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Proton Nuclear Magnetic Resonance Study of *N*,*N*-Dimethylformamide Exchange on (*N*,*N*-Dimethylformamide)(2,2′,2″-tris(dimethylamino)triethylamine)manganese(II) and Its Cobalt(II) and Copper(II) Analogues

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Proton NMR studies of dmf exchange on $[M(Me_6tren)dmf]^{2+}$, where M = Mn, Co, and Cu, respectively yield the following: $k_{ex}(298.2\ K) = (2.7 \pm 0.4) \times 10^6$, 51.4 ± 4.2, $555 \pm 39\ s^{-1}$; $\Delta H^{*} = 18.0 \pm 1.9$, 52.4 ± 1.1, $43.3 \pm 1.1\ kJ\ mol^{-1}$; $\Delta S^{*} = -61.2 \pm 7.4$, -36.5 ± 3.04, $-47.0 \pm 3.1\ J\ K^{-1}\ mol^{-1}$; $\Delta V^{*} = -6 \pm 2$, -2.71 ± 0.17, $6.5 \pm 0.2\ cm^3\ mol^{-1}$. These data are interpreted in terms of associative (a) activation modes operating when M = Mn and Co and a dissociative (d) activation mode operating when M = Cu. The possible effects of stereochemistry and d-orbital occupancy on lability and mechanism are discussed.

Introduction

It has been established in the case of nickel(II) and to a lesser extent for other bivalent first-row transition-metal ions that the coordination of a *n*-dentate polyamine, L, usually labilizes solvent in $[ML(solvent)_{6-n}]^{2+}$ complexes by several orders of magnitude in comparison to the lability of $[M(solvent)_6]^{2+}$.[1,2] In contrast 2,2′,2′-tris(dimethylamino)triethylamine (Me_6tren) causes the five-coordinate complexes $[M(Me_6tren)solvent]^{2+}$ (where M = Co, Ni, Cu and Zn) to exhibit markedly decreased labilities by comparison to $[M(solvent)_6]^{2+}$, decreases which have largely been attributed to the sterically constraining nature of Me_6tren.[3-6] These $[M(Me_6tren)solvent]^{2+}$ complexes offer an unusual opportunity to examine the solvent-exchange process in a five-coordinate environment and further to consider the effect of changing the identity of M and the consequent stereochemical changes[7-9] on the lability and mechanism of this process. Direct determinations of solvent-exchange kinetic parameters have been reported only for $[Cu(Me_6tren)dmf]^{2+}$ (dmf = *N*,*N*-dimethylformamide) and its zinc(II) analogues,[5,6] however, and it is therefore necessary to determine solvent-exchange parameters for other metal ions to facilitate a more systematic study. Accordingly dmf (which was chosen largely as a consequence of its large liquid temperature range, 212–426 K) exchange studies over a range of temperature and pressure are now reported for $[Mn(Me_6tren)dmf]^{2+}$ and its cobalt(II) and copper(II) analogues.

Experimental Section

Materials. 2,2′,2″-Tris(dimethylamino)triethylamine (Me_6tren) was prepared as previously described.[7] *N*,*N*-Dimethylformamide was purified by fractional distillation at reduced pressure over anhydrous copper sulfate. Cyclohexane and benzene were purified by distillation at atmospheric pressure. All liquid reagents were stored in dark bottles over previously activated Linde 4A molecular sieves.

Preparation of $[M(Me_6tren)dmf](ClO_4)_2$ (M = Mn, Co). The appropriate hydrated metal perchlorate salt (1.6 g, Fluka, purum) was dissolved in approximately 20 cm^3 of triethyl orthoformate (Fluka) and stirred at 330 K for 1 h. A solution of Me_6tren (1.1 g in 3 cm^3 of dmf) was then added whereupon immediate precipitation of $[M(Me_6tren)dmf](ClO_4)_2$ occurred. The crystals were filtered and washed with three 20-cm^3 portions of sodium-dried ether prior to drying under a stream of dry nitrogen overnight. The yields of products were essentially quantitative. Whereas the very pale pink manganese complex is both oxygen and water sensitive, the green cobalt complex appears to be air stable. Anal. Calcd for $[Mn(Me_6tren)dmf](ClO_4)_2$: Mn, 9.86. Found: Mn, 9.73. Anal. Calcd for $[Co(Me_6tren)dmf](ClO_4)_2$: Co, 10.41. Found: Co, 10.25. The copper(II) complex was prepared in a similar manner, but preparation of the iron(II) complex was thwarted by the rapid oxidation of iron(II) to iron(III).

All operations were carried out under a dry nitrogen atmosphere. *Perchlorate salts of metal complexes may be explosive under some circumstances and should be handled with caution.* No explosion hazard was encountered during this study.

Preparation of Solutions for NMR Studies. Cobalt(II) and copper(II) solutions were prepared by weight in a drybox, but owing to their high oxygen sensitivity manganese(II) solutions were prepared by vacuum-line mixing techniques after weighing out known quantities of complex and solvent independently. No appreciable oxidation of the manganese(II) solutions could be detected with use of this procedure.

^1H NMR Measurements. Ambient-pressure variable-temperature NMR measurements were carried out on solutions sealed in 2-mm diameter NMR tubes that were positioned concentrically in 5-mm NMR tubes containing either $(CD_3)_2CO$ or $(CD_3)_2SO$, depending on the temperature range investigated. Spectra were run on a Bruker HX90E spectrometer under the same conditions as described in an earlier study.[5] Variable-pressure experiments were carried out in Lausanne with a Bruker WP-60 spectrometer equipped with a previously described[10] high-pressure probe. Typically the sweep width was 1440 Hz with an 8K data table, and approximately 200 transients were collected prior to Fourier transformations. 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 Hz at half-maximum amplitude of the Lorentzian line shape. All solutions contained 1% cyclohexane and 0.3% benzene, which acted as shift references and as monitors of field homogeneity. Solutions of $[Zn(Me_6tren)dmf](ClO_4)_2$[6] were studied under identical conditions and provided reference chemical shifts and line widths for subsequent calculations.

At ambient pressure the line width variation with temperature obtained as the temperature was progressively increased was found to be the same as that when the temperature was progressively decreased. At a given temperature the line width variation observed as the pressure was progressively increased was identical with that observed as the pressure was progressively decreased.

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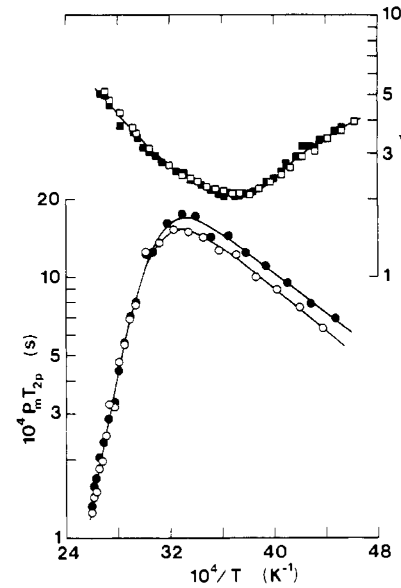

Figure 1. Variation of P_mT_{2p} with $1/T$. The [Mn(Me$_6$tren)dmf]$^{2+}$ data are shown as the upper data set of the figure where open and solid squares refer to data derived from solutions in which P_m = 0.000339 and 0.000627, respectively. The magnitudes of these data appear on the right-hand scale. The lower data set refers to [Co(Me$_6$tren)dmf]$^{2+}$, and the solid and open circles refer to data derived from solutions in which P_m = 0.0191 and 0.0306, respectively. The magnitudes of these data appear on the left-hand scale.

Results

^{1}H NMR Studies. General Aspects. The relaxation parameter, T_{2p}, is related to the transverse relaxation times of the formyl proton of bulk dmf in the [Co(Me$_6$tren)dmf]$^{2+}$ solutions and those of its manganese(II) analogue, T_2, and that of the [Zn(Me$_6$tren)dmf]$^{2+}$ reference solutions, $T_{2\text{ref}}$, through eq 1. The relationship between T_{2p} and the dmf exchange

$$T_{2p}^{-1} = T_2^{-1} - T_{2\text{ref}}^{-1} \qquad (1)$$

process is given by eq 2,[11] where τ_m ($=1/k_{ex} = (h/k_BT)\exp(\Delta H^*/RT - \Delta S^*/R)$) is the mean lifetime of coordinated

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

dmf, P_m is the mole fraction of coordinated dmf, T_{2m} ($=A_m^{-1}\exp(-E_m/RT)$) is the transverse relaxation time of coordinated dmf, $\Delta\omega_m$ is the chemical shift between coordinated and bulk dmf, and T_{2o} ($=A_o^{-1}\exp(-E_o/RT)$) is the contribution to T_{2p} arising from interactions outside the first coordination sphere. The T_{2p} data for [Mn(Me$_6$tren)dmf]$^{2+}$ (Figure 1) were fitted to eq 2 with use of a conventional nonlinear least-squares fitting program, and the derived parameters appear in Table I. The variation of the chemical shift of bulk dmf, $\Delta\omega$, with temperature is as predicted from eq 3, which may be derived

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

through eq 2. However, the magnitude of $\Delta\omega_m$ ($=B_1/T$; Table I) is such that its influence on the proton relaxation process is negligible over the experimental temperature range as is also the case for other manganese(II) systems.[12] It may be seen from Figure 1 that T_{2o} begins to make a contribution to T_{2p} at the low-temperature extreme. Unfortunately, E_o could not be reliably derived over the experimental temperature range and accordingly was set equal to E_m as a reasonable approximation in the data-fitting procedure.

Table I. Parameters[a] for dmf Exchange on [M(Me$_6$tren)dmf]$^{2+}$ and [M(dmf)$_6$]$^{2+}$

[M(Me$_6$tren)dmf]$^{2+}$

	M		
	Mn	Co	Cu[b]
k_{ex}(298.2 K), s^{-1}	(2.7 ± 0.4) × 10^6	51.4 ± 4.2	555 ± 39
$\Delta H^‡$, kJ mol^{-1}	18.0 ± 1.9	52.4 ± 1.1	43.3 ± 1.1
$\Delta S^‡$, J K^{-1} mol^{-1}	−61.2 ± 7.4	−36.5 ± 3.0	−47.0 ± 3.1
$\Delta V^‡$, cm^3 mol^{-1}	−6 ± 2[c]	−2.7 ± 0.2	6.5 ± 0.2
$\Delta V_0^‡$, cm^3 mol^{-1}	...	−2.5 ± 0.6	7.4 ± 0.4
$\Delta\beta^‡$, cm^3 mol^{-1} MPa^{-1}	...	(0.2 ± 0.5) × 10^{-2}	(0.9 ± 0.3) × 10^{-2}
P', MPa^{-1}	(1.63 ± 0.07) × 10^{-3}	...	...
A_o, s^{-1}	(4.9 ± 1.9) × 10^2	28.6 ± 4.2[d] 27.5 ± 4.3[e]	17.0 ± 3.0
E_o, kJ mol^{-1}	10.0 ± 0.5	7.3 ± 0.3[d] 7.7 ± 0.3[e]	12.5 ± 0.4
A_m, s^{-1}	(7.5 ± 1.1) × 10^3	...	...
E_m, kJ mol^{-1}	10.0 ± 0.5	...	...
B_1 rad K s^{-1}	(4.8 ± 0.3) × 10^7	...	...

[M(dmf)$_6$]$^{2+}$

	M		
	Mn[f]	Co[g]	Cu[h]
k_{ex}(298.2 K), s^{-1}	2.4 × 10^6	3.9 × 10^5	>10^7
$\Delta S^‡$, kJ mol^{-1}	37.2	56.9 ± 2.1	...
$\Delta H^‡$, J K^{-1} mol^{-1}	−3.1	52.7 ± 8.4	...
$\Delta V^‡$, cm^3 mol^{-1}	...	6.7 ± 0.3 (296 K)	...

[a] Errors represent 1 standard deviation determined through least-squares fits of the raw data to the appropriate equations as described in the text unless stated otherwise. [b] k_{ex}, $\Delta H^‡$, and $\Delta S^‡$ values from ref 5. [c] Error estimated as in ref 14. [d] Value for solution in which P_m = 0.0306. [e] Value for solution in which P_m = 0.0191. [f] Data from ref 12. [g] Data from: Matwiyoff, N. *Inorg. Chem.* 1966, *5*, 788; and ref 18. [h] Data from ref 5.

For [Co(Me$_6$tren)dmf]$^{2+}$ eq 2 reduces to eq 4 over the

$$(P_mT_{2p})^{-1} = \tau_m^{-1} + T_{2o}^{-1} \qquad (4)$$

experimental temperature range consistent with both τ_m^{-2} and $T_{2m}^{-2} << \Delta\omega_m^2$.[11] A nonlinear least-squares fit of the T_{2p} data (Figure 1) to eq 4 yields the parameters in Table I. It is seen that the more concentrated [Co(Me$_6$tren)dmf]$^{2+}$ solution (P_m = 0.0306) is characterized by the shorter T_{2o}. This may reflect a greater viscosity and consequently longer correlation time for this solution, but it is important to note that there is no significant variation of T_{2p} between the two solutions in the high-temperature region, where τ_m^{-1} dominates eq 4 and in consequence the variation observed in T_{2o} for the two solutions has no significant effect on the derived kinetic parameters. Up to 315 K no chemical shift of the bulk solvent $\Delta\omega$ was observed, but above this temperature $\Delta\omega$ increased with temperature as anticipated from eq 3 but the magnitudes of $\Delta\omega$ were small as a consequence of the domination of eq 3 by the relatively large magnitude of τ_m. The raw T_{2p} data for the cobalt(II) and manganese(II) systems and $\Delta\omega$ data for the latter system are available in the suupplementary data tables S3, S1, and S2, respectively. (A study of solutions of [Ni(Me$_6$tren)-dmf](ClO$_4$)$_2$ was also made, and the variation of T_{2p} with temperature suggested the presence of two nickel(II) species in solution, but this system is not further discussed here.)

High-Pressure NMR Studies. The [Co(Me$_6$tren)dmf]$^{2+}$ system and the analogous copper(II) system were studied at 371.9 and 373.1 K and 350.3 and 364.6 K, respectively, where

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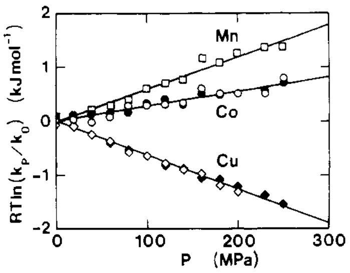

Figure 2. Variation of k_p/k_0 with pressure. The open squares represent data derived from $[Mn(Me_6tren)dmf]^{2+}$ for which $P_m = 0.000468$ at 263.6 K. The open and solid circles represent data derived from $[Co(Me_6tren)dmf]^{2+}$ solutions for which $P_m = 0.0203$ (373.1 K) and 0.0255 (371.9 K), respectively, at the temperatures indicated in parentheses. The open and solid diamonds represent data derived from $[Cu(Me_6tren)dmf]^{2+}$ solutions for which $P_m = 0.0452$ (350.3 K) and 0.0166 (364.6 K), respectively.

the T_{2o}^{-1} contribution to eq 4 is negligible such that $P_mT_{2p} = \tau_m$. This may be seen from Figure 1 and from an earlier report on the copper(II) system.[5] The variation in k_{ex} with pressure for the two systems is both marked and different as can be seen from Figure 2. Here, $RT \ln (k_p/k_0)$ is plotted against the applied pressure, P, and k_p is k_{ex} at pressure P while k_0 is the zero-pressure exchange rate constant. The T_{2p} data were fitted to eq 5, where $\Delta V^{\ddagger}$ is the volume of activation.[13] Fits

$$\ln (k_p/k_0) = -P(\Delta V^{\ddagger})/RT \qquad (5)$$

to the quadratic equation (6)[13] were also carried out and

$$\ln (k_p/k_0) = -P(\Delta V_0^{\ddagger})/RT + P^2(\Delta\beta^{\ddagger})/2RT \qquad (6)$$

showed the derived compressibilities of activation, $\Delta\beta^{\ddagger}$, to be indistinguishable from zero in the case of $[Co(Me_6tren)dmf]^{2+}$ and close to zero in the case of $[Cu(Me_6tren)dmf]^{2+}$. Accordingly, only the $\Delta V^{\ddagger}$ data derived through eq 5 are discussed; however, the derived zero-pressure volumes of activation, $\Delta V_0^{\ddagger}$, and $\Delta\beta^{\ddagger}$ also appear in Table I.

High-pressure studies were also carried out on the $[Mn(Me_6tren)dmf]^{2+}$ system at 263.6 and 331.7 K, but as there is no temperature at which eq 2 simplifies to $P_mT_{2p} = \tau_m$ for this system (Figure 1), the data interpretation is not as straightforward as in the case for the analogous cobalt(II) and copper(II) systems. However, as $\Delta\omega_m$ makes no significant contribution to the variation of T_{2p}, and T_{2o} contributions are insignificant at 263.6 and 331.7 K, the only pressure dependencies that can affect T_{2p} are those of T_{2m} and τ_m. At 331.7 K the T_{2m} term dominates eq 2 such that $P_mT_{2p} \approx T_{2m}$, on which basis the pressure dependence of T_{2m} is given by eq 7,

$$(P_mT_{2p})^{-1} \approx T_{2mp}^{-1} = T_{2m0}^{-1}(1 + P'P) \qquad (7)$$

where T_{2mp} and T_{2m0} are T_{2m} at the applied pressure and at zero pressure, respectively. The parameter P' takes into account changes in T_{2m}^{-1} with pressure. At 263.6 K the contribution of τ_m to T_{2p} is substantial, and assuming $\Delta V^{\ddagger}$ and P' to be independent[14] of temperature, the pressure dependence of τ_m may be derived. A simultaneous least-squares fit of the T_{2p} data at 331.7 and 263.6 K to eq 2, 5, and 7 yielded the P' and $\Delta V^{\ddagger}$ values given in Table I. The magnitude of T_{2m0} was allowed to vary while k_0 was fixed, but fits obtained when k_0 was allowed to vary and T_{2m0} was fixed did not produce significantly different values of P' and $\Delta V^{\ddagger}$. Experimental P_mT_{2p} values obtained at 263.6 K were also used to calculate individual k_p values through eq 2 and 7. In these calculations the values for T_{2m0}, k_0, and P' in Table I were used. The variation of $RT \ln (k_p/k_0)$ is shown in Figure 2. Raw variable-pressure T_{2p} data for the manganese(II), cobalt(II), and copper(II) systems are available in supplementary data tables S4, S5, and S6, respectively.

Discussion

The coordination of Me_6tren causes a substantial decrease in the lability of dmf in $[M(Me_6tren)dmf]^{2+}$ by comparison to $[M(dmf)_6]^{2+}$ when M = Co or Cu but very little change in lability when M = Mn, and the $\Delta V^{\ddagger}$ data are consistent with the activation mode changing from associative (a) when M = Mn and Co to dissociative (d)[15] when M = Cu (Table I). The origin of these variatiaons may be attributed to the somewhat interconnected causes of stereochemical and d-orbital occupancy variations.

Solid-state studies[7-9] of the trigonal-bipyramidal series $[M(Me_6tren)Br]^+$ (M = Mn, Fe, Co, Ni, Cu, Zn) indicate that the effects of Me_6tren steric constraints and d-orbital occupancy are superimposed on the the expected decrease in bond distances with increase in atomic number. In each case Br occupies an axial position with the three $-NMe_2$ groups in equatorial positions. For the sequence M = Mn, Fe, Co, Ni, Cu, Zn the following distances are found: M–Br = 2.491 (6), 2.482 (3), 2.431 (4), 2.467 (2), 2.393 (3), 2.449 (3) Å; $M-N_{(equatorial)}$ = 2.27 (2), 2.15 (1), 2.08 (2), 2.13 (1), 2.14 (1), 2.11 (2) Å; $M-N_{(axial)}$ = 2.19 (3), 2.21 (1), 2.15 (2), 2.10 (1), 2.07 (1), 2.19 (2) Å. It is assumed that dmf also occupies an axial position in $[M(Me_6tren)dmf]^{2+}$ and that this complex exhibits bond distance variations similar to those of the bromo analogue. The $M-N_{(equatorial)}$ distances determine the radius of the annulus formed by the six methyl groups about coordinated dmf and thereby the accessibility of M to an entering dmf molecule. Increase in the M–dmf distance should both increase the accessibility of M to entering dmf and weaken the M–dmf interaction. On this basis $[Mn(Me_6tren)dmf]^{2+}$ ought to be more amenable to dmf exchange through an a activation mode and also more labile than its cobalt(II) and copper(II) analogues. These stereochemical arguments take some account of d-orbital occupancy through its influence on stereochemistry as discussed elsewhere,[9] but a more direct influence of d-orbital occupancy on mechanism is possible. For a trigonal-bipyramidal structure in which the equatorial ligands lay in the xy plane the sequence of orbital energies is as follows: $d_{z^2} > d_{x^2-y^2} = d_{xy} > d_{xz} = d_{yz}$.[16] Thus the progressive filling of the d_{xz} and d_{yz} orbitals in particular and the d_{xy} orbital to a lesser extent is expected to electrostatically hinder the approach of a second dmf to any of the three faces of the trigonal bipyramid adjacent to the coordinated dmf. Hence the d^5 $[Mn(Me_6tren)dmf]^{2+}$ complex is also expected to be more amenable to an a activation mode on this basis. This argument is similar to that proposed for $[M(solvent)_6]^{2+}$ species, where the progressive filling of the d_{xy}, d_{xz}, an d_{yz} orbitals is considered to be a major cause of the decreasing associative character Mn > Fe > Co > Ni observed for solvent exchange as deduced from $\Delta V^{\ddagger}$ data.[13,17] However, in the case of $[M(solvent)_6]^{2+}$ $\Delta V^{\ddagger}$ is negative when M = Mn but becomes increasingly positive in the sequence Fe < Co < Ni, when the

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(14) To estimate the possible errors arising from the assumption that $P'_{331.7} = P'_{263.6}$, the value of P' was fixed at 8×10^{-4} and 3×10^{-3} MPa^{-1} and $\Delta V^{\ddagger}$ was derived through a simultaneous data fit to eq 2, 5, and 7. When $P' = 8 \times 10^{-4}$ MPa^{-1}, $\Delta V^{\ddagger} = -7.9 \pm 1.8$ cm^3 mol^{-1}, and when $P' = 3 \times 10^{-3}$ MPa^{-1}, $\Delta V^{\ddagger} = -4.9 \pm 1.2$ cm^3 mol^{-1}. Such changes in P' with temperature are almost certainly overestimates, and thus the error of ±2 cm^3 mol^{-1} quoted for $\Delta V^{\ddagger}$ in Table I is likely to be the maximum error limit. Very small variations in T_{2m} and T_{2o} may occur with change in operating frequency from 90 to 60 MHz and could cause small variations in P'. Such variations should be encompassed well within the variations in P' considered above.

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solvent is water, and this trend is also seen in other solvents. The observation that ΔV^* is positive only when M = Cu in the $[M(Me_6tren)dmf]^{2+}$ species studied further indicates that Me_6tren influences the mechanistic tendencies of M. Within the simple theory applied to the interpretation of ΔV^* the observation[18] that $\Delta V^* = 9.1$ cm^3 mol^{-1} for $[Ni(dmf)_6]^{2+}$, which is of similar size to $[M(Me_6tren)dmf]^{2+}$, suggests that ΔV^* values of this magnitude at least should be observed for associative (A) or dissociative (D) mechanisms.[15] As the ΔV^* magnitudes observed for $[M(Me_6tren)dmf]^{2+}$ are <9.1 cm^3 mol^{-1}, it is concluded that when M = Mn or Co an associative-interchange (I_a) mechanism operates for dmf exchange and when M = Cu a dissociative-interchange (I_d) mechanism operates.[15]

The sign of ΔS^* is sometimes used as an aid to assignment of a and d activation modes on the basis that these modes respectively come close to producing one entity from two and two entities from one, which should result in negative and positive contributions to ΔS^*. Mechanistic assignment on this basis may be valid if these contributions are dominant. If substantial solvent rearrangements outside the first coordination sphere,[19] and vibrational and rotational changes within the first coordination sphere,[20] make significant contributions to ΔS^*, however, the use of the sign of this parameter becomes unreliable in the assignment of activation mode. In this study the observed ΔS^* values are all negative (Table I) and it is concluded that several of the interactions discussed above make contributions to ΔS^*, and in consequence ΔV^* has been used as the major criterion for mechanistic assignment.

The greater lability of $[Mn(Me_6tren)dmf]^{2+}$ compared to its cobalt(II) and copper(II) analogues is largely a consequence of its smaller ΔH^* (Table I), which is consistent with the greater accessibility of the manganese(II) center to dmf exchange as a consequence of the steric and d-orbital occupancy factors previously discussed. It is pertinent, however, to examine the possibility that crystal field activation energy (CFAE)[17,21,22] contributions to ΔH^*, while being absent in high-spin d^5 $[Mn(Me_6tren)dmf]^{2+}$, could influence the relative labilities of the cobalt(II) and copper(II) analogues. For trigonal-bipyramidal $[ML_5]^{2+}$ undergoing L exchange through an A mechanism (octahedral transition state) high-spin d^7 and d^9 systems are characterized by CFAE = $-1.72Dq$ and $0.21Dq$, respectively, and by CFAE = $0.26Dq$ and $2.41Dq$, respectively, for an A mechanism proceeding through a trigonal-prismatic transition state. (The latter transition-state geometry seems unlikely on steric grounds, and a distortion toward a trigonal antiprism produces a geometry similar to that of the octahedron.) For high-spin d^7 and d^9 systems undergoing exchange through a D mechanism (triangular-pyramidal transition state) CFAE = $0.56Dq$ and $3.42\ Dq$ arise. These CFAE values are calculated for $\rho = 1$.[16] On the basis that I_a and I_d transition states substantially resemble A and D transition states, respectively, as far as CFAE calculations are concerned, it is seen that the d^7 (cobalt(II)) system is unlikely to exhibit a decreased lability as a consequence of a CFAE contribution ($-1.72Dq$) to ΔH^* for an I_a mechanism whereas a substantial CFAE ($3.42Dq$) contribution could decrease the lability of the d^9 (copper(II)) system (copper(II) (copper(II)) undergoing exchange through an I_d mechanism. While these deductions (based on CFAE calculations which ignore the presence of three different types of coordinating groups and the steric constraints of the multidentate ligand) can only be considered as qualitative guides at best when applied to the $[M(Me_6tren)dmf]^{2+}$ species, it appears that a significant CFAE contribution may arise when M = Cu. Nevertheless, the possibility that the greatly decreased lability of $[Cu(Me_6tren)dmf]^{2+}$ compared to that of $[Cu(dmf)_6]^{2+}$ arises solely from the decrease in coordination number from 6 to 5 and any attendant CFAE changes (or from the presence and absence of the labilizing Jahn-Teller effect in the six- and five-coordinate ground states, respectively) appears to be eliminated by the earlier observations that five-coordinate $[Cu(tren)solvent]^{2+}$ (where tren = 2,2′,2″-triaminotriethylamine and solvent = acetonitrile[3] or water[1,23]) is several orders of magnitude more labile than $[Cu(Me_6tren)solvent]^{2+}$. Similar observations on the analogous cobalt(II)[3] and zinc(II)[6] systems in acetonitrile and dmf, respectively, also indicate that the steric effects of the methyl groups are important in decreasing the lability of $[M(Me_6tren)solvent]^{2+}$.

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Registry No. $[Mn(Me_6tren)dmf](ClO_4)_2$, 88686-49-1; $[Mn(Me_6tren)dmf]^{2+}$, 88686-47-9; $[Co(Me_6tren)dmf](ClO_4)_2$, 88686-50-4; $[Co(Me_6tren)dmf]^{2+}$, 88686-48-0; $[Cu(Me_6tren)dmf](ClO_4)_2$, 86632-76-0; $[Cu(Me_6tren)dmf]^{2+}$, 86632-75-9; dmf, 68-12-2.

Supplementary Material Available: Variable-temperature T_{2p} and $\Delta\omega$ (Tables S1–S3) and variable-pressure T_{2p} data (Tables S4–S6) (6 pages). Ordering information is given on any current masthead page.

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