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Appendix

The average bond distances (Å) and other parameters of $[Au_2S_2PR_2)_2]_n$[10] and $[Au(CH_2)_2PR_2]_2$[12] are listed in Table V.

Our calculations used the extended Hückel method,[21] with weighted H_{ij}'s.[22] The Coulomb integrals and wave functions are specified[5] in Table VI.

Registry No. $[Au_2(S_2PH_2)_2]_2$, 94645-16-6; $[Au_2(S_2PH_2)_2]_x$, 94645-18-8; $Au(S_2PH_2)_2$, 94645-19-9.

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Associative Nature of Substitution Reactions of Manganese(II) in Aqueous Solution

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The forward and reverse rate constants for the complex formation of Mn^{2+} with terpy (2,2′:6′,2″-terpyridine) were studied as a function of pressure up to 200 MPa with stopped-flow techniques. From an analysis of the metal ion concentration dependence of the observed rate constant, the calculated volumes of activation are $\Delta V_f^{\ddagger} = -3.4 \pm 0.7$ and $\Delta V_r^{\ddagger} = -7.7 \pm 2.2$ cm^3 mol^{-1} at 288.1 K. The volume of activation for the reverse reaction was also obtained directly by studying the spontaneous aquation of $Mn(terpy)^{2+}$ in the presence of a much better complexing metal ion. The corresponding value is $\Delta V_r^{\ddagger} = -10.1 \pm 0.4$ cm^3 mol^{-1} at 298.1 K. In addition, the overall reaction volume was determined spectrophotometrically from the pressure dependence of the equilibrium constant. These results underline the associative nature of substitution on Mn^{2+} as concluded from the variable-pressure water-exchange data. They further confirm that, in water, the earlier members of the second-row transition-metal series react according to associative activation modes.

Introduction

High-pressure NMR techniques have been applied very successfully in the elucidation of the intimate nature of solvent-exchange processes of solvated transition-metal ions.[2] A remarkable finding is the gradual mechanistic changeover from I_a to I_d for solvent-exchange reactions on divalent first-row transition-metal ions along the series Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} for methanol and acetonitrile exchange[3,4] and from V^{2+} to Ni^{2+} for water exchange.[5,6] This contradicts the earlier generally accepted idea that complex formation reactions on all octahedral divalent metal ions proceed via I_d mechanisms. The dissociative character was assigned on the basis of small changes in the substitution rates for a number of ligands of the same charge.[7-10] Obviously, the volume of activation is a more sensitive parameter, leading to a better understanding of the nature of the substitution processes and, therefore, of the chemistry of such metal ions.

Consequently, the question arises as to whether ligand substitution reactions, viz. complex formation and solvolysis processes, also exhibit this mechanistic changeover along the first-row elements. Only a few pressure-dependence studies of such fast substitution reactions have been reported to date. The majority concern complex formation reactions of Co^{2+} and Ni^{2+},[11-19] for which a good correlation with the volume of activation for the solvent-exchange reaction was observed, confirming the I_d character of the substitution processes on these ions. Only two studies[20,21] concern complex formation reactions of V^{2+} and Mn^{2+} (with thiocyanate[20] and bipyridine,[21] respectively), and here again, the reported volumes of activation (-2.1 ± 0.8 and -1.2 ± 0.2 cm^3 mol^{-1}, respectively) parallel the solvent-exchange data, underlining the I_a nature of substitution processes on the early elements of the series.

We have extended our earlier measurements[20,21] and now report volumes of activation as well as reaction-volume data for the formation and aquation reactions of $Mn(terpy)^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) in aqueous solution.

Experimental Section

$Mn(ClO_4)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$ and terpyridine were used as supplied by Fluka (p.a.). Stock solutions were prepared volumetrically at room temperature with doubly distilled water. The concentrations were not corrected for volume changes with varying temperature or

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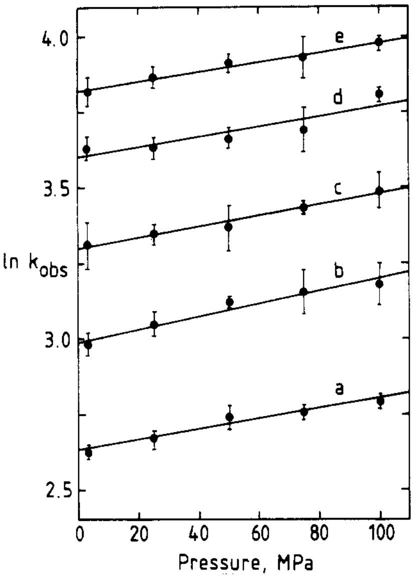

Figure 1. Pressure dependence of ln k_{obsd} for the reaction Mn^{2+} + terpy $\rightleftharpoons$ $Mn(terpy)^{2+}$. Experimental conditions: T = 288.1 K; I = 0.1 M; λ = 325 nm; (a) [Mn] = 0.1 mM, [terpy] = 0.015 mM; (b) [Mn] = 0.2 mM, [terpy] = 0.015 mM; (c) [Mn] = 0.3 mM, [terpy] = 0.015 mM; (d) [Mn] = 0.4 mM, [terpy] = 0.015 mM; (e) [Mn] = 0.5 mM, [terpy] = 0.03 mM.

pressure.[22,23] Kinetic measurements at ambient pressure were performed on conventional Aminco and HI-TECH stopped-flow instruments, whereas specially designed high-pressure stopped-flow setups[20,24] were used for measurements at pressures up to 200 MPa. First-order rate constants were calculated from absorbance/time traces in the usual way, and the corresponding first-order plots proved to be linear for at least 2–3 half-lives of the reaction. Equilibrium measurements were performed on a Zeiss DMR 10 spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell.[25]

Results and Discussion

The complex formation reaction between Mn^{2+} and terpy in the presence of an excess of Mn^{2+} can be formulated as in eq 1.

$$\mathrm{Mn(H_2O)_6^{2+} + terpy \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Mn(terpy)(H_2O)_3^{2+} + 3H_2O} \qquad (1)$$

Kinetic analysis has shown the formation of the first bond to terpy to be rate determining in the forward reaction.[26] The $Mn(terpy)_2^{2+}$ species is only produced in the presence of an excess of terpy.[26] Under pseudo-first-order conditions as in the present study, i.e. $[Mn^{2+}] \gg [terpy]$, eq 2 applies, from which it follows

$$k_{obsd} = k_f[Mn^{2+}] + k_r \qquad (2)$$

that k_f and k_r can be determined from the $[Mn^{2+}]$ dependence of k_{obsd}. The reverse rate constant k_r can also be measured independently by addition of a large excess of Co^{2+}, a much more efficient complexing metal ion ($K_1 = k_f/k_r = 10^{4.4}$, $K_3 = k_r/k_{-r} = 10^{8.4}$).[26] The reaction then follows eq 3.

$$\mathrm{Mn(terpy)(H_2O)_3^{2+} + Co(H_2O)_6^{2+} \underset{k_{-r}}{\overset{k_r}{\rightleftharpoons}} Mn(H_2O)_6^{2+} + Co(terpy)(H_2O)_3^{2+}} \qquad (3)$$

Preliminary kinetic measurements at ambient pressure were performed at different temperatures and excesses of Mn^{2+} and underlined the validity of eq 2.[27] Plots of k_{obsd} vs. $[Mn^{2+}]$ resulted in $k_f = (8.3 \pm 0.6) \times 10^4\ M^{-1}\ s^{-1}$ and $k_r = 4 \pm 2\ s^{-1}$ at 288.1 K and $k_f = (1.5 \pm 0.1) \times 10^5\ M^{-1}\ s^{-1}$ and $k_r = 6 \pm 1\ s^{-1}$ at 298.1 K.[28] These results are in close agreement with the earlier reported data ($k_f = 1.1 \times 10^5\ M^{-1}\ s^{-1}$ and $k_r = 3.8\ s^{-1}$ at 298.1 K).[26] In addition, the temperature dependence of k_r was studied in the presence of excess Co^{2+} and resulted in $\Delta H^{\ddagger} = 54.1 \pm 1.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -52 \pm 4$ J K^{-1} mol^{-1}.

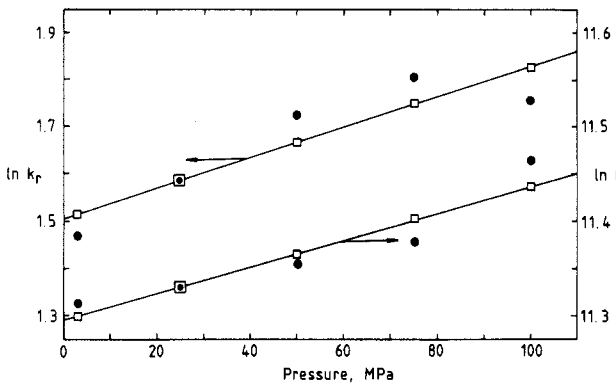

Figure 2. Pressure dependence of the forward and reverse rate constants for the reaction shown below. Experimental conditions: see Figure 1.

$$\mathrm{Mn^{2+} + terpy \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Mn(terpy)^{2+}}$$

Symbols: (●) k_f and k_r estimated from the experimental values of k_{obsd} according to eq 2; (□) k_f and k_r estimated from calculated values of k_{obsd} according to the lines in Figure 1—see Discussion.

The pressure dependence of k_{obsd} was studied at five concentrations of Mn^{2+}, each data point being the mean value of at least six kinetic runs. These measurements were performed at 288.1 K since the rate of the reactions at the higher Mn^{2+} concentrations were too fast to measure accurately with our instrument[24] at higher temperatures. The standard deviation of up to 7% on the mean value of k_{obsd} is partly due to the relatively high rate of the process even at 288.1 K. The plots of ln k_{obsd} vs. pressure (Figure 1) are linear within the experimental error limits, and the corresponding volumes of activation, $\Delta V^{\ddagger}$ ($= -RT\ \mathrm{d}\ln k/\mathrm{d}P$),[23] range from −4.9 to −3.7 cm^3 mol^{-1} for the various lines in Figure 1. k_{obsd}, however, is a composite quantity (eq 2) such that its pressure dependence must be analyzed in terms of the pressure dependencies of k_f and k_r. The latter were calculated from the slope and intercept of the corresponding k_{obsd} vs. $[Mn^{2+}]$ plot as a function of pressure. It follows from Figure 2 that $\Delta V_f^{\ddagger} = -3.4 \pm 0.7$ and $\Delta V_r^{\ddagger} = -7.7 \pm 2.2$ cm^3 mol^{-1}. It must however be kept in mind that the pressure dependence of k_{obsd} was determined at different $[Mn^{2+}]$ in separate experiments; i.e., a series of kinetic runs as a function of pressure was performed at each $[Mn^{2+}]$. Combining such data in the way outlined above is expected to result in rather large error limits especially when the individual values of k_{obsd} are subject to relatively high error limits. An alternative data treatment procedure adopted previously[29] is to use the least-squares-fitted lines in Figure 1 to calculate k_{obsd} at each pressure as a function of $[Mn^{2+}]$. The values of k_f and k_r obtained in this way are included in Figure 2 and result in $\Delta V_f^{\ddagger} = -3.4 \pm 0.1$ and $\Delta V_r^{\ddagger} = -7.6 \pm 0.1$ cm^3 mol^{-1}, respectively. It is seen that an excellent agreement between the two sets of $\Delta V^{\ddagger}$ values exists, the latter treatment resulting in smaller error limits. The values of k_f and k_r extrapolated to 0.1 MPa are in very good agreement with those quoted above.

An alternative way to determine the pressure dependence of k_r is to measure this rate constant directly. As outlined above,

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Table I. Volumes of Activation[a] and Volumes of Reaction[a] for Ligand-Exchange Reactions on V^{2+} and Mn^{2+}

				$\Delta\bar{V}$		
metal	ligand	$\Delta V_f^{\ddagger}$	$\Delta V_r^{\ddagger}$	kinetic	spectroscopic	ref
V^{2+}	H_2O	-4.1 ± 0.1^b				6
	SCN^-	-2.1 ± 0.8^c	-11.5 ± 0.9	$+9.5\ (+6.2)^d$		20
Mn^{2+}	H_2O	-5.4 ± 0.1^b				5
	bpy[e]	-1.2 ± 0.2	-4.1 ± 0.4^f		$+3.0 \pm 0.4$	21
	terpy	-3.4 ± 0.7	-7.7 ± 2.2	$+4.3$	$+4.7 \pm 0.3$	this work
			-10.1 ± 0.4^g	$+6.7$		this work

[a] In $cm^3\ mol^{-1}$. Errors quoted are standard deviations. [b] $\Delta V_I^{\ddagger}$. [c] $\Delta V_I^{\ddagger} = -5.3 \pm 0.8\ cm^3\ mol^{-1}$ (see text). [d] Volume of reaction for the interchange step, $\Delta\bar{V}_I = \Delta\bar{V} - \Delta\bar{V}_{OS}$, to be compared with $\Delta\bar{V}$ for reactions involving uncharged ligands ($\Delta\bar{V}_{OS} = 0$). [e] 2,2′-Bipyridine. [f] Calculated from $\Delta V_r^{\ddagger} = \Delta V_f^{\ddagger} - \Delta\bar{V}$. [g] Measured independently by addition of an excess of Co^{2+} (see text).

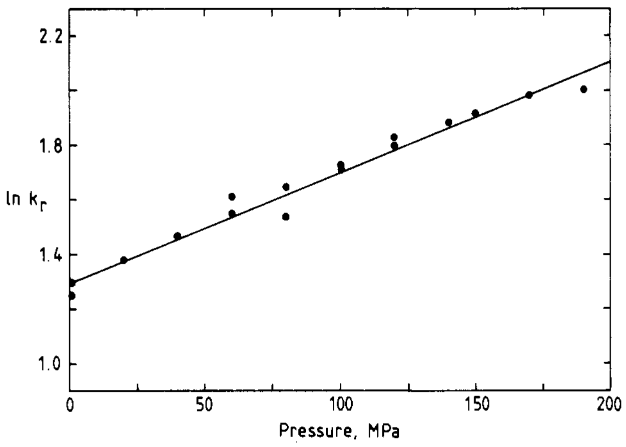

Figure 3. Pressure dependence of k_r for the reaction shown below.

$$Mn(terpy)^{2+} + Co^{2+} \underset{k_d}{\overset{k_r}{\rightleftharpoons}} Mn^{2+} + Co(terpy)^{2+}$$

Experimental conditions: $T = 298.1$ K; $\lambda = 390$ nm; [Mn] = 0.2 mM; [Co] = 2.6 mM.

such a determination has the advantage that k_r is not obtained from an extrapolation procedure that adds to the error limits involved. The pressure dependence of k_r was studied in this way in the absence of $NaClO_4$, and the results are summarized in Figure 3. The plot of ln k_r vs. pressure is once again linear, and $\Delta V_r^{\ddagger} = -10.1 \pm 0.4\ cm^3\ mol^{-1}$ at 298.1 K. The extrapolated value of k_r at ambient pressure is $3.6 \pm 0.1\ s^{-1}$, which is in excellent agreement with Wilkins' value[26] of $3.8\ s^{-1}$. The values of $\Delta V_r^{\ddagger}$ obtained by the two methods are in good agreement, especially when the differences in experimental conditions (temperature and ionic strength) are taken into account.

In addition, we have determined the reaction volume ($\Delta\bar{V}$) for reaction 1 from the pressure dependence of the equilibrium constant K by using a spectrophotometric technique.[30-32] K was determined from absorbance measurements at 325 nm by steadily increasing the $[Mn^{2+}]$ in excess over the [terpy]. No $NaClO_4$ could be added to such solutions since $[Mn(terpy)](ClO_4)_2$ tended to precipitate over the longer times required for the corresponding measurements under pressure. The value of K obtained in this way (average of eight measurements) is $(8 \pm 2) \times 10^4\ M^{-1}$ at 288.1 K and ambient pressure, which is higher than the value estimated from the ratio of k_f over k_r, viz. $2.1 \times 10^4\ M^{-1}$. This difference could partly be due to the difference in ionic strength and the fact that such spectrophotometrically determined equilibrium constants are in this case subjected to significantly larger error limits than the individual rate constants.[33] At elevated pressure,[23,31,32] K values of 7.74×10^4, 7.34×10^4, 6.97×10^4, 6.63×10^4, and $6.42 \times 10^4\ M^{-1}$ at 3, 25, 50, 75, and 100 MPa, respectively, were obtained, from which it follows[23,32] that $\Delta\bar{V} = +4.7 \pm 0.3\ cm^3\ mol^{-1}$. This value is in good agreement with those obtained from the relationship $\Delta\bar{V} = \Delta V_f^{\ddagger} - \Delta V_r^{\ddagger}$, which range between +4.3 and $+6.7\ cm^3\ mol^{-1}$ depending on the selected value of $\Delta V_r^{\ddagger}$. This agreement is, despite the difference in ionic strength, not surprising since $\Delta\bar{V}$ is not expected to depend on ionic strength for a reaction in which no changes in charge occur.[34,35]

We now turn to the interpretation of the $\Delta V^{\ddagger}$ and $\Delta\bar{V}$ data. Very important for the mechanistic interpretation is the negative sign of $\Delta V^{\ddagger}$ for both the forward and reverse steps, showing that this ligand substitution process has a distinct associative character and is most probably of the I_a type. The present data are in good agreement with the corresponding data ($\Delta V^{\ddagger}$ and $\Delta\bar{V}$) for the complexation of Mn^{2+} by bipyridine[21] as shown in Table I, where a summary of the available data for ligand-exchange reactions on V^{2+} and Mn^{2+} in aqueous solution is given. The value of $\Delta V_f^{\ddagger}$ quoted for $V(SCN)^+$ complex formation should be corrected for outer-sphere ion-pair formation, before a comparison can be made with reactions involving uncharged ligands. This outer-sphere contribution can be estimated to be $\Delta\bar{V}_{os} = +3.2\ cm^3\ mol^{-1}$,[20] and it follows that the volume of activation for the interchange step ($\Delta V_I^{\ddagger} = \Delta V_f^{\ddagger} - \Delta\bar{V}_{os}$) is $-5.3\ cm^3\ mol^{-1}$. For both metal centers, the substitution data correlate well with the corresponding water-exchange data, thus underlining the I_a nature of these substitution processes. It is quite remarkable that, although the results have been obtained for two different metal centers with ligands of various sizes and bonding properties, each of the parameters $\Delta V_f^{\ddagger}$, $\Delta V_r^{\ddagger}$, and $\Delta\bar{V}$ are of similar size for the systems studied. The absolute values for bpy are smaller than for terpy, but the number of systems studied is not sufficient to draw any distinct conclusions from this observation. The $\Delta V_r^{\ddagger}$ values are throughout more negative than the corresponding values of $\Delta V_f^{\ddagger}$, indicating that the entering water molecule can be better accommodated by the complex ion during the reverse process than by the entering ligand during the formation reaction.

We conclude that all the volume of activation data available to date for water-exchange and ligand-substitution processes on V^{2+} and Mn^{2+} firmly establish the associative nature of these reactions and, once again, demonstrate the mechanistic discriminating ability of this activation parameter.

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Registry No. $Mn(H_2O)_6^{2+}$, 15365-82-9; $Co(H_2O)_6^{2+}$, 15276-47-8; terpy, 1148-79-4.

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