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# Monocomplex formation and dissociation of some first row divalent transition metal ions with 2-chloro-1,10-phenanthroline by the high-pressure stopped-flow technique*

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## Abstract

The kinetics of the monocomplex formation and dissociation of $[Co(Cl\text{-}phen)]^{2+}$ and $[Ni(Cl\text{-}phen)]^{2+}$ (Cl-phen = 2-chloro-1,10-phenanthroline) in aqueous solution have been studied as a function of temperature, pressure and excess metal ion. The dissociation of these complexes was followed by adding $Cu^{2+}$ to a solution of the complex $[Co(Cl\text{-}phen)]^{2+}$ or $[Ni(Cl\text{-}phen)]^{2+}$. The rate constants, activation enthalpies, entropies and volumes, and the corresponding thermodynamic parameters obtained for $[Co(Cl\text{-}phen)]^{2+}$ (and for $[Ni(Cl\text{-}phen)]^{2+}$) are as follows: $k_f^{298}$ ($M^{-1}$ $s^{-1}$) = $5.7\times10^4$ ($1.3\times10^3$); $k_r^{298}$ ($s^{-1}$) = 7.1 (0.025); $\Delta H_f^\ddagger$ (kJ $mol^{-1}$) = 47.1 (53.5); $\Delta H_r^\ddagger$ (kJ $mol^{-1}$) = 59.2 (80.7); $\Delta S_f^\ddagger$ (J $K^{-1}$ $mol^{-1}$) = +4 (−6); $\Delta S_r^\ddagger$ (J $K^{-1}$ $mol^{-1}$) = −30 (−5); $\Delta V_f^\ddagger$ ($cm^3$ $mol^{-1}$) = +6.6 (+6.0); $\Delta V_r^\ddagger$ ($cm^3$ $mol^{-1}$) = +0.2 (+2.1); log $K^{298}$ ($M^{-1}$) = 3.91 (4.71); $\Delta H^\circ$ (kJ $mol^{-1}$) = −12.1 (−27.2); $\Delta S^\circ$ (J $K^{-1}$ $mol^1$) = +34 (−1); $\Delta V^\circ$ ($cm^3$ $mol^{-1}$) = +6.4 (+3.9). It is concluded that the complex formation reactions on both metal ions take place *via* dissociative interchange $I_d$ mechanisms.

## Introduction

During recent years, a large number of variable-pressure kinetic studies of solvent exchange and complex formation reactions have been reported [1–3]. The results for water exchange on octahedral high spin first row divalent transition metal ions, have recently been completed by data for the Jahn–Teller distorted copper(II) ion [4]. A definite trend in activation volumes is observed across the series. The $\Delta V^\ddagger$ values, negative at the beginning and positive at the end of the series, indicate that the mechanism for water exchange is not unique, but progressively changes from an associative activation mode for the early elements to a dissociative activation mode for the later ones. The mechanistic changeover occurs after the iron(II) ion.

It is also becoming clear from available data that, for a given metal ion, simple complex formation reactions take place via the same mechanism in aqueous solution as does water exchange. A complication in the study of complex formation reactions is in the asymmetry of the reaction pathway, which means that the knowledge of the full volume profile is necessary for a mechanistic description. To simplify the mechanistic interpretation it is wise to use a neutral ligand which will minimize the electrostrictive component, $\Delta V_{elec}^\ddagger$, of the observed volume of activation. For this reason we have recently carried out a variable-pressure kinetic and equilibrium study of the monocomplex formation of copper(II) and zinc(II) with 2-chloro-1,10-phenanthroline in aqueous solution [5].

## Experimental

2-Chloro-1,10-phenanthroline was synthesized from 1,10-phenanthroline (Fluka) *via* *o*-phenanthroline methiodide and 1-methyl-2-*o*-phenanthrolone. The purity was checked as described previously [5]. $Co(ClO_4)_2\cdot6H_2O$ and $Ni(ClO_4)_2\cdot6H_2O$ (Fluka) were dissolved in doubly distilled water, to prepare the metal perchlorate stock solutions. The metal ion concentrations were checked by complexometric titration with EDTA. The ionic strength was fixed to $I$ = 0.05 M by $NaClO_4$ (Merck, recrystallized from doubly distilled water). A pH between 5.7 and 5.9 was chosen for the samples, to avoid ligand protonation ($pK_a$ = 4.17 for Cl-phen [6]) and metal ion hydrolysis. The experimental set-ups for kinetic experiments for the high pressure stopped-flow measurements are similar to those described elsewhere [7]. For each set of experimental

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conditions, series of five to nine kinetic data were averaged. The errors quoted are one standard deviation.

## Results

The kinetics of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$ monocomplex formation (reaction (1)) were investigated as a function

$$[\mathrm{M(H_2O)_6}]^{2+} + \mathrm{Cl\text{-}phen} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [\mathrm{M(Cl\text{-}phen)(H_2O)_4}]^{2+} + 2\mathrm{H_2O} \qquad (1)$$

of the metal concentration $C_M$ (M = Co, Ni). Under pseudo-first-order conditions of at least five times excess $M^{2+}$, the monocomplex is the only species formed. The rate constants for the formation, $k_f$, and dissociation, $k_r$, of the complex are usually calculated from the slopes and intercepts of the dependence of $k_{obs}$ on $C_M$ (eqn. (2)). The observed pseudo-first-order rate constants,

$$k_{obs} = k_r + k_f C_M \qquad (2)$$

$k_{obs}$, for the formation of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$, as a function of metal concentration and temperature, are illustrated in Fig. 1(a) and (b). The measurements were performed at 298 nm, and the corresponding molar absorptivities were $\epsilon$(Cl-phen) = 4620 ± 150 $M^{-1}$ $cm^{-1}$, $\epsilon$(Co(Cl-phen) = 11260 ± 80 $M^{-1}$ $cm^{-1}$, $\epsilon$(Ni(Cl-phen)) = 10240 ± 150 $M^{-1}$ $cm^{-1}$.

As can be seen from Fig. 1(a) and (b), the extrapolated $k_r$ values are not well-defined. To obtain the rate constant of dissociation of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$, $\mathrm{Cu}^{2+}$ was added to solutions of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$. The formation of $[\mathrm{Cu(Cl\text{-}phen)}]^{2+}$ is much faster than the dissociation of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$, and more favourable ($K_{\mathrm{Cu}}^{298}/K_{\mathrm{Co}}^{298} = 13$; $K_{\mathrm{Cu}}^{298}/K_{\mathrm{Ni}}^{298} = 2.1$). Moreover, it has been shown that $\mathrm{Cu}^{2+}$ has no influence on the dissociation rate of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$ complex (see Fig. 1(c) and (d)). The equilibrium is completely displaced toward the formation of $[\mathrm{Cu(Cl\text{-}phen)}]^{2+}$, with the dissociation of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$ as the rate-controlling step. The dissociation of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$ was followed at 310 nm, where the difference in molar absorbances between the complexes is maximum ($\epsilon$(Cu(Cl-phen)) − $\epsilon$(Co(Cl-phen)) = 2050 $M^{-1}$ $cm^{-1}$; $\epsilon$(Cu(Cl-phen)) − $\epsilon$(Ni(Cl-phen)) = 2390 $M^{-1}$ $cm^{-1}$). The $k_r$ data as a function of temperature (Co: 278.2–318.2 K; Ni: 298.2–328.2 K) are reported in Fig. 1(c) and (d).

The $k_{obs}$ and $k_r$ values obtained at various temperatures for the formation and the dissociation of $[\mathrm{M(Cl\text{-}phen)}]^{2+}$, were analysed using eqns. (2) and (3). A four-parameter simultaneous analysis of the data

$$k = k_B T/h \exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT) \qquad (3)$$

yielded the $\Delta S_f^{\ddagger}$ (or $k_f^{298}$), $\Delta S_r^{\ddagger}$ (or $k_r^{298}$), $\Delta H_f^{\ddagger}$ and $\Delta H_r^{\ddagger}$ values listed in Table 1, where $k_f^{298}$ and $k_r^{298}$ are the rate constants, $\Delta H_f^{\ddagger}$ and $\Delta H_r^{\ddagger}$ the activation enthalpies and $\Delta S_f^{\ddagger}$ and $\Delta S_r^{\ddagger}$ the activation entropies, for the formation and the dissociation of the monocomplex. The corresponding thermodynamic parameters $K^{298}$, $\Delta H^{\circ}$, $\Delta S^{\circ}$ and their standard deviations were obtained by replacing $k_r^{298}$ by $K^{298}/k_f^{298}$, $\Delta H_r^{\ddagger}$ by $\Delta H_f^{\ddagger} - \Delta H^{\circ}$, and $\Delta S_r^{\ddagger}$ by $\Delta S_f^{\ddagger} - \Delta S^{\circ}$.

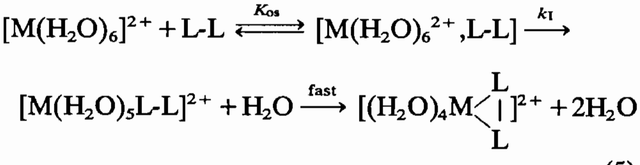
The variation of $k_f$ and $k_r$ as a function of pressure was determined at 298.2 K, up to 152 MPa. The pressure dependence of the $[\mathrm{M(Cl\text{-}phen)}]^{2+}$ dissociation was performed, as for the temperature dependence, by adding excess $\mathrm{Cu}^{2+}$. The experimental results are reported in Fig. 2(a) and (b). The $k_f$ and $k_r$ data were fitted simultaneously to eqn. (4), where $k_0$ is the rate

$$\ln k = \ln k_0 - \Delta V^{\ddagger} P/RT \qquad (4)$$

constant zero pressure, and $\Delta V^{\ddagger}$ the activation volume. $\Delta V^{\circ}$ was obtained by replacing $\Delta V_r^{\ddagger}$ by $\Delta V_f^{\ddagger} - \Delta V^{\circ}$. The high-pressure results are also listed in Table 1. To check the temperature independence of $\Delta V_f^{\ddagger}$ for the $\mathrm{Ni}^{2+}$–Cl-phen system, it was measured at 273.2, 298.2 and 338.2 K, giving $\Delta V_f^{\ddagger}$ values of 6.6 ± 0.5, 6.8 ± 0.3 and 6.7 ± 0.5, respectively. The error quoted is the standard deviation, but it is clear that, due to possible non-random errors, volumes of activation can only be determined to within 1 $cm^3$ $mol^{-1}$.

## Discussion

The mechanism assumed to take place for the formation of complexes of divalent metal aqua ions, is that developed in the sixties by Eigen, Wilkins and their associates [8]. This mechanism was proposed on the basis of observations that rates and activation parameters were generally similar for complex formation reactions and water exchange for a given metal ion. The reaction pathway can be decomposed into successive steps (eqn. (5)).



$$[\mathrm{M(H_2O)_6}]^{2+} + \mathrm{L\text{-}L} \overset{K_{os}}{\rightleftharpoons} [\mathrm{M(H_2O)_6}^{2+},\mathrm{L\text{-}L}] \xrightarrow{k_I}$$

$$[\mathrm{M(H_2O)_5L\text{-}L}]^{2+} + \mathrm{H_2O} \xrightarrow{\text{fast}} [\mathrm{(H_2O)_4M}\langle\mathrm{L{-}L}\rangle]^{2+} + 2\mathrm{H_2O} \qquad (5)$$

The initial diffusion-controlled approach of the incoming ligand in the vicinity of the solvated cation to form an outer-sphere association complex is followed by the inner-sphere, rate limiting, concerted exchange of a solvent molecule for the entering ligand molecule, and, in our case, for the bidentate 2-chloro-1,10-phenanthroline ligand, there is a final ring closure step with

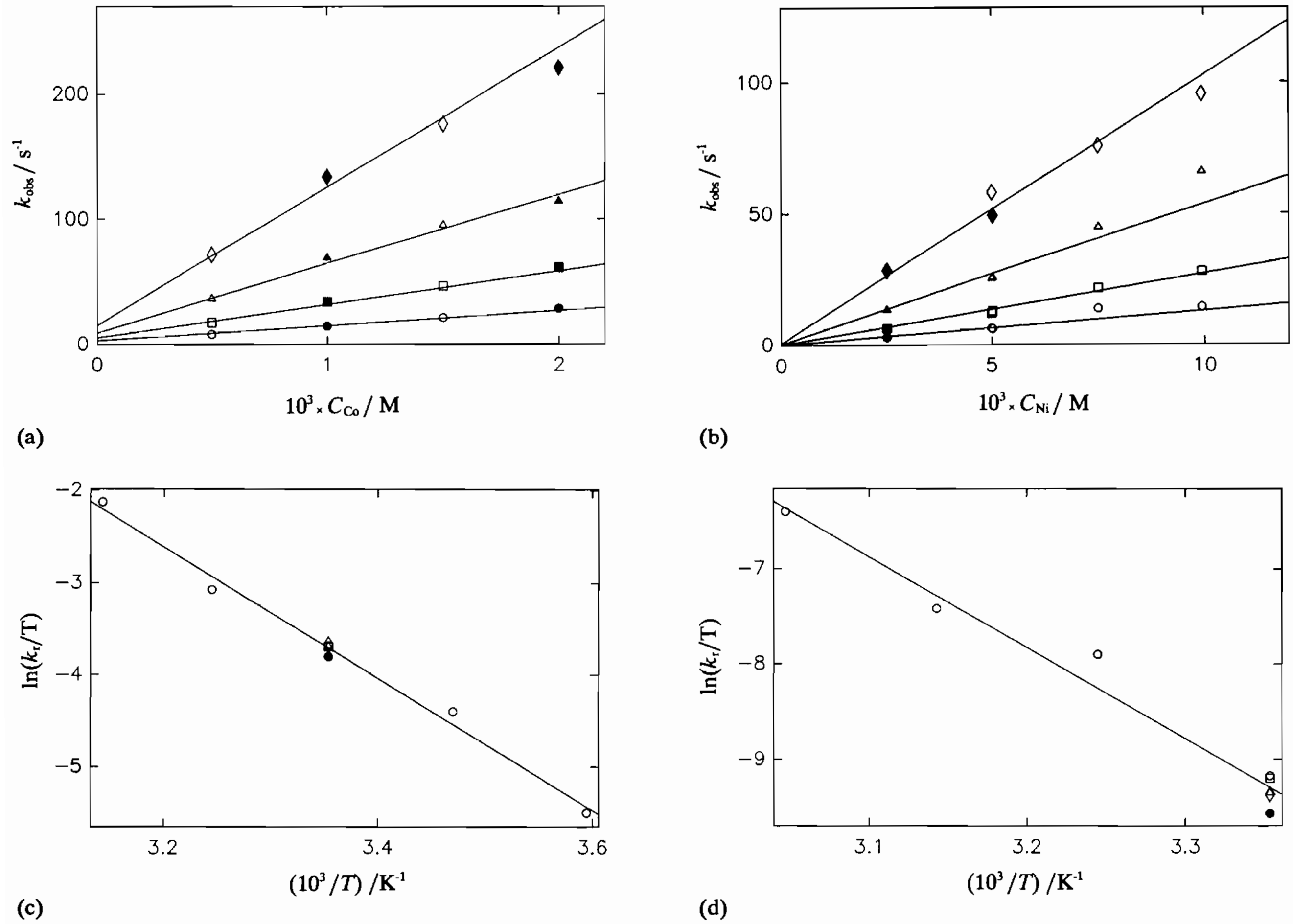


Fig. 1. Temperature dependences of the observed pseudo-first-order rate constant, $k_{obs}$, for the formation of $[M(Cl\text{-}phen)]^{2+}$ as a function of $C_M$: (a) $[Co(Cl\text{-}phen)]^{2+}$: $C_{Cl\text{-}phen}=1\times10^{-4}$ M, $T=278.2$ (●), 288.2 (■), 298.2 (▲) and 308.2 (◆) K; $C_{Cl\text{-}phen}=5\times10^{-5}$ M, $T=278.2$ (○), 288.2 (□), 298.2 (△) and 308.2 (◇) K; (b) $[Ni(Cl\text{-}phen)]^{2+}$: $C_{Cl\text{-}phen}=3\times10^{-4}$ M, $T=298.2$ (●), 308.2 (■), 318.2 (▲) and 328.2 (◆) K; $C_{Cl\text{-}phen}=5\times10^{-4}$ M, $T=298.2$ (○), 308.2 (□), 318.2 (△) and 328.2 (◇) K. Eyring plots of the dissociation rate constant, $k_r$, of $[M(Cl\text{-}phen)]^{2+}$: (c) $[Co(Cl\text{-}phen)]^{2+}$: $C_{Co(Cl\text{-}phen)}=5\times10^{-4}$ M, $C_{Cu}=1\times10^{-2}$ M (○); $C_{Co(Cl\text{-}phen)}=3\times10^{-4}$ M, $C_{Cu}=8.5\times10^{-3}$ M (●); $C_{Co(Cl\text{-}phen)}=5\times10^{-4}$ M, $C_{Cu}=5\times10^{-2}$ M, $I=0.11$ M (◇); $C_{Co(Cl\text{-}phen)}=1\times10^{-4}$ M, $C_{Cu}=1\times10^{-2}$ M (□); $C_{Co(Cl\text{-}phen)}=1\times10^{-4}$ M, $C_{Cu}=5\times10^{-2}$ M, $I=0.10$ M (△); (d) $[Ni(Cl\text{-}phen)]^{2+}$: $C_{Ni(Cl\text{-}phen)}=5\times10^{-4}$ M, $C_{Cu}=1\times10^{-2}$ M (○); $C_{Ni(Cl\text{-}phen)}=3\times10^{-4}$ M, $C_{Cu}=8.5\times10^{-3}$ M (●); $C_{Ni(Cl\text{-}phen)}=1\times10^{-4}$ M, $C_{Cu}=1\times10^{-2}$ M (◇); $C_{Ni(Cl\text{-}phen)}=5\times10^{-4}$ M, $C_{Cu}=5\times10^{-2}$ M, $I=0.11$ M (□); $C_{Ni(Cl\text{-}phen)}=1\times10^{-4}$ M, $C_{Cu}=5\times10^{-2}$ M, $I=0.10$ M (△). The ionic strength is fixed to $I=0.05$, except where stated.

the displacement of a second solvating water molecule from the metal ion. It is generally accepted that the ring closure step is more probable than the first coordination step, so that the entering of the ligand into the first coordination sphere is the rate limiting step. This assumption would seem to be justified by the observation that water exchange rate on a mono- or disubstituted cation is usually faster than on the corresponding hexaaquaion [8]. The second-order rate constant for complex formation, $k_f$, is related to $K_{os}$ and $k_I$ by eqn. (6), assuming $K_{os}\times[M(H_2O)_6^{2+}]\ll1$. The derivative of eqn. (6) as function of pressure gives

$$k_f=K_{os}k_I \qquad (6)$$

$$\Delta V_f^{\ddagger}=\Delta V_{os}^{\circ}+\Delta V_I^{\ddagger} \qquad (7)$$

eqn. (7), relating the activation volume for the forward reaction, $\Delta V_f^{\ddagger}$, to the volume change during the outer-sphere complex formation, $\Delta V_{os}^{\circ}$, and to the activation volume for the interchange step, $\Delta V_I^{\ddagger}$. It should be stressed that $k_I$ may vary for a series of ligands and may differ from the water exchange rate constant, $k_{ex}$, for a given metal ion and that $\Delta V_I^{\ddagger}$ may be negative, such observations indicate an associative activation mode (see for example: vanadium(II) [9], manganese(II) [10], titanium(III) [11], vanadium(III) [12], etc.).

The present results and the literature values of $k_{ex}$, $k_f$ and the corresponding activation parameters, for some divalent first-row transition-metal ions with a few selected ligands, are reported in Table 2 (for a survey,

TABLE 1. Thermodynamic and kinetic parameters for $[Co(Cl\text{-}phen)]^{2+}$ and $[Ni(Cl\text{-}phen)]^{2+}$

| | $[Co(Cl\text{-}phen)]^{2+}$ | $[Ni(Cl\text{-}phen)]^{2+}$ |
|---|---|---|
| $\log K^{298}$ ($M^{-1}$) | $3.91 \pm 0.14^{a}$ | $4.71 \pm 0.05^{a}$ |
| $k_f^{298}$ ($M^{-1}\,s^{-1}$) | $(5.7 \pm 0.1) \times 10^4$ | $(1.3 \pm 0.1) \times 10^3$ |
| $k_r^{298}$ ($s^{-1}$) | $7.1 \pm 0.2$ | $(2.5 \pm 0.2) \times 10^{-2}$ |
| $\Delta H^\circ$ (kJ $mol^{-1}$) | $-12.1 \pm 0.2^{a}$ | $-27.2 \pm 5.1^{a}$ |
| $\Delta H_f^\ddagger$ (kJ $mol^{-1}$) | $47.1 \pm 1.2$ | $53.5 \pm 2.4$ |
| $\Delta H_r^\ddagger$ (kJ $mol^{-1}$) | $59.2 \pm 1.6$ | $80.7 \pm 4.4$ |
| $\Delta S^\circ$ (J $K^{-1}$ $mol^{-1}$) | $+34 \pm 7^{a}$ | $-1 \pm 16^{a}$ |
| $\Delta S_f^\ddagger$ (J $K^{-1}$ $mol^{-1}$) | $+4 \pm 4$ | $-6 \pm 8$ |
| $\Delta S_r^\ddagger$ (J $K^{-1}$ $mol^{-1}$) | $-30 \pm 5$ | $-5 \pm 14$ |
| $\Delta V^{\circ,298}$ ($cm^3$ $mol^{-1}$) | $+6.4 \pm 0.8^{a}$ | $+3.9 \pm 0.6^{a}$ |
| $\Delta V_f^{\ddagger,298}$ ($cm^3$ $mol^{-1}$) | $+6.6 \pm 0.3$ | $+6.0 \pm 0.1$ |
| $\Delta V_r^{\ddagger,298}$ ($cm^3$ $mol^{-1}$) | $+0.2 \pm 0.4$ | $+2.1 \pm 0.2$ |

[a] Derived from kinetic data.

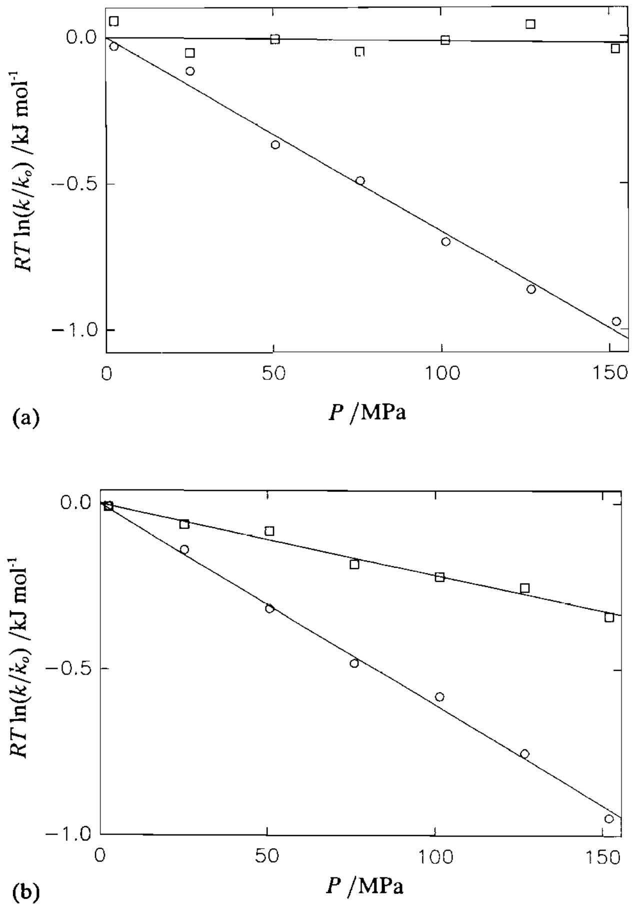


Fig. 2. Pressure effect on the normalized logarithm of the rate constant of formation, $k_f$ (○), and of the rate constant of dissociation, $k_r$ (□), of $[M(Cl\text{-}phen)]^{2+}$ ($T = 298.2$ K): (a) $[Co(Cl\text{-}phen)]^{2+}$, (b) $[Ni(Cl\text{-}phen)]^{2+}$. ○: $C_{Cl\text{-}phen} = 3 \times 10^{-4}$ M, $C_M = 2.5 \times 10^{-3}$ M; □: $C_{M(Cl\text{-}phen)} = 3 \times 10^{-4}$ M, $C_{Cu} = 8.5 \times 10^{-3}$ M.

see refs. 8 and 26). $NH_3$ is the simplest monodentate ligand binding via nitrogen, and 1,10-phenanthroline (phen) is similar to the investigated 2-chloro-1,10-phenanthroline (Cl-phen) ligand. Glycinate anion ($gly^-$) and 2,2′-bipyridine (bipy) data are listed because these are the only ligands for which activation volumes have been determined for $Cu^{2+}$ and/or for $Zn^{2+}$.

The complex formation reactions with the neutral ligands $NH_3$, bipy, phen and Cl-phen and the water exchange reactions, do not involve charge separation or cancellation on going to the transition state. Thus, for the polar solvent water, the outer-sphere contribution, $\Delta V_{os}^\circ$, can be neglected [27], and the mechanistic indicator $\Delta V_I^\ddagger$ is equal to the observed value $\Delta V_f^\ddagger$. In the case of the complex formation reactions with $gly^-$, neutralization of charge occurs, and the difference $\Delta V_f^\ddagger - \Delta V_{os}^\circ$ has to be calculated to obtain the activation volume for the interchange step, $\Delta V_I^\ddagger$. For the reaction of a divalent cation with an uninegatively charged anion, with a distance of closest approach of 500 pm, Grant [18] uses an estimated $\Delta V_{os}^\circ$ value of +3.2 $cm^3$ $mol^{-1}$ in the calculation of $\Delta V_I^\ddagger$. The $\Delta V_{ex}^\ddagger$ and $\Delta V_I^\ddagger$ data reported in Table 2 are all positive from $Co^{2+}$ to $Zn^{2+}$ indicating that all reactions proceed according to dissociative activation modes. This is also confirmed by the presence of maxima in the reaction profiles drawn in Fig.3, despite the relatively large reaction volumes $\Delta V^\circ$ observed for the displacement of two water molecules in the formation of the Cl-phen complexes. The observed $\Delta V_{ex}^\ddagger$ values, much smaller than the value of +13.1 $cm^3$ $mol^{-1}$ suggested by Swaddle and Mak [14] for D mechanism, were taken as evidence for dissociative interchange $I_d$ mechanisms. The similarity of the activation volumes for solvent exchange $\Delta V_{ex}^\ddagger$, with those for the interchange step $\Delta V_I^\ddagger$ are indicative of a similar mechanism for complex formation, in which the metal–water bond rupture plays the major role. This is also an indication that the first substitution step, and not the ring closure, is rate determining for the bidentate ligands bipy and Cl-phen.

The sequence $k_f(Ni^{2+}) < k_f(Co^{2+}) < k_f(Zn^{2+}) < k_f(Cu^{2+})$, parallels that observed for the water-exchange rate, $k_{ex}$, and provides further evidence for the paramount role of metal–water bond breaking at the transition state for complex formation with these metal aquaions. This sequence confirms also the indirect relation between $k_f$ and $k_{ex}$. More precisely, the comparison should be made between the first-order rate constants $k_I$ and $k_{ex}$. Using eqn. (6), the first-order rate constants $k_I$ can be calculated via the outer-sphere stability constants $K_{os}$, which have been experimentally determined only in few cases [8], or which can be estimated using the Fuoss equation [28, 29], based on statistical arguments and on the theory of diffusion. The problems inherent in the use of this equation have

TABLE 2. Formation rate constants, $k_f^{298}$ ($M^{-1}$ $s^{-1}$), activation and reaction volumes, $\Delta V_f^{\ddagger}$ and $\Delta V^{\circ}$ ($cm^3$ $mol^{-1}$), for reactions of some selected octahedral first row $[M(H_2O)_6]^{2+}$ with entering ligands L[a]

| | | Mn($d^5$) | Co($d^7$) | Ni($d^8$) | Cu($d^9$) | Zn($d^{10}$) |
|---|---|---|---|---|---|---|
| $H_2O^b$ | $k_{ex}$ | $2.1\times10^7$ | $3.2\times10^6$ | $3.2\times10^4$ | $4.4\times10^{9w}$ | $(0.3–6)\times10^{8c}$ |
| | $\Delta V_{ex}^{\ddagger}$ | $-5.4$ | $+6.1$ | $+7.2$ | $\leq +6^d$ | $+6^d$ |
| $NH_3$ | $k_f$ | | $1.5\times10^{5e}$ | $4.5\times10^{3c}$ | $2\times10^{9f}$ | $8\times10^{6g}$ |
| | $\Delta V_f^{\ddagger}$ | | $+4.8^h$ | $+6.0^h$ | | |
| | $\Delta V^{\circ}$ | | $-8.6^h$ | $-2.3^h$ | | |
| $gly^{-i}$ | $k_f$ | | $3\times10^6$ | $2.1\times10^4$ | $3.4\times10^9$ | $1.5\times10^{8j}$ |
| | $\Delta V_f^{\ddagger k}$ | | $+5$ | $+7$ | $+9$ | $+4$ |
| | $\Delta V^{\circ}$ | | $+7.3$ | $+2.1$ | $+13.4$ | $+5.2$ |
| bipy | $k_f$ | $2.8\times10^{5l}$ | $6.3\times10^{4m}$ | $1.6\times10^{3m}$ | $5\times10^{7n}$ | $2.3\times10^{6o}$ |
| | $\Delta V_f^{\ddagger}$ | $-1.2^p$ | $+5.9^r$ | $+5.3^r$ | | $+7.1^o$ |
| | $\Delta V^{\circ}$ | $+3.0^p$ | | | | $+3.5^o$ |
| phen | $k_f$ | $2\times10^{5s}$ | $3\times10^{5m}$ | $3.9\times10^{3m}$ | $6.4\times10^{7n}$ | $2\times10^{6m}$ |
| Cl-phen | $k_f$ | | $5.7\times10^{4t}$ | $1.3\times10^{3t,u}$ | $1.1\times10^{7v}$ | $1.1\times10^{6v}$ |
| | $\Delta V_f^{\ddagger}$ | | $+6.6^t$ | $+6.0^t$ | $+7.1^v$ | $+5.0^v$ |
| | $\Delta V^{\circ}$ | | $+6.4^t$ | $+3.9^t$ | $+1.9^v$ | $+0.9^v$ |

[a] Abbreviations: $gly^-$ = glycinate$^-$, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Cl-phen = 2-chloro-1,10-phenanthroline. [b] Water exchange data from ref. 13 ($k_{ex}$ in $s^{-1}$ refers to the exchange of one particular water molecule). [c] Estimated value from ref. 5. [d] Predicted values from ref. 14. [e] Ref. 15. [f] Ref. 16. [g] Value from ref. 13 (measured at 284 K) corrected to 298 K, using an estimated value of $\Delta H_f^{\ddagger} = 30$ kJ $mol^{-1}$. [h] Ref. 17. [i] Ref. 18. [j] Ref. 19. [k] $\Delta V_I^{\ddagger} = \Delta V_f^{\ddagger} - \Delta V_{os}^{\circ}$, see text. [l] Ref. 20. [m] Ref. 21. [n] Ref. 22. [o] Ref. 23. [p] Ref. 24. [r] Ref. 25. [s] Value from ref. 20 (measured at 284 K) corrected to 298 K, using an estimated $\Delta H_f^{\ddagger} = 30$ kJ $mol^{-1}$. [t] This work. [u] Estimated value from ref. 20, $1\times10^3$. [v] Ref. 5. [w] Ref. 4.

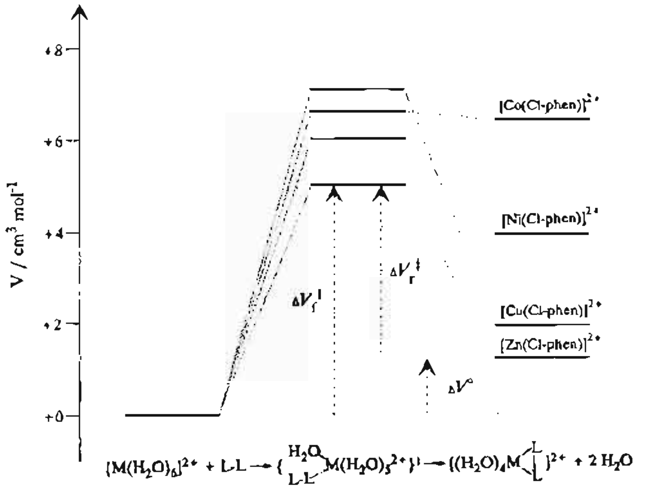


Fig. 3. Volume reaction profiles for the complex formation and dissociation reactions between Cl-phen and $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, in aqueous solution.

been discussed frequently: the theory treats the ion and ligand as charged spheres in a dielectric continuum, and thus its use for irregularly shaped, neutral, or dipolar ligands is highly speculative. Another complication appears in comparing $k_I$ with $k_{ex}$, because in the outer-sphere complex, the exchange of certain water molecules, due to their unfavourable position, is less likely to bring about the complex formation.

Using the Fuoss equation for a divalent cation with a uninegatively charged ligand, the $K_{os}$ value is around 1.6 $M^{-1}$ [28, 29] with a distance of closest approach $a$ of 500 pm, and an ionic strength of 0.2 M. For a divalent cation with an uncharged ligand, the equation gives a $K_{os}$ value of 0.32 $M^{-1}$ (0.16 $M^{-1}$), with $a = 500$ pm (400 pm). Using a $K_{os}$ value of 1.6 $M^{-1}$ for $gly^-$, 0.16 $M^{-1}$ $NH_3$ and 0.32 $M^{-1}$ for the bipy and phen ligands, the range of the first-order rate constant $k_I$ for $Co^{2+}$ ($Ni^{2+}$) is 0.2 to $1.9\times10^6$ $s^{-1}$ (0.5 to 2.8–$10^4$ $s^{-1}$). The same calculation, using a $K_{os}$ value of 0.32 $M^{-1}$ for Cl-phen, gives a $k_I$ value of $0.18\times10^6$ and $0.4\times10^4$ $s^{-1}$ for $Co^{2+}$ and $Ni^{2+}$, respectively. These calculations show that the $k_I$ values determined for Cl-phen ligand are at the lower limit of the above $k_I$ value ranges. One of the reasons for the relatively small $k_I$ in the case of Cl-phen can be the lower probability of the first nitrogen coordination compared to the bipy or phen, considering the steric hindrance of the chlorine atom next to one of the two nitrogen atoms.

## Conclusions

As for the water exchange reactions [30], the complex formation reactions between 2-chloro-1,10-phenanthroline and $Ni^{2+}$, $Co^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ take place via dissociative interchange $I_d$ mechanisms, and the dissociation of one water molecule and the simultaneous formation of the first metal–nitrogen bond are the rate determining step. During recent years, the water exchange rate constants $k_{ex}$ have been determined for $Mn^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cu^{2+}$ and $Zn^{2+}$. It was found that the water exchange reaction for $Mn^{2+}$ takes place via an associative interchange $I_a$ mechanism. Therefore it would be interesting to extend this study of complex formation to $Mn^{2+}$ with Cl-phen, using the T-Jump method under variable pressure. For the first time, with the same ligand, this would permit a comparison of the mechanisms between the complex formation reactions and the water exchange reactions for $Mn^{2+}$ ($I_a$ mechanism), $Ni^{2+}$, $Co^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ ($I_d$ mechanism).

## Supplementary material

Observed pseudo-first-order rate constants, $k_{obs}$, for the formation of $[M(Cl\text{-}phen)]^{2+}$ as a function of temperature (Table SI–SII); observed pseudo-first-order rate constants, $k_{obs}$, for the dissociation of $[M(Cl\text{-}phen)]^{2+}$ as a function of temperature (Table SIII); observed pseudo-first-order rate constants, $k_{obs}$, for the formation of $[M(Cl\text{-}phen)]^{2+}$ as a function of pressure (Table SIV); and observed pseudo-first-order rate constants, $k_{obs}$, for the dissociation of $[M(Cl\text{-}phen)]^{2+}$ as a function of pressure (Table SV) are available from the authors on request.

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