{2+}$ . Dissociation of  $\text{Cd}(\text{H}_2\text{O})_4\text{bpy}^{2+}$  was followed between 273.2 and 293.2 K at 305 nm, for different concentrations in added  $\text{Cu}^{2+}$ . Variable-pressure data were collected up to 200 MPa at 273.2 K. Series of 2–12 data sets were collected for each of the experimental conditions. For equilibrium measurements, the temperature range was 273.2–328.2 K. A study of the change in the  $\text{Zn}(\text{H}_2\text{O})_4\text{bpy}^{2+}$  stability constant with pressure was made up to 200 MPa at 298.2 by using equimolar concentrations ( $2 \times 10^{-5}$  M) of  $\text{Zn}^{2+}$  and bpy. The errors quoted throughout the text and Table I are  $\pm 1$  standard deviation.

## Results

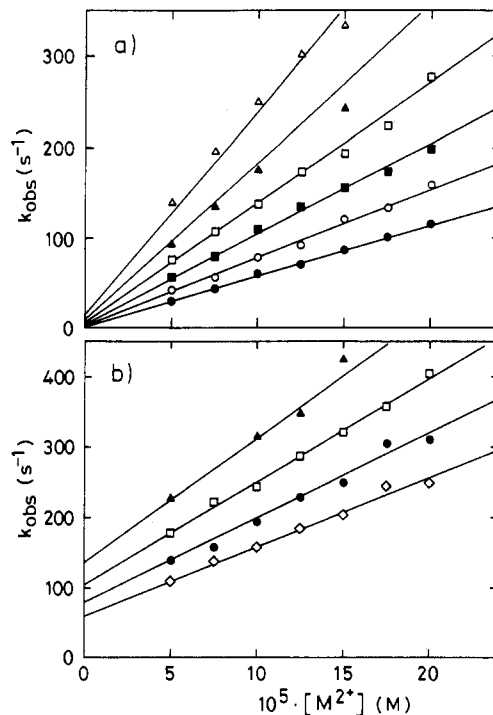
The reaction between excess  $\text{M}(\text{H}_2\text{O})_6^{2+}$  ( $\text{M} = \text{Cd}, \text{Zn}$ ) and bpy in aqueous solution follows (1). Kinetic analysis shows



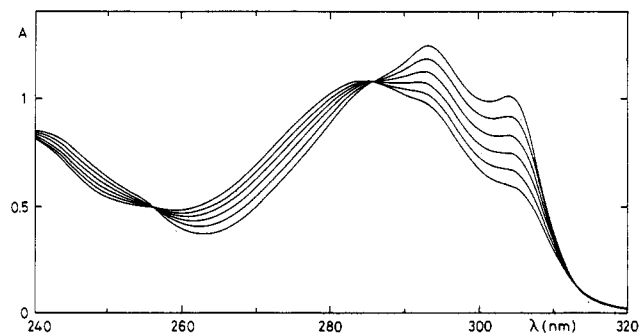
binding of the first nitrogen of bpy to the metal cation to be the rate-determining step in forming the bidentate complex. The subsequent ring closure occurs much faster.<sup>9,10</sup> The mono complex is the only species formed when  $\text{M}^{2+}$  is in excess. In the kinetic study, a 10-fold excess metal over ligand concentration, or more, was always enforced. It was considered a minimum requirement to ensure the pseudo-first-order conditions necessary for the application of eq 2. The  $k_{\text{obsd}}$  values were obtained by using the

$$k_{\text{obsd}} = k_f[\text{M}^{2+}] + k_r \quad (2)$$

first four half-lives of reaction at least. The  $k_f$  values were ex-



**Figure 1.**  $\text{M}^{2+}$  concentration dependence of observed first-order rate constants for formation of  $\text{M}(\text{H}_2\text{O})_4(\text{bpy})^{2+}$  at various temperatures. (a)  $\text{M} = \text{Zn}$ : (●) 273 K; (○) 278 K; (■) 283 K; (□) 288 K; (▲) 293 K; (△) 298 K. (b)  $\text{M} = \text{Cd}$ : (◇) 273 K; (●) 278 K; (□) 283 K; (▲) 288 K.



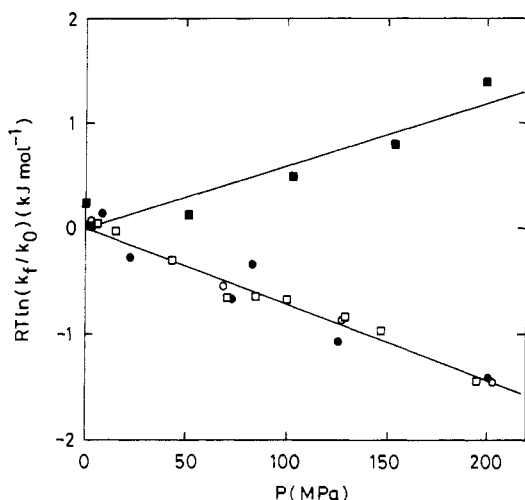
**Figure 2.** Absorption spectra of an equilibrated  $10^{-4}$  M solution of  $\text{Cd}^{2+}$  and bpy at 273, 285, 296, 309, 316, and 328 K (top to bottom curves at 304 nm).

tracted from the slopes of the dependence of  $k_{\text{obsd}}$  on  $\text{M}^{2+}$  concentration by use of a weighed least-squares analysis. Figure 1 shows the concentration dependence of  $k_{\text{obsd}}$  at several temperatures.

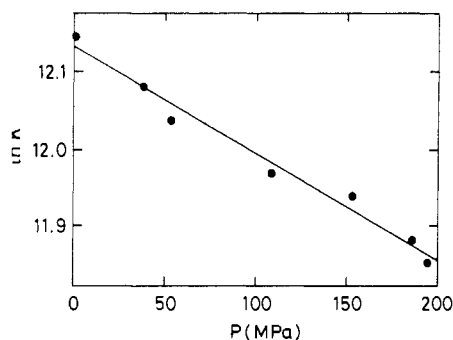
The stability constants of  $\text{Zn}(\text{H}_2\text{O})_4\text{bpy}^{2+}$  and  $\text{Cd}(\text{H}_2\text{O})_4\text{bpy}^{2+}$  were determined spectrophotometrically in addition to the kinetic measurements. Equilibrium constants were obtained from absorbance measurements at various excess metal concentrations by use of a least-squares minimizing program.<sup>11</sup> The best fit was obtained in both cases for one complex, with stability constants  $K^{298} = (1.7 \pm 0.2) \times 10^5 \text{ M}^{-1}$  and  $K^{298} = (2.2 \pm 0.3) \times 10^4 \text{ M}^{-1}$  and molar absorptivities  $\epsilon^{298} = (1.68 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 305.5 nm and  $\epsilon^{298} = (1.46 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 304 nm for the  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  mono complexes, respectively. The  $K^{298}$  values are in perfect agreement with those quoted in the literature<sup>12</sup> and with the values obtained from the kinetics as  $k_f/k_r$ . Simultaneous fits of all variable-temperature kinetic and equilibrium data were consequently made by combining the adjustable pa-

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**Figure 3.** Pressure effect on the normalized natural logarithm of the rate constant for formation of  $M(H_2O)_4(bpy)^{2+}$  at 273 K by high-pressure stopped flow:  $M = Zn$ ,  $[bpy] = 5 \times 10^{-5} M$ ,  $[Zn^{2+}] = 5 \times 10^{-5} M$  ( $\square$ ),  $10^{-4} M$  ( $\bullet$ ),  $1.5 \times 10^{-4} M$  ( $\circ$ );  $M = Cd$  ( $\blacksquare$ ),  $[bpy] = 10^{-5} M$  or  $5 \times 10^{-6} M$ ,  $5 \times 10^{-5} M \leq [Cd^{2+}] \leq 2 \times 10^{-4} M$ .

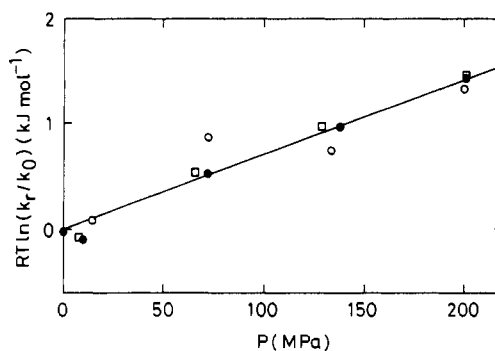


**Figure 4.** Pressure dependence of the logarithm of the stability constant for a solution  $2 \times 10^{-5} M$  in  $Zn^{2+}$  and  $bpy$  at 298 K.

rameters in groups of four ( $\Delta S_f^\ddagger$ ,  $\Delta S_r^\ddagger$  or  $\Delta S^\circ$ ,  $\Delta H_f^\ddagger$ , and  $\Delta H_r^\ddagger$  or  $\Delta H^\circ$ ). They yielded the values listed in Table I. A series of absorption spectra for an equimolar solution of  $Cd^{2+}$  and  $bpy$  at various temperatures is shown in Figure 2.

The pressure dependences of  $k_r$  in normalized logarithmic scale are shown in Figure 3. The pressure dependences of the intercepts in the  $k_{obsd}$  versus  $[M^{2+}]$  plots were too small to allow an accurate determination of the  $k_r$  values. In the zinc case, they were not significantly different from zero and were neglected in the analysis. The variation of the equilibrium constant with pressure gave absorbance changes large enough to obtain  $\Delta V^\circ$ , the overall volume change during the reaction (Figure 4). In the cadmium case, the  $k_r$  values could be obtained from rate measurements made after addition of  $Cu^{2+}$  to the solutions. The  $Cu(H_2O)_4bpy^{2+}$  complex is about  $8 \times 10^3$  times more stable ( $K^{298} = 1.6 \times 10^8 M^{-1}$ )<sup>13</sup> than the  $Cd^{2+}$  one, and the rate constant for its formation is much larger ( $k_f \geq 10^7 M^{-1} s^{-1}$ ).<sup>10</sup> The dissociation of  $Cd(H_2O)_4bpy^{2+}$  hence becomes the rate-limiting step, and  $k_r$  can be measured directly. The pressure dependence of  $k_r$  obtained in this way is shown in normalized logarithmic scale in Figure 5. The absorbance change with increasing pressure was small and the standard deviations on the equilibrium measurements as a function of pressure were too large to allow an accurate determination of the reaction volume  $\Delta V^\circ$ . It was therefore calculated as the difference between the kinetically obtained activation volumes.

The measured activation volumes and the volume of reaction listed in Table I were obtained from fits of all the variable-pressure



**Figure 5.** Pressure effect on the normalized natural logarithm of the rate constant for dissociation of  $Cd(H_2O)_4(bpy)^{2+}$  at 273 K by high-pressure stopped flow after addition of  $Cu^{2+}$ : ( $\square$ )  $[Cd(bpy)^{2+}] = 5 \times 10^{-5} M$ ,  $[Cu^{2+}] = 2.5 \times 10^{-3} M$ ; ( $\circ$ )  $[Cd(bpy)^{2+}] = 5 \times 10^{-5} M$ ,  $[Cu^{2+}] = 7.5 \times 10^{-3} M$ ; ( $\bullet$ )  $[Cd(bpy)^{2+}] = 10^{-4} M$ ,  $[Cu^{2+}] = 5 \times 10^{-3} M$ .

data to eq 3 and 4 ( $Cd^{2+}$ ) or eq 3 and 5 ( $Zn^{2+}$ ), with  $k_f^\circ$ ,  $k_r^\circ$  (or  $K^\circ$ ),  $\Delta V_f^\ddagger$ , and  $\Delta V_r^\ddagger$  (or  $\Delta V^\circ$ ) as adjustable parameters.

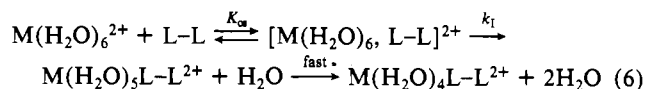
$$\ln k_f = \ln k_f^\circ - \Delta V_f^\ddagger P / RT \quad (3)$$

$$\ln k_r = \ln k_r^\circ - \Delta V_r^\ddagger P / RT \quad (4)$$

$$\ln K = \ln K^\circ - \Delta V^\circ P / RT \quad (5)$$

## Discussion

Coordination of a neutral ligand such as  $bpy$  on the hexaaquated zinc or cadmium cation is expected to follow an interchange mechanism.<sup>13</sup> As depicted in reaction 6, the reaction pathway



can be decomposed into successive steps.<sup>14</sup> The initial diffusion-controlled approach of the incoming ligand in the vicinity of the aqua ion to form an outer-sphere association complex is followed by the inner-sphere, rate-limiting, concerted exchange of water for the entering ligand molecule and, in our case of a bidentate ligand, by the final, much faster ring closure. This scheme is independent of the activation mode of reaction. If a dissociative interchange ( $I_d$ ) takes place, the rate constant  $k_f$  should be comparable to the rate of exchange of water on the studied cation, possibly with a statistical factor being taken into account. For an associative interchange ( $I_a$ ), a much larger dependence of  $k_f$  on the nature of the incoming group, including water, is expected. Reaction 6 will be valid only if the metal complex remains octahedral at every stage of the reaction, since changes in coordination number and geometry about the metal ion have been shown to lead to anomalous kinetic behavior when the configurational change is rate-limiting.<sup>14</sup> Such structural modifications in the course of the reaction have been observed for zinc and cadmium, from octahedral to tetrahedral geometry.<sup>15</sup> In water, though, they occur only at the stage of tris complex formation<sup>16</sup> and can be ruled out for formation of mono complexes as in the present cases.

Several kinetic studies of cadmium in aqueous solution have been reported, most of them involving multidentate ligands,<sup>17</sup> with formation rate constants ranging from  $10^5$  to  $5 \times 10^9 M^{-1} s^{-1}$ . This large spread in  $k_f$  values has suggested an associative mechanism for reactions of this cation, but none of these studies have been

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**Table II.** Activation Volumes  $\Delta V_1^\ddagger$  ( $\text{cm}^3 \text{mol}^{-1}$ ) for the Interchange Step in Dissociatively Activated Substitution Reactions of L on Octahedral First-Row  $\text{M}(\text{H}_2\text{O})_6^{2+}$ 

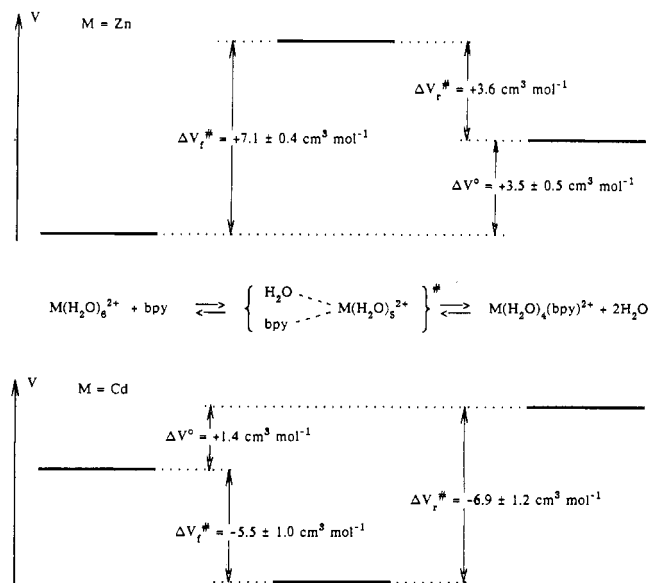
L	M; $r_i$ , pm		
	$\text{Co}^{2+}$ ( $d^7$ ); 74	$\text{Ni}^{2+}$ ( $d^8$ ); 69	$\text{Zn}^{2+}$ ( $d^{10}$ ); 74
$\text{H}_2\text{O}$	+6.1 <sup>a</sup>	+7.2 <sup>a</sup>	(+6) <sup>b</sup>
bpy	+5.9 <sup>c</sup>	+5.3 <sup>c</sup>	+7.1
gly <sup>-d</sup>	+5	+7	+4

<sup>a</sup> Reference 26. <sup>b</sup> Theoretical prediction using a semiempirical approach;<sup>20</sup> see text. <sup>c</sup> Reference 27. <sup>d</sup> From ref 28, after deduction of  $3 \text{ cm}^3 \text{mol}^{-1}$  to account for outer-sphere reaction volume; see text.

conducted at variable temperature or pressure, and the mechanistic information is thus extremely limited. In nonaqueous solvents, the temperature dependence of the rate constant for formation of cadmium nitrate has been studied in methanol, dimethylformamide (DMF), and dimethyl sulfoxide.<sup>18</sup> From the large negative values of the activation entropies, the authors suggested that an associative interchange mechanism is operative for this process in the three solvents and anticipated an increased dissociative character in aqueous solution. For insertion of  $\text{Cd}^{2+}$  into a large phenyl-substituted porphine in DMF, Funahashi et al.<sup>19</sup> concluded that the activation process had a dissociative character on the basis of the large positive activation volume obtained ( $\Delta V_1^\ddagger = +8.9 \text{ cm}^3 \text{mol}^{-1}$ ), although they found a negative activation entropy of a size comparable to that for nitrate complexation. In the two studies, interpretation of the results is complicated by electrostatic contributions to the overall rate constant due to partial charge neutralization in forming the complex.

Formation of bpy complexes does not involve charge separation or cancellation. The electrostrictive influence of an uncharged ligand on the surrounding solvent should not change significantly in forming the precursor outer-sphere complex, and this effect can be neglected, at least in polar solvents. Accordingly, this preequilibrium should produce a negligible contribution to the activation volume  $\Delta V_1^\ddagger$  of the forward process. In the reverse reaction, no outer-sphere precursor complex occurs, but there is also a preequilibrium, corresponding to the replacement of the first bpy nitrogen by a water molecule before the rate-determining substitution of the second nitrogen. The portion of the overall activation volume  $\Delta V_1^\ddagger$  due to this preequilibrium cannot be quantified, but it should be smaller than the reaction volume for replacement of the two bpy nitrogens by water. This all implies that the measured activation volumes mainly reflect the variations in volume due to changes in bond distances and angles in the transition steps. The values of  $\Delta V_1^\ddagger$  and  $\Delta V_2^\ddagger$  can therefore be used directly for mechanistic assignment, as in the simpler cases of solvent exchange. Positive activation volumes will be taken as a strong indication that the reaction proceeds dissociatively, and conversely, negative activation volumes will be a good support for an associative activation mode for the reaction.

For the two reactions of concern, the activation and reaction volumes listed in Table I define three points in the diagram of the volume changes occurring along the reaction path, represented in Figure 6. For formation and dissociation of  $\text{Zn}(\text{H}_2\text{O})_4(\text{bpy})^{2+}$ , with both activation volumes positive, the diagram is characteristic of a dissociative interchange mechanism. Volumes of activation  $\Delta V_1^\ddagger$  for the interchange step of  $I_d$  processes should be fairly independent of the nature of the entering ligand. Table II shows the activation volumes associated with water exchange and simple substitution reactions on dissociatively activated first-row hexaaqua cations. For water exchange and bpy complexation, the volumes of activation can be compared directly because both reactions involve uncharged incoming ligands. For  $\text{Zn}^{2+}$ , however, the activation volume for water exchange cannot be obtained experimentally, as discussed above, and the quoted value is a predicted number proposed by Swaddle<sup>20</sup> as the result of a semi-

**Figure 6.** Volume profiles for formation and dissociation of  $\text{M}(\text{H}_2\text{O})_4(\text{bpy})^{2+}$  complexes.

empirical treatment based on correlations with partial molar volumes. For formation of complexes with the glycinate anion (gly<sup>-</sup>), the activation volumes in Table II had to be corrected before comparison, since this process involves partial neutralization of charges. The ion-pairing contribution to  $\Delta V_1^\ddagger$ ,  $\Delta V_{os}^\ddagger$ , can be estimated to about  $3 \text{ cm}^3 \text{mol}^{-1}$  from model calculations<sup>21</sup> based on the Fuoss equation.<sup>22</sup> This electrostrictive term must be deducted from the apparent volume of activation to obtain the contribution from the interchange step ( $\Delta V_1^\ddagger = \Delta V_1^\ddagger - \Delta V_{os}^\ddagger$ ), which can be now compared with the other values in Table II. Note that the confidence in the indirectly obtained value for  $\text{Zn}^{2+}$  is rather low.<sup>23</sup> Except for this last number, and with an accepted uncertainty in volumes of activation of  $\pm 1 \text{ cm}^3 \text{mol}^{-1}$  taken into account,<sup>24</sup> all results show that the three cations have a comparable dissociative character.

As one goes down the periodic table from  $\text{Zn}^{2+}$  ( $d^{10}$ ,  $r_i = 74 \text{ pm}$ ) in the first row to  $\text{Cd}^{2+}$  ( $d^{10}$ ,  $r_i = 95 \text{ pm}$ ), the corresponding isoelectronic second-row element, the mechanistic situation drastically changes. It is clear from the negative activation volumes in Figure 6 and from the very negative activation entropies that the mechanism for formation and dissociation of  $\text{Cd}(\text{H}_2\text{O})_4(\text{bpy})^{2+}$  is associative and is very likely to be an interchange. In aqueous solution, it is the first time that a changeover in mechanism between rows can be clearly shown from directly comparable data. In nonaqueous solution, a similar behavior had however been observed down the main group IIIA,<sup>3</sup> from the dissociatively activated trimethyl phosphate (TMP) exchange on  $\text{Ga}(\text{TMP})_6^{3+}$  ( $r_i = 62 \text{ pm}$ ,  $\Delta V^\ddagger = +20.7 \text{ cm}^3 \text{mol}^{-1}$ ) to the associatively exchanging TMP on  $\text{In}(\text{TMP})_6^{3+}$  ( $r_i = 80 \text{ pm}$ ,  $\Delta V^\ddagger = -21.4 \text{ cm}^3 \text{mol}^{-1}$ ). In absence of differences in electronic configuration, these changes of mechanism can solely be attributed to size effects. In the present case, the large  $\text{Cd}^{2+}$  center has

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enough room around itself to accommodate all or part of a seventh molecule at the transition state, contrary to the more compact  $Zn^{2+}$  ion. We can say accordingly that the isoelectronic octahedral divalent and trivalent cations of the second row, being larger than their first-row analogues, will probably all react with much more associative character than their first-row counterparts.

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**Registry No.**  $Cd(H_2O)_6^{2+}$ , 14752-06-8;  $Zn(H_2O)_6^{2+}$ , 15906-01-1;  $Cd(H_2O)_4bpy^{2+}$ , 61917-96-2;  $Zn(H_2O)_4bpy^{2+}$ , 61918-16-9; bpy, 366-18-7.

**Supplementary Material Available:** Equilibrium measurements (Tables SI, SII, and SVII-SIX) and observed first-order rate constants (Tables SIII-SVI, SX, and SXI) (11 pages). Ordering information is given on any current masthead page.

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## Calorimetric Study of Thiocyanato Complexes of the Cobalt(II) Ion in Micellar Solutions of a Nonionic Surfactant

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Complex formation equilibria between cobalt(II) and thiocyanate ions have been studied calorimetrically in an aqueous solution and in micellar solutions of the nonionic surfactant Triton X-100 containing  $MClO_4$  ( $M = Li, Na, NH_4$ ) as ionic media at 25 °C. Calorimetric data were well explained in terms of the formation of  $[Co(NCS)]^+$  and  $[Co(NCS)_2]$  and of  $[Co(NCS)]^+$ ,  $[Co(NCS)_2]$ , and  $[Co(NCS)_4]^{2-}$  in water and in micellar solutions, respectively. The formation of  $[Co(NCS)_3]^-$  was found to be practically negligible in any of the solutions examined. The formation constant and enthalpy of formation of  $[Co(NCS)_4]^{2-}$  change with the concentration of the surfactant and with the ionic media in the micellar solutions, while those of  $[Co(NCS)]^+$  remain practically constant. It is suggested that the  $[Co(NCS)]^+$  complex is formed only in the aqueous phase, while  $[Co(NCS)_4]^{2-}$  is formed mainly in micelles as ion pairs.

### Introduction

One of the present authors<sup>1-5</sup> studied liquid-liquid extraction of metal ions with poly(ethylene glycol) and poly(oxyethylene)-type nonionic surfactants as extractants. In aqueous solution of a nonionic surfactant, neutral micelles are formed above the critical micelle concentration (cmc) of the surfactant; the polar hydrophilic groups, such as those of poly(oxyethylene), are directed toward the aqueous bulk phase and the hydrophobic hydrocarbon chains are directed away from the aqueous phase to make up the central cores of micelles. It has been elucidated from the liquid-liquid extraction experiments<sup>1-5</sup> that metal ions such as Co(II), Zn(II), Mo(II), and U(VI) are highly extractable from their thiocyanate micellar solutions by inert polar solvents such as 1,2-dichloroethane and nitrobenzene and that Cd(II), Hg(II), and Pb(II) ions are extractable from their iodide solutions, while Mn(II) and Ni(II) ions as well as alkali-metal and alkaline-earth-metal ions are hardly extracted from either thiocyanate or iodide solution. In the cobalt(II) thiocyanate system with the nonionic surfactant Triton X-100 ( $C_8H_{15}C_6H_4(C_2H_4O)_nH$  ( $n = 10$ )), it was suggested that the metal ion is extracted by an organic solvent in the form of  $M_2[Co(NCS)_4] \cdot 2(\text{Triton X-100})$  ( $M^+ = \text{alkali-metal ions or } NH_4^+$ ). The same conclusion was drawn for the zinc(II) thiocyanate system. The distribution ratios  $D$  of the Zn(II) ion with various MSCN micellar solutions increased in the order  $LiNCS < NaNCS < NH_4NCS < KNCS$  (the respective  $\log D$  values are -0.5, 1.0, 1.7, and 2.3 in micellar solutions of 0.1% w/v Triton X-100 for example), i.e. in the order of decreasing hydration energies of the monovalent cations. Although the complex formation equilibria between cobalt(II) and thiocyanate ions in micellar solutions have not been investigated, cobalt(II) thiocyanate micellar solutions of Triton X-100 show absorption spectra originating from the tetrahedral  $[Co(NCS)_4]^{2-}$  complex. It is thus supposed that the  $[Co(NCS)_4]^{2-}$  complex is present in the form of the  $M_2[Co(NCS)_4]$  ion pairs in micelles of Triton X-100 that have a polar surface zone of poly(oxyethylene) groups with an effective dielectric constant of  $\epsilon \approx 30$ .<sup>6</sup>

In order to throw more light on the mechanism of extraction of metal(II) ions with nonionic surfactants, we have investigated complex formation equilibria between cobalt(II) and thiocyanate ions in micellar solutions of the nonionic surfactant Triton X-100. Although such a surfactant solution, on the macroscopic scale, is homogeneous as an aqueous-organic mixed solvent, it might microscopically be a pseudo-two-phase system consisting of micellar and aqueous bulk phases, as will be discussed later. A calorimetric titration procedure that has been used for studying complex formation equilibria of metal ions in various nonaqueous solvents was employed in this work.<sup>7</sup>

### Experimental Section

Calorimetric measurements were carried out in a room thermostated at  $25 \pm 0.5$  °C. Test solutions were prepared by dissolving cobalt(II) perchlorate hexahydrate crystals in an aqueous Triton X-100 solution of a given concentration over the range 1-10% w/w. As the cmc of Triton X-100 is about  $2.5 \times 10^{-4}$  mol  $dm^{-3}$ , the surfactant molecules were present mostly as micelles in the solutions. The ionic strength of the test solutions was kept at 0.5 mol  $dm^{-3}$  throughout the measurements by using  $MClO_4$  ( $M = Li, Na, NH_4$ ). A cobalt(II) perchlorate solution (50  $cm^3$ ) was placed in a stainless steel vessel, the inside wall of which was coated with Teflon, and the vessel was inserted into an aluminum block thermostated at  $25 \pm 0.0001$  °C in an air bath. The concentration of cobalt(II) perchlorate in the initial solutions was varied over the range 5-40 mmol  $dm^{-3}$ . This solution was titrated with a 0.5 mol  $dm^{-3}$  MNCS ( $M = NH_4, Na, Li$ ) solution by using an autoburet (APB-118, Kyoto Electronics). Heats observed at each titration point were about 1 J with a certainty of  $\pm 0.02$  J. The heat of reaction thus determined was corrected for heats of dilution of the titrant, which had been determined by separate experiments and found to be very small. Micellar solutions remained

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