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Nuclear Magnetic Resonance Study of Solvent Exchange on Hexakis(*N*,*N*-dimethylacetamide)cobalt(II), Hexakis(*N*,*N*-diethylformamide)cobalt(II), and Their Nickel(II) Analogues. Effect of Solvent Molecular Size on Lability

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^1H NMR studies of *N*,*N*-diethylformamide (def) exchange on $[Co(def)_6]^{2+}$ and $[Ni(def)_6]^{2+}$ yield $10^{-3}k(298.2\ K) = 120 \pm 16$ and $1.15 \pm 0.08\ s^{-1}$, $\Delta H^{\ddagger} = 51.4 \pm 2.0$ and $74.2 \pm 1.1\ kJ\ mol^{-1}$, and $\Delta S^{\ddagger} = 24.8 \pm 7.0$ and $62.6 \pm 3.4\ J\ K^{-1}\ mol^{-1}$, respectively. ^{13}C NMR studies of *N*,*N*-dimethylacetamide (dma) exchange on $[Co(dma)_6]^{2+}$ and $[Ni(dma)_6]^{2+}$ yield $10^{-6}k(298.2\ K) = 23.1 \pm 3.5$ and $3.52 \pm 0.70\ s^{-1}$, $\Delta H^{\ddagger} = 32.7 \pm 0.8$ and $40.4 \pm 1.8\ kJ\ mol^{-1}$, and $\Delta S^{\ddagger} = 5.8 \pm 3.0$ and $16.0 \pm 10.0\ J\ K^{-1}\ mol^{-1}$, respectively. These systems are also characterized by equilibria between tetrakis- and hexakis(solvent) species, and the latter species are considered to undergo exchange through D mechanisms. The greater lability of the dma species is attributed to the increased steric crowding caused by the acetyl moiety. These results are discussed in conjunction with reported studies of the effects of solvent molecular size on the lability toward solvent exchange of several other metal ions.

Introduction

The process of solvent exchange has been extensively studied for metal ions ranging from beryllium(II) to uranium(VI) in many different solvents.[1-11] The bivalent first-row transition-metal ions have been the most intensively studied, and their solvent-exchange mechanisms are now quite well established.[1,5] For the $[M(solvent)_6]^{2+}$ species in water[6] and methanol[7] the activation mode changes from associative (a) for Mn^{2+} to dissociative (d) for Fe^{2+}, with the transition state becoming increasingly dissociative for Co^{2+} and Ni^{2+}, and this trend in mechanistic variation appears to persist in other solvents also.[5] Within this mechanistic framework the lability of $[M(solvent)_6]^{2+}$ varies with the nature of the solvent. This latter variation may arise from differences in the electron-donating power and the molecular size of the solvent, but as most of the solvents studied are of different chemical type, separate identification of the effects of these two solvent characteristics on lability is not readily achieved. However, the oxygen-donor solvents *N*,*N*-dimethylformamide (dmf), *N*,*N*-diethylformamide (def), and *N*,*N*-dimethylacetamide (dma) are of similar chemical type and exhibit a small range of electron-donating power, as indicated by their Gutmann donor numbers[12] (D_N) of 26.6, 30.9, and 27.8, respectively; therefore, any differences in lability of their $[M(solvent)_6]^{2+}$ species should be largely attributable to steric differences among the three solvents. The kinetic parameters characterizing $[Co(dmf)_6]^{2+}$ and $[Ni(dmf)_6]^{2+}$ are well established, and both undergo solvent exchange through a d activation mode usually interpreted in terms of a dissociative interchange (I_d) mechanism,[8,9] which may closely approach the dissociative (D) mechanism for $[Ni(dmf)_6]^{2+}$, as suggested in a recent ligand substitution study.[13] In the study reported here the rates of solvent exchange are determined on the analogous dma species, in which a substantial increase in steric crowding occurs close to the metal center, and the analogous def species, in which an increase in steric crowding occurs at a greater distance from the metal center, to ascertain the effect of these stereochemical differences on lability.

Experimental Section

The solid complexes were obtained by heating the hydrated metal perchlorate salts at 325 K for 2 h and, after the salts were allowed to cool to room temperature, adding the stoichiometric amount of def or dma calculated for six-coordination in a manner similar to that described in the literature.[10,14] The resulting hygroscopic crystalline products were filtered off, washed with dry ether in a dry-nitrogen-flushed glovebox, and dried on a vacuum line for 3 h. The yields of the complexes were in the range 65–75%. Anal. Calcd for $[Co(dma)_4](ClO_4)_2$: Co, 9.72. Found: Co, 9.66. Calcd for $[Ni(dma)_{5.3}](ClO_4)_2$: Ni, 8.18. Found: Ni, 8.18. Calcd for $[Co(def)_{4.36}](ClO_4)_2$: Co, 8.43. Found: Co, 8.43. Calcd for $[Ni(def)_6](ClO_4)_2$: Ni, 6.79. Found: Ni, 6.82. Analyses for Co and Ni as the bivalent ions were carried out by using an ion-exchange technique[15] and were reproducible to within ±3 of the third figure of the percentages quoted above. In the two cases where noninteger metal: solvent ratios are obtained, it is possible that this is a consequence of the isolated solid consisting of a mixture of four- and six-coordinate complexes, as is discussed below. Analyses for C, H, and N were performed on all four complexes by commercial analytical companies, but in all cases the H analyses were high and the C and N analyses were low, consistent with absorption of water by the hygroscopic solids during handling in the analytical procedure. (*Caution*! Perchlorate salts of metal complexes may be explosive under some circumstances and should be handled with caution. No explosion hazard was encountered in this study.) The infrared spectra of these complexes in Nujol mulls exhibited no O–H bands, consistent with the absence of significant amounts of water.

Solutions of the complexes for UV–visible and NMR spectroscopic study were prepared by weight in a dry-nitrogen-flushed glovebox. UV–visible spectra of these solutions in tightly stoppered 1 cm path length quartz cells were run on a Zeiss DMR-10 spectrophotometer equipped with a thermostated cell block (±0.1 K). NMR spectra were run on solutions of the complexes and solvent reference samples (which were 2% in either benzene or cyclohexane, which acted as chemical shift references and as monitors of field homogeneity) sealed under vacuum in either 2-mm (^1H) or 7-mm (^{13}C) tubes mounted coaxially in either 5-mm (^1H) or 10-mm (^{13}C) tubes that, depending on the temperature range studied, contained either $(CD_3)_2CO$ or $(CD_3)_2SO$, which provided the deuterium lock signal. The mole fractions of coordinated solvent, P_m, were 0.006 19, 0.0185, and 0.0571 in the $[Co(def)_6]^{2+}$ solutions, 0.0149, 0.0168, and 0.0351 in the $[Ni(def)_6]^{2+}$ solutions, 0.0183 in the $[Co(dma)_6]^{2+}$ solution, and 0.0127 and 0.0229 in the $[Ni(dma)_6]^{2+}$ solutions. (These P_m values are calculated on the basis of six-coordinate complexes existing exclu-

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Table I. Kinetic Parameters[a] for Solvent (S) Exchange on $[MS_6]^{2+}$

M	S	$10^{-3}k$(298.2 K), s^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta V^\ddagger$, cm^3 mol^{-1}	ref
Co	dmf	390	56.9 ± 2.1	52.7 ± 8.4	6.7 ± 0.3	8, 9
Co[b]	def	120 ± 16	51.4 ± 2.0	24.8 ± 7.0		this work
Co	dma	23100 ± 3500	32.7 ± 0.8	5.8 ± 3.0		this work
Ni	dmf	3.8	62.8 ± 2.1	33.5 ± 8.4	9.1 ± 0.3	8, 9
Ni[b]	def	1.15 ± 0.08	74.2 ± 1.1	62.6 ± 3.4		this work
Ni	dma	3520 ± 700	40.4 ± 1.8	16 ± 10		this work

[a] Errors represent one standard deviation determined through least-squares fits of the raw data to the appropriate equations as described in the text. [b] The first and second values given for the parameters that follow pertain to Co and Ni, respectively: $A_m = 60 \pm 17$ and $1200 \pm 460\ s^{-1}$; $E_m = E_o = 3.1 \pm 1.5$ and 3.3 ± 1.3 kJ mol^{-1} (the approximation $E_m = E_o$ was used in the data-fitting procedure); $B = (1.67 \pm 0.03) \times 10^6$ and $(1.55 \pm 0.02) \times 10^6$ Hz K s^{-1}; $A_0 = 72 \pm 14$ and $125 \pm 34\ s^{-1}$; $C_o = 0.081 \pm 0.005$ and 0.059 ± 0.007.

sively in solution. It will be seen below that equilibria between four- and six-coordinate dma complexes exist, whereas the def complexes are predominantly six-coordinate in solution.)

^1H (90-MHz) and ^{13}C (75.47-MHz) NMR spectra were run on Bruker HX-90E and CXP-300 spectrometers, respectively, in which sample temperature was maintained to ±0.03 K by Bruker B-VT 1000 temperature controllers and was monitored by platinum resistance thermometers. ^1H NMR spectra were run in the temperature range 220–370 K and 25–1000 transients were collected into a 8192-data-point block prior to Fourier transformation depending on the sample. Broad-band proton-decoupled ^{13}C NMR spectra were run in the temperature range 255–370 K and 1000–5000 transients were collected into 8192-data-point blocks prior to Fourier transformation depending on the sample. The experimental transverse relaxation times, T_2, were calculated through the relationship $T_2 = 1/(\pi W_{1/2})$, where $W_{1/2}$ is the full line width in hertz at half-maximum amplitude of the Lorentzian line shape. Computing was carried out on a Cyber 173 computer.

Results

NMR and UV-visible spectroscopic studies[8,17] have shown six-coordinate $[Co(dmf)_6]^{2+}$ and $[Ni(dmf)_6]^{2+}$ to be the only detectable species in dmf solutions of cobalt(II) and nickel(II) perchlorate respectively. In contrast, in dma solution the equilibrium between $[Co(dma)_4]^{2+}$ and $[Co(dma)_6]^{2+}$ has been shown to move toward the former species as the temperature is increased.[16] The temperature variation of the spectrum of a dma solution of $[Ni(dma)_{5.3}](ClO_4)_2$ shown in Figure 1 is qualitatively consistent with the equilibrium between $[Ni(dma)_4]^{2+}$ and $[Ni(dma)_6]^{2+}$ moving toward the former species as the temperature is increased. Below 298.2 K the spectrum shows only small changes with temperature, consistent with $[Ni(dma)_6]^{2+}$ becoming the greatly predominant species,[17] and below 278.2 K no further change in the spectrum was observed. Repeated attempts to isolate the $[Ni(dma)_4]^{2+}$ species as a crystalline perchlorate salt in a manner similar to that described for its cobalt(II) analogue[16,18] produced a yellow hygroscopic oil that analyzed for a Ni^{2+}:dma ratio of 1:4. While this result supports the postulation of $[Ni(dma)_4]^{2+}$ in solution above ca. 278.2 K, it does not establish the nature of this species as tetrahedral or square planar nor does it permit the reliable determination of the UV–visible spectrum of this species necessary for the spectrophotometric estimation of the four-coordinate/six-coordinate equilibrium constant above 278.2 K. (In light of these observations it seems possible that the stoichiometry of the isolated solid $[Ni(dma)_{5.3}](ClO_4)_2$ characterizes a mixture of four- and six-coordinate nickel(II) species, and a similar explanation may apply for the $[Co(def)_{4.36}](ClO_4)_2$ solid stoichiometry.) Def solutions of $[Co(def)_{4.36}](ClO_4)_2$ and $[Ni(def)_6](ClO_4)_2$ were characterized by UV-visible spectra at 298.2 K with λ_{max} at 522 and 398 nm, respectively (with molar absorbances of 19.9 and 17.0 dm^3 mol^{-1} cm^{-1}, respectively), consistent with $[Co(def)_6]^{2+}$ and $[Ni(def)_6]^{2+}$ being the predominant species in solution.[16,18,19] As the temperature is increased from 298.2 to 344.2 K, the spectra of both cobalt(II) and nickel(II) def solutions change qualitatively in the same manner as the dma solutions but only to a slight extent, probably indicating the production of very low concentrations of the four-coordinate species. These observations are consistent with the stability of the six-coordinate species relative to the four-coordinate species, decreasing as the steric crowding around the metal center increases in the sequence dmf < def ≪ dma. (It is noteworthy that even in the case of the smaller solvent molecule, H_2O, evidence has been presented for the existence of $[Co(OH_2)_4]^{2+}$ as a minor species in equilibrium with $[Co(OH_2)_6]^{2+}$.[20])

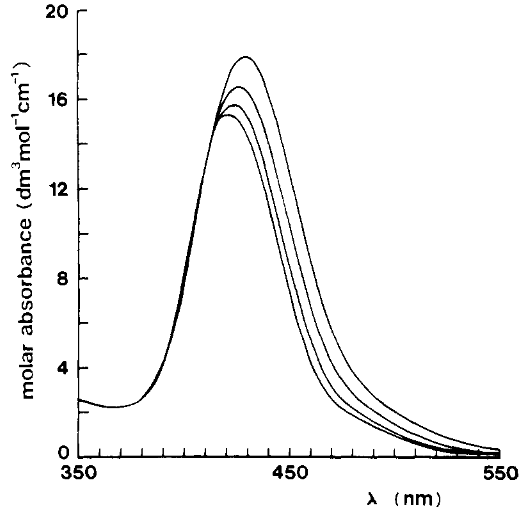

Figure 1. Temperature variation of the UV–visible spectrum of a 0.0265 mol dm^{-3} solution of $[Ni(dma)_{5.3}](ClO_4)_2$ in dma. The temperatures at which the spectra were recorded decrease in the order 338.2, 318.2, 298.2, and 278.2 K as molar absorbance decreases at 450 nm.

The kinetic parameters for dma and def exchange on hexakis(solvent)cobalt(II) and -nickel(II) were determined from the temperature variation of the transverse relaxation times and the chemical shifts of the ^1H formyl resonance of bulk def and the ^{13}C carbonyl resonance of bulk dma in solutions of their metal complexes. The relaxation parameter, T_{2p}, is related to the transverse relaxation times of the bulk solvent resonance in solutions of the complexes and reference solutions of the solvent alone, T_2 and T_{2ref}, respectively, through eq 1.[21,22] The relationship

$$T_{2p}^{-1} = T_2^{-1} + T_{2ref}^{-1} \tag{1}$$

between T_{2p} and the solvent-exchange rate is given by eq 2, where

$$T_{2p}^{-1} = \frac{P_m}{\tau_m}\left(\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + (\Delta\omega_m)^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + (\Delta\omega_m)^2}\right) + \frac{P_m}{T_{2o}} \tag{2}$$

τ_m $(=1/k = (h/k_BT)\exp(\Delta H^\ddagger/RT - \Delta S^\ddagger/R))$ is the mean lifetime of a single coordinated solvent molecule, P_m is the mole fraction of coordinated solvent, T_{2m} $(=A_m^{-1}\exp(-E_m/RT))$ is the

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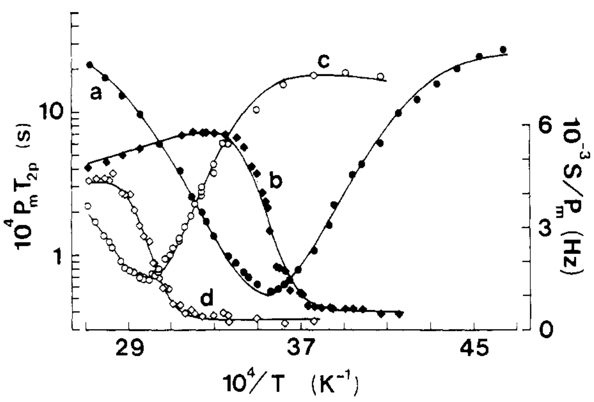

Figure 2. Variation with temperature of T_{2p} (a) and S (b) for [Co-(def)$_6$]$^{2+}$ and T_{2p} (c) and S(d) for [Ni(def)$_6$]$^{2+}$, determined from the formyl ^{1}H resonance of bulk def at 90 MHz. The solid curves represent the best fit of these data to eq 2 and 3.

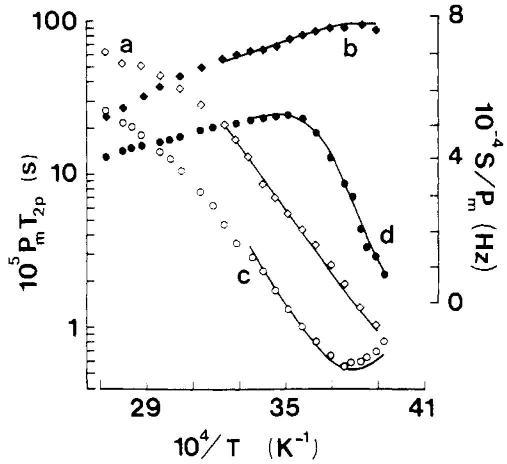

Figure 3. Variation with temperature of T_{2p} (a) and S (b) for [Co-(dma)$_6$]$^{2+}$ and T_{2p} (c) and S (d) for [Ni(dma)$_6$]$^{2+}$, determined from the carbonyl ^{13}C resonance of bulk dma at 75.47 MHz. The solid curves represent the best fit of these data to eq 2 and 3.

transverse relaxation time of coordinated solvent, $\Delta\omega_m$ ($=B/T$) is the chemical shift between coordinated and bulk solvent, and T_{2o} ($=A_o^{-1}\exp(-E_o/RT)$) is the contribution to T_{2p} arising from interactions outside the first coordination sphere.[21,22] The variations of T_{2p} with temperature for all four systems studied are seen in Figures 2 and 3. The variations of the chemical shift of bulk solvent, S, with temperature are also seen in Figures 2 and 3 and are described by eq 3, in which $C_o(\Delta\omega_m)$ is the chemical

$$S = \frac{(\Delta\omega_m)P_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m^2(\Delta\omega_m)^2} + C_o(\Delta\omega_m)P_m \qquad (3)$$

shift between the bulk solvent resonance of the reference solution and that of the paramagnetic complex solution, which arises from the interactions outside the first coordination sphere, and C_o is a proportionality constant. The best fit curves for the simultaneous fitting of the [Co(def)$_6$]$^{2+}$ and [Ni(def)$_6$]$^{2+}$ T_{2p} and S data to eq 2 and 3 are shown in Figure 2, and the kinetic parameters characterizing def exchange on these two species appear in Table I. Solvent exchange on [Co(dma)$_6$]$^{2+}$ and [Ni(dma)$_6$]$^{2+}$ is more rapid than on their def analogues, but the derivation of the kinetic parameters is complicated by the four-coordinate/six-coordinate equilibria. The tetrahedral [Co(dma)$_4$]$^{2+}$ species is paramagnetic and, depending on the rate of dma exchange, may contribute significantly to the ^{13}C relaxation and shift variation with temperature. To avoid the complications arising from this source, only T_{2p} and S data below 309.4 K (where [Co(dma)$_4$]$^{2+}$ exists as <4% of the total cobalt(II) concentration[16]) were used in deriving the kinetic parameters for dma exchange on [Co(dma)$_6$]$^{2+}$ through eq 2. The rapidity of dma exchange is such that the T_{2o} term of eq 2 makes no detectable contribution to T_{2p}, and accordingly, it was dropped from eq 2 in the data-fitting procedure. The resulting simultaneous best fit curves for the T_{2p} and S data are shown in Figure 3, and the kinetic parameters for dma exchange appear in Table I. To similarly avoid complications arising from the four-coordinate/six-coordinate equilibrium, only the T_{2p} and S data below 298.7 K (where the previously discussed UV-visible spectral temperature dependence indicates that [Ni-(dma)$_4$]$^{2+}$ exists as <5% of the total nickel(II) concentration) were used in deriving the kinetic parameters for dma exchange on [Ni(dma)$_6$]$^{2+}$ through eq 2 from which the term in T_{2o} was dropped. The resulting simultaneous best fit curves for the T_{2p} and S data are shown in Figure 3, and the kinetic parameters for dma exchange appear in Table I. (No contribution to S from the $C_o(\Delta\omega_m)$ term was detected for the dma systems, but a small contribution was detected for the def systems as indicated by the C_o values in Table I.)

Discussion

It is seen from Table I that [Co(solvent)$_6$]$^{2+}$ exhibits a greater lability and smaller ΔH^* for solvent exchange in dmf, def, and dma by comparison with [Ni(solvent)$_6$]$^{2+}$, as expected as a consequence of the greater crystal field activation energy of the latter species undergoing exchange through a five-coordinate intermediate.[23,24] For a given metal ion it is seen that while the labilities of the dmf and def species differ slightly, the dma species is much more labile as a consequence of a decreased ΔH^*. As the electron-donating power of dmf differs more from that of def than from that of dma (D_N = 26.6, 30.9, and 27.8, respectively[12]), it seems unlikely that this is a factor of major importance in determining the relative labilities of the coordinated solvents. Thus, the substantially greater steric crowding close to the metal center caused by the acetyl group of dma relative to that caused by the formyl group of dmf or def is the most likely cause of the greater lability of [Co(dma)$_6$]$^{2+}$ and [Ni(dma)$_6$]$^{2+}$ relative to those of their dmf and def analogues. The positive activation volumes, ΔV^*, characterizing dmf exchange on [Co(dmf)$_6$]$^{2+}$ and [Ni-(dmf)$_6$]$^{2+}$ (Table I) are convincing evidence that the exchange process is dissociatively (d) activated in each case. As ΔV^* characterizing solvent exchange on [Ni(solvent)$_6$]$^{2+}$ is generally greater than that characterizing the analogous earlier first-row transition-metal species, it is usually considered that the [Ni-(solvent)$_6$]$^{2+}$ solvent-exchange mechanism most closely approaches the D mechanism,[5,25,26] and when the solvent is dmf, it has been suggested that a D mechanism operates.[13] The observation of [Ni(dma)$_4$]$^{2+}$ in equilibrium with [Ni(dma)$_6$]$^{2+}$ is substantial evidence for the operation of a D solvent-exchange mechanism for the latter species; and given the increase in size of def over dmf and the probable existence of [Ni(def)$_4$]$^{2+}$ in equilibrium with [Ni(def)$_6$]$^{2+}$, it is reasonable to assign a D mechanism to the def exchange process also. By use of a similar rationale, D mechanisms are assigned to the solvent-exchange processes on both [Co(dma)$_6$]$^{2+}$ and [Co(def)$_6$]$^{2+}$. The operation of a D mechanism for solvent exchange on [M(solvent)$_6$]$^{2+}$ conventionally requires the generation of a [M(solvent)$_5$]$^{2+}$ reactive intermediate. (For M = Co and Ni there seem to be no reports of [M(solvent)$_5$]$^{2+}$ ground-state species in solution, which suggests that the related four- and six-coordinated species are favored through a combination of steric and crystal field effects. The five-coordinate [ML(dmf)]$^{2+}$ species, where L = the tetradentate 2,2',2''-tris-(dimethylamino)triethylamine and 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane ligands, are stable in solution however.[27,28]) The observation of ground-state [M(solvent)$_4$]$^{2+}$

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species raises the possibility of the occurrence of either sequential or simultaneous loss of two solvent molecules from $[M(solvent)_6]^{2+}$, both of which provide D pathways for solvent exchange on $[M(solvent)_6]^{2+}$. Evidence for the sequential loss of two solvent molecules from $[NiL(solvent)_2]^{2+}$ (where L is a tetradentate ligand) has been presented,[29,30] and while no direct evidence is available for such a process occurring on $[M(solvent)_6]^{2+}$, it presents no conceptual difficulties. The simultaneous loss of two solvent molecules from $[M(solvent)_6]^{2+}$ to produce tetrahedral $[M(solvent)_4]^{2+}$ could be envisaged to involve the simultaneous departure of two trans solvent molecules along the C_4 axis of $[M(solvent)_6]^{2+}$ while the two remaining pairs of cis solvent molecules contrarotate about a common C_2 axis as their bond angles increase from 90 to 109.5°. (A square-planar product is more simply obtained by omission of the contrarotation of the cis pairs.) The reverse process requires a reactive three-body collision. Unless there is a highly concerted involvement of solvent both in and outside the first coordination spheres (as a recently published computer modeling of solvent exchange suggests is the case for exchange of a single solvent molecule[31]), the simultaneous process would seem to be less favored than the sequential process, but the available data provide no basis for a definitive choice between the two processes. Nevertheless, this study clearly demonstrates that an increase in crowding at the metal center in $[M(solvent)_6]^{2+}$ not only labilizes the solvent for a d-activated mechanism when M = Ni or Co but also in the case of the latter metal causes the mechanism to change from I_d to D when the solvent is changed from dmf[5] to dma or def.

It is appropriate to compare the findings of this study with those from other studies in which the nature of the solvent was varied. Dma exchange on $[Sc(dma)_6]^{3+}$ in acetonitrile diluent is characterized by first- and second-order exchange processes, respectively, assigned to D and A mechanisms, whereas the exchange of dmf and def on scandium(III) is found to be too fast for determination by NMR methods.[10] This increased lability is thought to be a consequence of either the less sterically crowding dmf and def facilitating very rapid solvent exchange on $[Sc(solvent)_6]^{3+}$ through an A mechanism or the formation of very labile $[Sc(solvent)_7]^{3+}$. Evidence for the labilization of $[M(solvent)_n]^{3+}$ with an increase in n may be adduced from the observation that $k(298.2\ K) = 3.1 \times 10^7\ s^{-1}$ for $[Tm(dmf)_8]^{3+}$[32] whereas for $[Tm(tmu)_6]^{3+}$[33] $k(298.2\ K) = 145\ s^{-1}$ where tmu = 1,1,3,3-tetramethylurea ($D_N = 29.6$), both of which undergo exchange through a D mechanism. However, a change in coordination number may also result in a change in mechanism, as exemplified by $[UO_2(OP(NMe_2)_3)_4]^{2+}$, for which the predominant solvent-exchange process occurs through an A mechanism, and $[UO_2(OP(OMe)_3)_5]^{2+}$, for which a D mechanism operates.[3,4]

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Registry No. def, 617-84-5; dma, 127-19-5; $[Co(def)_6]^{2+}$, 100485-68-5; $[Ni(def)_6]^{2+}$, 45318-23-8; $[Co(dma)_6]^{2+}$, 38213-56-8; $[Ni(dma)_6]^{2+}$, 48077-69-6.

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Mechanism of Reduction of Bound Nitrite to Ammonia

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Electrochemical experiments on the oxidation of $[(tpy)(bpy)M(NH_3)]^{2+}$ (M = Ru, Os; tpy = 2,2′,2″-terpyridine; bpy = 2,2′-bipyridine) and reduction of $[(tpy)(bpy)M(NO_2)]^+$ have given insight into the mechanistic details of how bound nitrite is converted into ammonia. A critical feature is acid–base interconversion to the nitrosyl form, $[(tpy)(bpy)M(NO)]^{3+}$, which undergoes a series of stepwise, one-electron reductions. Direct experimental evidence has been obtained for a series of intermediates that can be formulated as $[(tpy)(bpy)M^{IV}(NH)]^{2+}$, $[(tpy)(bpy)M^{V}(N)]^{2+}$ or $[(tpy)(bpy)M^{II}(NH_2O)]^{2+}$, $[(tpy)(bpy)M^{II}(NHO)]^{2+}$, and $[(tpy)(bpy)M^{II}(NO\cdot)]^{2+}$.

In the overall reduction of nitrate to ammonia in green plants[1-4] an important step is the six-electron reduction of nitrite to ammonia. The reduction is catalyzed by the enzyme nitrite reductase, which is a complex protein consisting of an iron–sulfur unit and an iron–isobacteriochlorin group or siroheme. In the enzyme it appears that the iron–sulfur unit accepts electrons from reduced ferredoxin and subsequently transfers them to the siroheme site,[1] which is also the binding site for the nitrite ion. Two remarkable features of the enzymatic reduction are that it is facile even though six-electron in nature and that no evidence has been obtained for intermediate stages in the reduction.

Results have been reported on attempts to model the active site of nitrite reductase via synthetically accessible isobacteriochlorins.[5-7] In addition, certain features of the reactivity of the enzyme have been observed in simple metal complexes, most notably by Armor and co-workers, who found that $[(NH_3)_5Ru(NO)]^{3+}$ is reduced quantitatively[8] to $[(NH_3)_6Ru]^{2+}$ by Cr(II) and that $[(NH_3)_6Ru]^{2+}$ is oxidized in 30% yield to $[(NH_3)_5Ru(NO)]^{3+}$ by O_2 in basic solution.[9] More recently, Bottomley and Mukaida have shown that $[(py)_4Ru(NO)Cl]^{2+}$ (py = pyridine) undergoes two reversible one-electron reductions, followed by an irreversible four-electron reduction to give $[(py)_4Ru(NH_3)Cl]^+$.[10] It has also been reported[11] that $[(tpy)(bpy)Ru(NH_3)]^{2+}$ (tpy = 2,2′,2″-terpyridine; bpy = 2,2′-bipyridine) is rapidly and quantitatively oxidized to give $[(tpy)(bpy)Ru(NO)]^{3+}$, which is in

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