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Variable-Pressure Kinetic Study of Formation and Dissociation of Octahedral Divalent Metal Ion Monocomplexes in *N,N*-Dimethylformamide: Dissociative Reaction Mechanisms through the First Row from Manganese to Nickel

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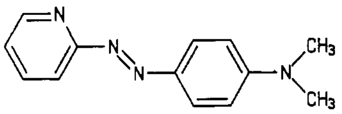
The kinetics of formation of $M(DMF)_4Et_2DTC^+$ (DMF = *N,N*-dimethylformamide; Et_2DTC = diethyldithiocarbamate; M = Mn, Fe, Co) and of formation and dissociation of $Fe(DMF)_4Pada^{2+}$ (Pada = *trans*-pyridine-2-azo(*p*-dimethylaniline)) have been studied in DMF medium by stopped-flow spectrophotometry as a function of excess metal concentration, temperature, and pressure. The rate constants and activation enthalpies and entropies obtained from the Mn^{2+}, Fe^{2+}, and Co^{2+} reactions with Et_2DTC^- are respectively $k_f^{298}/M^{-1}\ s^{-1} = 6.4 \times 10^7$, 1.2×10^7, and 4.3×10^6; $\Delta H_f^*/kJ\ mol^{-1} = 47.5$, 38.8, and 39.1; and $\Delta S_f^*/J\ K^{-1}\ mol^{-1} = +64$, +20, and +26. For the Fe^{2+} reaction with Pada, the parameters are $k_f^{298}/M^{-1}\ s^{-1} = 4.3 \times 10^5$, $k_r^{298}/s^{-1} = 2.7 \times 10^3$, $\Delta H_f^*/kJ\ mol^{-1} = 52.1$, $\Delta H_r^*/kJ\ mol^{-1} = 48.9$, $\Delta S_f^*/J\ K^{-1}\ mol^{-1} = +38$, and $\Delta S_r^*/J\ K^{-1}\ mol^{-1} = -15$. The activation volume corresponding to the substitution of DMF by Et_2DTC^+ to form $Mn(DMF)_4Et_2DTC^+$ ($\Delta V_f^*/cm^3\ mol^{-1} = +9.5$) is smaller than the activation volumes for the corresponding Fe^{2+} ($\Delta V_f^*/cm^3\ mol^{-1} = +12.3$) or Co^{2+} ($\Delta V_f^*/cm^3\ mol^{-1} = +12.1$) reactions. For the reaction between $Fe(DMF)_6{}^{2+}$ and Pada, a complete volume diagram is obtained ($\Delta V_f^*/cm^3\ mol^{-1} = +7.5$, $\Delta V_r^*/cm^3\ mol^{-1} = +9.5$, $\Delta V^0/cm^3\ mol^{-1} = -2.0$). The changeover from the associative to the dissociative interchange mechanism observed in other solvents does not take place in DMF, probably because hexakis(dimethylformamide) solvates are too sterically hindered to allow association, even in the case of the larger manganese cation. However, a mechanistic changeover may also occur in this solvent, from the I_d to the D mechanism on going from Mn^{2+} to Ni^{2+}.

Introduction

It has now been more than 8 years since we have found strongly cation-dependent activation volumes for the highly symmetrical reactions of water, acetonitrile, or methanol exchange on divalent hexasolvates of the first-row transition series.[2-4] The spectrum of volumes of activation, spreading from negative values for vanadium and manganese to positive values for iron, cobalt, and nickel, was only slightly solvent dependent.[5] These observations were strong evidence that the cationic size and the electronic configuration of the 3d shell are governing a mechanistic changeover from associative to dissociative activation mode along the series, and this idea is now firmly established. Confirmation of the gradual mechanistic trend came unsurprisingly when the attention of variable-pressure experimentalists focused on formation of monocomplexes from hexaaqua ions of these same metallic centers in water.[6] With a similar changeover found for solvent exchange on trivalent d-metal hexasolvates,[7] it became clear that it was a generic behavior among first-row transition-series cations. For DMF, however, both solvent exchange[3] and complex formation[8] data on Ni^{2+} led to the suspicion that substitution on this cation might follow a more dissociative pathway in this particular solvent. In this context, we decided to explore solvent exchange and complex formation reactions in DMF on the largest possible number of divalent octahedral d cations. In a recent publication from this laboratory,[9] positive activation volumes were reported for DMF exchange on $Mn(DMF)_6{}^{2+}$, $Fe(DMF)_6{}^{2+}$, and $Co(DMF)_6{}^{2+}$, substantiating the presumption that exchange reactions in DMF are indeed more dissociatively activated than in aqueous, acetonitrile, or methanol solutions. The present study is concerned with the closely related although slightly less simple reactions of replacement of DMF for bidentate ligands on the hexasolvento species.

Experimental Section

Chemicals and Solutions. *N,N*-Dimethylformamide (DMF, Fluka, p.a.) was dried over 4-Å molecular sieves for 24 h, stored over KOH pellets for the same time, distilled at reduced pressure, and stored over 4-Å molecular sieves under a nitrogen atmosphere. The water content was checked by Karl Fischer titration to be less than 30 ppm. Solvated $Mn(DMF)_6(ClO_4)_2$ and $Co(DMF)_6(ClO_4)_2$ were prepared from $Mn(ClO_4)_2{\cdot}6H_2O$ (Fluka, purum) and $Co(ClO_4)_2{\cdot}6H_2O$ (Fluka, purum), following the method proposed by Selbin et al. for preparation of dimethyl sulfoxide salts.[10] Complexometric titrations with EDTA gave % Mn = 8.02 (calcd 7.93) and % Co = 8.50 (calcd 8.46). Solvated $Fe(DMF)_6(CF_3SO_3)_2$ was prepared by reacting $Fe(H_2O)_6(CF_3SO_3)_2$ with triethyl orthoformate, adding DMF, precipitating the DMF solvate by addition of diethyl ether, and vacuum-drying of the crystals. Oxydimetric titration with potassium dichromate[11] gave % Fe = 7.25 (calcd 7.05). $NaClO_4{\cdot}H_2O$ (Merck, p.a.) was dried at 170 °C for 24 h and stored over $CaCl_2$. Sodium diethyldithiocarbamate trihydrate (Fluka, p.a.) was recrystallized from acetone/diethyl ether shortly before use. *trans*-Pyridine-2-azo(*p*-dimethylaniline) (Pada (**1**), Sigma, p.a.,) was used as received. Stock solutions were prepared volumetrically in a nitrogen-atmosphere drybox at room temperature. In all cases, concentrations were expressed in molarities at 0.1 MPa[12] and the ionic strength was fixed at 0.10 M with $NaClO_4$.



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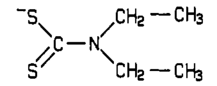

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Kinetic and Equilibrium Measurements. The experimental setups for kinetic and equilibrium experiments were as described previously,[13,14] except for the inner part of the variable-pressure stopped-flow instrument, which was modified to incorporate a commercial Durrum mixer with four tangential jets before the observation chamber. This improvement allows more efficient mixing of the reactants solutions and reactions with half-lives as short as 4 ms can now be studied as a function of pressure. Appearance of the complex was monitored at 300 nm for the diethyldithiocarbamate anion (Et_2DTC^- (**2**)) reactions and at 550 nm for the Pada reaction, wavelengths at which the ligand does not absorb significantly. The temperature dependences of the kinetics at ambient pressure

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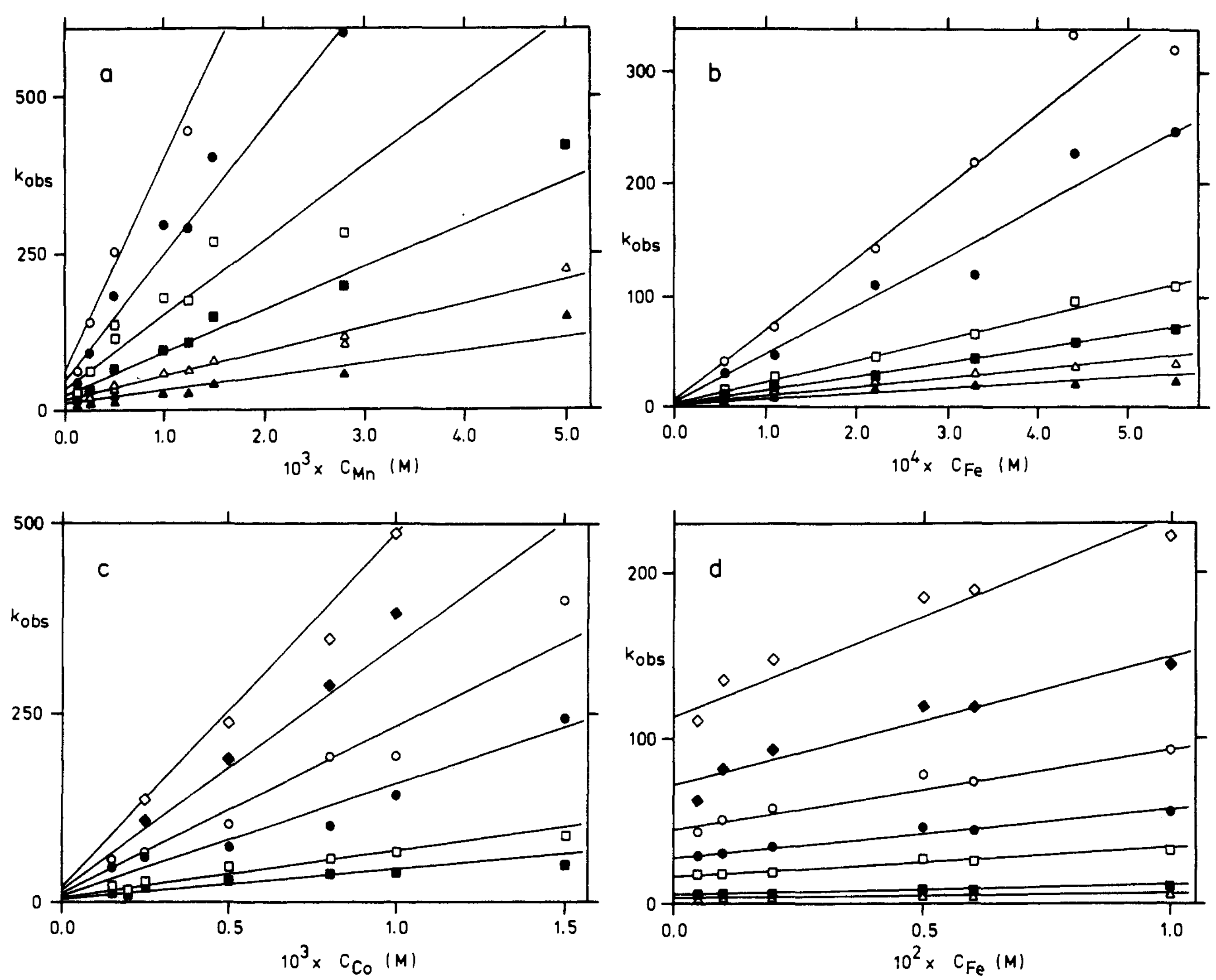

Figure 1. M^{2+} concentration dependence of observed first-order rate constants at various temperatures (from bottom to top, with 5-deg intervals between indicated limits) for $M(DMF)_4Et_2DTC^+$: (a) M = Mn, 213–238 K; (b) M = Fe, 223–253 K; (c) M = Co, 233–263 K; (d) $Fe(DMF)_4Pada^{2+}$, 223–258 K.

were studied over 25–35 deg ranges. Variable-pressure kinetic data were collected up to 120 MPa at 228.2 K for $Mn(DMF)_4Et_2DTC^+$, and up to 160 MPa at 238.2 K for $Fe(DMF)_4Pada^{2+}$, $Fe(DMF)_4Et_2DTC^+$, and $Co(DMF)_4Et_2DTC^+$. Series of 2–14 data sets were collected for each experimental condition. A study of the change in the $Fe(DMF)_4Pada^{2+}$ stability constant with pressure at 550 nm was made up to 175 MPa at 238.2 K, using a 10^{-5} M Pada solution and various concentrations of Fe^{2+}, $0 \leq C_{Fe} \leq 2 \times 10^{-2}$ M. The partial molar volume of Pada in DMF was obtained from density measurements at 298 K, collected with a PAAR DMA 60 densitometer. The errors quoted through text and tables correspond to 1 standard deviation.

Results

The kinetics of monocomplex formation and dissociation from $M(DMF)_6^{2+}$ (M = Mn, Fe, or Co) were studied as a function of concentration in excess metal ion, temperature, and pressure. Under these pseudo-first-order conditions (eq 1) of at least 10-fold

$$k_{obs} = k_f C_M + k_r \qquad (1)$$

excess metal concentration C_M, the reactions were found to follow first-order kinetics over more than 4 half-lives. They are reversible, and the rate constants for formation (k_f) and dissociation (k_r) of the complexes were extracted from the slopes and intercepts of the k_{obs} dependence on M^{2+} concentration by use of a weighed least-squares analysis. As discussed in the literature,[15] traces of amine-type decomposition impurities in the DMF solvent can form stable complexes with some metal ions and increase the magnitude of the intercept owing to simultaneous formation of ternary complexes. In the present study, the standard deviations on the dissociation rate constants are large for the iron and cobalt reactions with Et_2DTC^-, possibly due to this effect, but more probably because the k_r terms represent a minor contribution in the overall observed rate constant. The reasonable agreement between the k_r values obtained from the intercepts of pseudo-first-order plots for the reaction of $Fe(DMF)_6^{2+}$ with Pada and those derived as the ratio of the experimentally obtained k_f and K values suggests that this effect is not significant in this system and for the more labile Mn^{2+} system. The k_{obs} obtained at various temperatures were least-squares analysed with four adjustable parameters to obtain k_f^{298} (or $\Delta S_f^{\ddagger}$), k_r^{298} (or $\Delta S_r^{\ddagger}$), $\Delta H_f^{\ddagger}$, and $\Delta H_r^{\ddagger}$ listed in Table I. Figure 1 shows the concentration dependencies of k_{obs} at several temperatures. It is noteworthy that the parameters for the dissociation of the $M(DMF)_4Et_2DTC^+$ complexes, obtained from very small intercepts in the k_{obs} vs metal concentration plots, are subject to large errors. Moreover, it should be noticed that k_f^{298} and k_r^{298} are in all cases extrapolated from low-temperature data (213–238 K for Mn^{2+}, 223–258 K for Fe^{2+}, and 233–263 K for Co^{2+}). The parameters obtained from linear least-square fits of the variable-pressure data to eq 2 (Et_2DTC^-, Pada; kinetic data), 3 (Pada; kinetic data) or 4 (Pada; spectrophotometric data) are also presented in Table I.

$$\ln k_f = \ln k_f^0 - \Delta V_f^{\ddagger} P/RT \qquad (2)$$

$$\ln k_r = \ln k_r^0 - \Delta V_r^{\ddagger} P/RT \qquad (3)$$

$$\ln K = \ln K^0 - \Delta V^0 P/RT \qquad (4)$$

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Table I. Kinetic, Thermodynamic, and Activation Parameters for Complex Formation and Dissociation of $M(DMF)_6^{2+}$ with L[a]

	M = Mn	M = Fe		M = Co
	L = Et_2DTC^-	L = Et_2DTC^-	L = Pada	L = Et_2DTC^-
$k_f^{298}/M^{-1}\ s^{-1}$	$(6.4 \pm 0.2) \times 10^7$	$(1.2 \pm 0.3) \times 10^7$	$(4.3 \pm 1.0) \times 10^5$	$(4.3 \pm 1.0) \times 10^6$
k_r^{298}/s^{-1}	651 ± 25	39.1 ± 11	$(2.7 \pm 0.3) \times 10^3$	102 ± 16
$\log (K^{238}/M^{-1})$			2.3 ± 0.8	
$\Delta H_f^\ddagger/kJ\ mol^{-1}$	47.5 ± 2.5	38.8 ± 1.3	52.1 ± 2.1	39.1 ± 2.2
$\Delta H_r^\ddagger/kJ\ mol^{-1}$	30.1 ± 9.2	17.9 ± 6.2	48.9 ± 0.9	27.3 ± 26.8
$\Delta S_f^\ddagger/JK^{-1}\ mol^{-1}$	$+64 \pm 11$	$+20 \pm 5$	$+38 \pm 8$	$+26 \pm 8$
$\Delta S_r^\ddagger/JK^{-1}\ mol^{-1}$	-90 ± 42	-154 ± 27	-15 ± 4	-115 ± 100
$\Delta V_f^\ddagger/cm^3\ mol^{-1}$	$+9.5 \pm 0.9^b$	$+12.3 \pm 0.8^c$	$+7.5 \pm 10^c$	$+12.1 \pm 0.6^c$
$\Delta V_f^\ddagger/cm^3\ mol^{-1}$			$+9.5 \pm 1.3^c$	
$\Delta V^0/cm^3\ mol^{-1}$			-2.0 ± 0.3^c	

[a] The errors in the parameters for dissociation of Et_2DTC complexes are probably larger than standard deviations; see text. [b] At 228 K. [c] At 238 K.

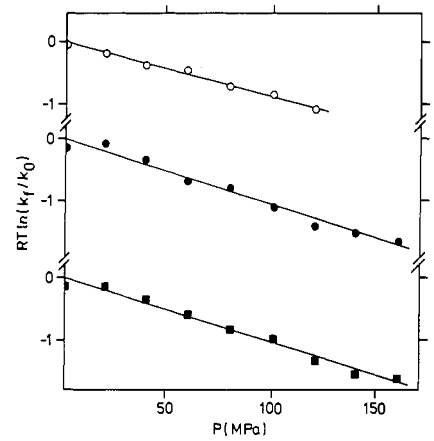

Figure 2. Effect of pressure on first-order rate constants for formation of $M(DMF)_4Et_2DTC^+$ in DMF: (●) M = Mn; (○) M = Fe; (■) M = Co.

Et_2DTC^- Reactions. The kinetics of formation and dissociation of $Fe(DMF)_4Et_2DTC^+$ follows eq 5. It was assumed that the first binding of the bidentate Et_2DTC^- ligand to the metal cation is

$$Fe(DMF)_6^{2+} + Et_2DTC^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Fe(DMF)_4Et_2DTC^+ + 2DMF \quad (5)$$

the slowest, rate-limiting step, followed by rapid chelation to form a stable 1:1 complex, as observed in dimethyl sulfoxide (DMSO).[16] It is noteworthy that for Ni^{2+}, a spin-state change occurs on bonding a second Et_2DTC^- ligand, which strongly favors formation of a stable bis complex in both DMF[8] and DMSO.[17] The Et_2DTC^- complexes of Mn^{2+}, Fe^{2+}, and Co^{2+} react with atmospheric oxygen to give the neutral tris(diethyldithiocarbamate) complexes $M(Et_2DTC)_3$, and care was taken to avoid oxidation in the preparation of solutions. For Mn^{2+} and Fe^{2+}, residual oxidation reactions occur much slower than the initial complexation, but for Co^{2+}, they are of comparable rates.[16] The pressure dependencies of k_f in normalized logarithmic scale are shown in Figure 2. Single concentrations were studied, chosen in a range where the k_f term does not contribute significantly to the observed rate constant.

Pada Reaction. The kinetics of substitution of DMF for Pada on $Fe(DMF)_6^{2+}$ follows eq 6. As in the Et_2DTC^- case, the first binding is rate determining,[18] but here, the k_r term of eq 1 is much

$$Fe(DMF)_6^{2+} + Pada \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Fe(DMF)_4Pada^{2+} + 2DMF \quad (6)$$

more important than for the Et_2DTC^- reaction, and it can thus be determined much more accurately. Spectrophotometric de-

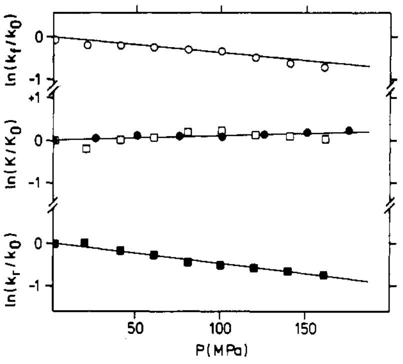

Figure 3. Pressure effect on formation and dissociation rate constants and on the equilibrium constant for the $Fe(DMF)_4Pada^{2+}$ reaction: (□) from kinetic data; (●) from spectrophotometric data.

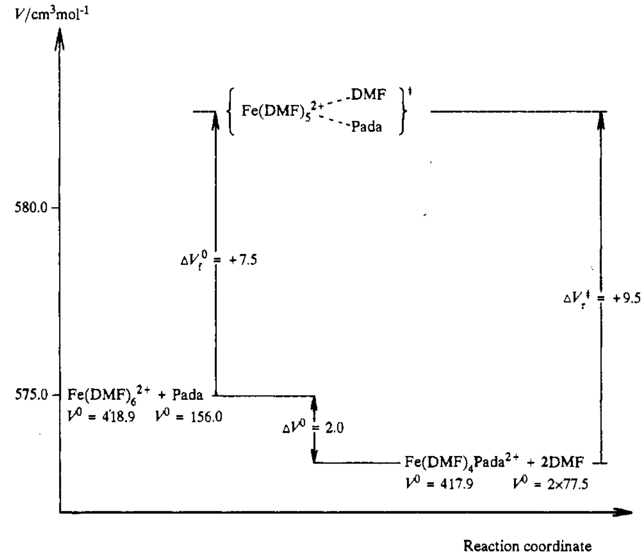

Figure 4. Volume diagram for the reaction between $Fe(DMF)_6^{2+}$ and Pada. Partial molar volumes V^0 at 298 K are obtained from literature data ($V^0(Fe(DMF)_6^{2+})/cm^3\ mol^{-1}$ = 418.9,[24] $V^0(DMF)/cm^3\ mol^{-1}$ = 77.5[23]) or measured ($V^0(Pada)/cm^3\ mol^{-1}$ = 156.0).

termination of the stability constant of $Fe(DMF)_4Pada^{2+}$ could be made in addition to the kinetic measurements. Equilibrium constants were determined from least-squares analysis of the absorbance measurements with the equilibrium constant and extinction coefficient as parameters of the minimizing program.[19] With our excess metal conditions, the best fit was obtained for a 1:1 complex, with stability constant $\log (K^{238}/M^{-1}) = 2.2 \pm 0.1$ and molar absorptivity $\epsilon^{238}/cm^{-1}\ M^{-1} = (4.02 \pm 0.05) \times 10^4$ at 550 nm, in reasonable agreement with the value estimated from the kinetics as $\log (k_f/k_r) = \log (K^{238}/M^{-1}) = 2.0$. The variation

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Table II. Rate Constants (k_{ex}^{298}/s^{-1} and k_f^{298}/M^{-1} s^{-1}) at 298 K and Activation Volumes for DMF Exchange (ΔV_{ex}^*/cm^3 mol^{-1}) and Substitution of DMF by L (ΔV_f^*/cm^3 mol^{-1}) on Divalent Octahedral First-Row M(DMF)$_6^{2+}$

	M = Mn (d^5) r_i = 82 pm		M = Fe (d^6) r_i = 78 pm		M = Co (d^7) r_i = 74 pm		M = Ni (d^8) r_i = 70 pm	
L	k	ΔV^*	k	ΔV^*	k	ΔV^*	k	ΔV^*
DMF	1.8 × 10^6	+2.7[a]	9.7 × 10^5	+8.5[b]	3.9 × 10^5	+9.2[c]	3.8 × 10^3	+9.1[d]
Isoq[e]							2.4 × 10^3[f]	+9.3[g]
Pada			4.3 × 10^5	+7.5[h]		+10.1[i]	1.2 × 10^3	+9.1[j]
Et$_2$DTC$^-$	6.4 × 10^7	+9.5[k] (+7.2)[n]	1.2 × 10^7	+12.3[l] (+9.7)[n]	4.3 × 10^6	+12.1[l] (+9.5)[n]	3.0 × 10^4	+12.4[m] (+7.4)[n]
SCN$^-$							3.1 × 10^4	+8.8[o] (+5.8)[n]

[a] Average of three reported values: ^{17}O NMR; 0.6 × 10^6 and +1.6 (310 K);[36] ^{13}C NMR, 2.2 × 10^6 and +2.4 (263-270 K);[9] ^{1}H NMR, 2.7 × 10^6 and +4.2 (318 K).[26] [b] Reference 9 (275–292 K). [c] Reference 9 (253 K). [d] Reference 3 (297 K). [e] Isoq = Isoquinoline. [f] Reference 37. [g] Reference 38 (298 K). [h] This work (238 K). [i] Reference 18 (323 K). [j] Average of reported values given in ref 18 (298–323 K). [k] This work (228 K). [l] This work (238 K). [m] Reference 8 (298 K). [n] $\Delta V_I^* = \Delta V_f^* - \Delta V_{os}^0$; see text. [o] Reference 8 (264 K).

of the equilibrium constant with pressure gave absorbance changes large enough to obtain ΔV^0 (the small overall volume change during the reaction) with a good accuracy. The pressure dependencies of k_f, k_r, and K in normalized logarithmic scale are shown in Figure 3.

Discussion

The data on the reaction between Fe(DMF)$_6^{2+}$ and Pada allow the construction of a complete volume diagram (Figure 4). This diagram clearly shows that an expansion occurs on going to the transition state, for the forward as well as for the reverse reaction, which is characteristic of dissociatively activated processes. The partial molar volumes for Fe(DMF)$_6^{2+}$ and DMF have been taken from literature[20,21] and that for Pada has been measured in our laboratory. It is noteworthy that the molar volume of Fe(DMF)$_4$Pada^{2+} calculated from the diagram is equal within error limits to that of Fe(DMF)$_6^{2+}$.

The activation volumes in Table II are all positive, reflecting dissociative modes of activation,[5] according to the Langford–Gray classification of substitution mechanisms.[22] It can be seen that the present complex formation results very nicely parallel the solvent-exchange data, and bring a strong confirmation that the reaction mechanisms are of dissociative nature, not only for cobalt and iron but also for manganese, contrary to the behavior in water, acetonitrile, or methanol. The more pronounced dissociative character of solvent exchange and complex formation reactions in DMF has been observed before[8,23–26] and has been attributed to the increased steric crowding brought by the presence of six coordinated DMF molecule around the central cation.

Coordination of a ligand molecule such as Et$_2$DTC$^-$ or Pada on an hexasolvated transition-metal ion is usually assumed to follow an interchange mechanism[27] of the Eigen–Wilkins type.[28] The reaction pathway can be decomposed into successive steps (eq 7). The initial diffusion-controlled approach of the incoming

$$\mathrm{M(S)_6^{2+} + L{-}L^{n-} \overset{K_{os}}{\rightleftharpoons} [M(S)_6,L{-}L]^{(2-n)+}} \xrightarrow{k_1}$$
$$\mathrm{M(S)_5L{-}L^{(2-n)+} + S \xrightarrow{fast} M(S)_4L{-}L^{(2-n)+} + 2S} \quad (7)$$

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 bidentate ligands, the final and supposedly much faster chelation step. The rate constant for the forward process can thus be written as $k_f = K_{os}k_I$, and the activation volume measured for this same process, ΔV_f^*, can be expressed in terms of the pressure derivative of $\ln k_f = \ln K_{os} + \ln k_I$ (eq 8). ΔV_{os}^0 represents the volume change in forming the

$$\Delta V_f^* = \Delta V_{os}^0 + \Delta V_I^* \quad (8)$$

outer-sphere complex and ΔV_I^* is the volume of activation for the subsequent substitution of a DMF molecule. The change in volume caused by the replacement of DMF by some uncharged ligand in the second coordination sphere of the solvated cation should be negligible. The ΔV_{os}^0 contribution to the activation volume can therefore be set to zero for Pada as incoming ligand, and ΔV_f^* equated to ΔV_I^*. Conversely, when a charged species like Et$_2$DTC$^-$ is approaching the solvated cation, a large change in solvent electrostriction should occur and produce substantial volume changes in the preequilibrium stage. Comparison of the activation volumes for DMF exchange or complex formation with uncharged ligands with those for Et$_2$DTC$^-$ suggests that the ΔV_{os}^0 contribution amounts to about 2–4 cm^3 mol^{-1} (Table II). This outer-sphere term can also be estimated from calculations based on the Fuoss equation[29] (eq 9), where K_F^0 is the equilibrium

$$K_F^0 = (4\pi a^3 N/3000)\exp(|z^+z^-|e_0^2/4\pi a\epsilon_0\epsilon kT) \quad (9)$$

constant at infinite dilution, z^+ and z^- are the charges of the two reacting species, e_0 is the charge of the electron, a is the distance of closest approach between the ligand and the solvated metal ion, ϵ^0 is the vacuum permittivity, and ϵ is the dielectric constant of the solution. Following Hemmes,[30] we can take the pressure derivative of eq 9 at constant temperature to obtain eq 10. The

$$\left(\frac{\mathrm{d}\ln K_F}{\mathrm{d}P}\right)_T = \frac{-\Delta V_F^0}{RT} = \frac{-|z^+z^-|e_0^2}{4\pi a\epsilon_0\epsilon kT}\left(\frac{\mathrm{d}\ln\epsilon}{\mathrm{d}P}\right)_T \quad (10)$$

pressure dependence of ϵ has not yet been measured for DMF. However, since the dielectric constant and the density ρ of the solution have a similar pressure dependence,[31] this term can, to a good approximation (±10%), be set equal to κ, the isothermal compressibility of the solution.[32] After unit conversion,[33] the volume change occurring in forming the outer-sphere complex, ΔV_{os}^0, can be expressed as eq 11. For a distance of closest

$$\Delta V_{os}^0 = R\kappa\left(\frac{|z^+z^-|e_0^2}{4\pi a\epsilon_0\epsilon k} - T\right) \quad (11)$$

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approach *a* of 0.7 nm (corresponding to the metal cation separated from the ligand by one solvent molecule), and the literature values of ε and κ,[34] the volume change accompanying the outer-sphere association can be calculated as $\Delta V_{os}^0 = +2.3$ cm^3 mol^{-1} at 228 K, +2.6 cm^3 mol^{-1} at 238 K, +3.0 cm^3 mol^{-1} at 264 K, and +5.0 cm^3 mol^{-1} at 298 K. For the two ligands with −1 charge, it seems therefore reasonable to subtract these calculated values from ΔV_f^* to obtain the activation volume corresponding to the interchange step, ΔV_I^*, displayed in parentheses in Table II.

The overall picture emerging from Table II is that a dissociative activation mode is the rule in DMF throughout the series of cations studied. On the basis of the present data, it is not possible to decide whether the mechanisms are dissociative interchanges for all cations or if a changeover from dissociative interchange mechanisms (I_d) to a limiting dissociative mechanism (D) takes place along the series. This latter proposition would confirm the earlier conclusion to a limiting dissociative mechanism proposed for Ni^{2+}, based on DMF exchange data.[35] It would not be in contradiction with the observations in water, methanol, and acetonitrile, in which easier bond-making capabilities displace the spectrum of mechanisms into an I_a–I_d changeover.

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Registry No. **1**, 77038-70-1; **2**, 392-74-5; Mn(DMF)$_6^{2+}$, 39016-85-8; Co(DMF)$_6^{2+}$, 34409-32-0; Fe(DMF)$_6^{2+}$, 62126-14-1.

Supplementary Material Available: Listings of observed first-order rate constants and calculated forward and reverse rate constants (Tables SI–SVII) and equilibrium measurements (Table SVIII) (8 pages). Ordering information is given on any current masthead page.

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New Synthetic Cobalt Schiff Base Complexes as Oxygen Carriers

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The synthesis and dioxygen affinities of ten new cobalt Schiff base complexes and two new cobalt complexes obtained by reduction of Schiff bases are reported and compared in a common solvent with two well-known parent Schiff base complexes and six Schiff base complexes recently reported. The cobalt(II) Schiff base complexes investigated are (bis(3-fluorosalicylaldehyde) ethylenediiminato)cobalt(II) (CoFLUOMINE), (bis(3-methoxysalicylaldehyde) ethylenediiminato)cobalt(II) (Co3MeOSALEN), (bis(3-fluorosalicylaldehyde) *o*-phenylenediimato)cobalt(II) (Co3FSALOPHEN), disodium (bis(5-sulfosalicylaldehyde) *o*-phenylenediiminato)cobaltate(II) (Co5SO$_3$NaSALOPHEN), (bis(2-hydroxyacetophenone) *o*-phenylenediiminato)cobalt(II) (CoαCH$_3$SALOPHEN), (bis(3-fluorosalicylaldehyde) tetramethylethylenediiminato)cobalt(II) (Co3FSALTMEN), (bis(3-methoxysalicylaldehyde) tetramethylethylenediiminato)cobalt(II) (Co3MeOSALTMEN), (*N*,*N*′-bis(salicylidene)-2,6-bis(aminomethyl)pyridinato)cobalt(II) (CoSALMP), (*N*,*N*′-bis(salicylidene)-2,6-bis(aminoethyl)pyridinato)cobalt(II) (CoSALEP), (*N*,*N*′-bis(2-hydroxybenzyl)-2,6-bis(aminoethyl)pyridinato)cobalt(II) (CoBHBEPTY), (*N*,*N*′-bis(salicylidene)bis(2-aminophenyl)methylaminato)cobalt(II) (CoMBA), and (*N*,*N*′-bis(2-hydroxybenzyl)bis(2-aminophenyl)methylaminato)cobalt(II) (CoMHBA). Oxygenation equilibria were measured by monitoring gaseous oxygen uptake by the cobalt(II) complexes in bis(2-methoxyethyl) ether (diglyme) as solvent. The seven tetradentate Schiff base complexes were studied in the presence of large excess (ca. 50 times) concentrations of 4-methylpyridine. The substitution of methyl groups on the Schiff bases (α-substitution, acetophenone derivatives) increases the affinity for dioxygen but also increases the rate of degradation. Fluorine substitution on the aromatic rings of the Schiff bases increases the affinity of the complexes for dioxygen by promoting 2:1 (binuclear) dioxygen complex formation. Sulfonation of the aromatic rings of the Schiff base seems to increase the rate of degradation of the cobalt dioxygen complexes studied. Methoxy groups on the aromatic rings of the Schiff bases tend to increase the affinity of the cobalt(II) complex for dioxygen and favor 1:1 dioxygen complex formation. Combination of dioxygen with the cobalt(II) complexes of the pentadentate Schiff bases seems to be partially inhibited by steric effects, which are relieved by hydrogenation of the ligands. The cobalt(II) complexes of reduced ligands have much higher affinities for dioxygen than do the complexes of the corresponding Schiff bases.

Introduction

Of the dioxygen carriers that have been studied as potential reagents for oxygen separation and transport, the cobalt(II) complexes of Schiff bases, such as bis(salicylaldehyde) ethylenediimine (salcomine) and its analogues, have been the first and the most extensively investigated.[1] The potential usefulness of such dioxygen carriers has long been recognized, in view of the fact that the separation factor for the removal of oxygen from a mixture of inert gases (N$_2$, CO, CO$_2$, etc.) is 100%. However dioxygen separation processes based on this type of complex formation have suffered from the fact that all dioxygen complexes synthesized thus far undergo degradation reactions to inert compounds incapable of carrying dioxygen.[2,3] The cobalt(II) complex of bis(3-fluorosalicylaldehyde) ethylenediimine (fluomine) shows the best performance achieved thus far,[3-5] with up to 3500 oxygenation–deoxygenation cycles before about 40% of the complex becomes inert. Although a variety of cobalt(II) dioxygen carriers have been investigated,[1,6] including several salcomine analogues,

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