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Proton Nuclear Magnetic Resonance Study of N,N-Diethylformamide Exchange on (N,N-Diethylformamide)(2,2′,2″-tris(dimethylamino)triethylamine)cobalt(II) and its Copper(II) Analogue

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Abstract

Proton NMR studies of N,N-diethylformamide (def) exchange on $[M(Me_6tren)def]^{2+}$ where M = Co and Cu yield: k_{ex} (298.2 K) = 26.3 ± 2.2, 980 ± 70 s^{-1}; $\Delta H^{\ddagger}$ = 58.3 ± 1.7, 36.3 ± 0.9 kJ mol^{-1}; $\Delta S^{\ddagger}$ = −22.2 ± 4.6, −65.9 ± 2.5 J K^{-1} mol^{-1}; and $\Delta V^{\ddagger}$ = −1.3 ± 0.2, 5.3 ± 0.3 cm^3 mol^{-1} respectively. These data which are consistent with **a** and **d** activation modes operating when M = Co and Cu respectively are compared with data for related systems.

Introduction

The coordination of the tetradentate tripod ligand 2,2′,2″-tris(dimethylamino)triethylamine (Me_6tren) to bivalent first row transition metal ions (M^{2+}) produces trigonal bipyramidal $[M(Me_6tren)solvent]^{2+}$ complexes in which the lability of the solvent molecule in the fifth coordination site is substantially decreased by comparison to that in the appropriate $[M(solvent)_6]^{2+}$ species when M = Co, Ni, and Cu [1–4]. The negative and positive $\Delta V^{\ddagger}$ values observed for N,N-dimethylformamide (dmf) exchange on $[Co(Me_6tren)dmf]^{2+}$ and its copper(II) analogue respectively indicate a change in activation mode from **a** to **d**, a conclusion which is supported by the selectivity and non-selectivity exhibited respectively by these complexes in their ligand substitution processes [3]. (Mechanistic conclusions for the nickel(II) system are complicated by the presence of more than one complex in solution [4].) These studies which included the first $\Delta V^{\ddagger}$ determinations for copper(II) indicated that steric effects induced by Me_6tren are important in decreasing the lability towards solvent exchange and ligand substitution. As the slow solvent exchange rates exhibited by $[M(Me_6tren)dmf]$ are unusual for cobalt(II) and copper(II) it is of interest to change the solvent to one of similar electron donating characteristics but of different size and thereby to facilitate an assessment of steric interactions on solvent lability and exchange mechanism. Accordingly a study of $[Co(Me_6tren)def]^{2+}$ and its copper(II) analogue (where def = N,N-diethylformamide) is now reported.

Experimental

N,N-Diethylformamide was purified by fractional distillation under vacuum from anhydrous copper sulphate. Cyclohexane and benzene were purified by fractional distillation at atmospheric pressure. All liquid reagents were stored under dry nitrogen in dark bottles over previously activated Linde 4A molecular sieves. $[Co(Me_6tren)def](ClO_4)_2$ and its copper(II) and zinc(II) analogues were prepared in a similar manner to that described for the dmf complexes [2, 3] and excellent analytical results were obtained. Ambient and high pressure proton NMR studies were carried out using previously described equipment and techniques, and data treatment methods were also as previously described [3]. The mol fractions of coordinated def (P_m) in the solutions studied were: $[Co(Me_6tren)def]^{2+}$, 0.0085, 0.0125 (ambient pressure), 0.0133, 0.0087 (variable pressure); $[Cu(Me_6tren)def]^{2+}$, 0.0081 (ambient pressure), 0.0083 (variable pressure).

Results

The relaxation parameter, T_{2p}, is related to the transverse relaxation times, T_2, of the formyl proton of bulk def in the $[M(Me_6tren)def]^{2+}$ (M = Co or Cu) solutions and those of the $[Zn(Me_6tren)def]^{2+}$ reference solutions, T_{2ref}, through eqn. (1):

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

The relationship between T_{2p} and the def exchange process is given by eqn. 2 where τ_m ($=1/k_{ex} = (h/k_BT)\exp(\Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R)$) is the mean lifetime of coordinated def, T_{2m} is the transverse relaxation time of coordinated def, $\Delta\omega_m$ is the chemical shift between coordinated and bulk def, and T_{2o} ($=A_o^{-1}\exp(-E_o/RT)$) is the contribution to T_{2p} arising from interactions outside the first coordination sphere [5, 6]. For both of the systems studied

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

eqn. 2 reduces to eqn. 3 over the experimental temperature range consitent with both τ_m^{-2} and $T_{2m}^{-2} \ll \Delta\omega_m^{2}$.

$$(P_mT_{2p})^{-1} = \tau_m^{-1} + T_{2o}^{-1} \qquad (3)$$

Non-linear least squares fits of the [Co(Me$_6$tren)-def]$^{2+}$ data and that of its copper(II) analogue (Fig. 1) to eqn. 3 yield the parameters in Table I. Eqn. 4 expresses the anticipated variation of the chemical shift of the bulk def, $\Delta\omega$:

$$\Delta\omega = \Delta\omega P_m/((\tau_m/T_{2m} + 1)^2 + \tau_m^{2}\Delta\omega_m^{2}) \qquad (4)$$

In both systems variation of $\Delta\omega$ qualitatively consistent with eqn. 4 was observed at temperatures >320 K but the domination of eqn. 4 by τ_m over the experimental temperature range caused the magnitude of $\Delta\omega$ to be too small for reliable incorporation into the derivation of kinetic parameters.

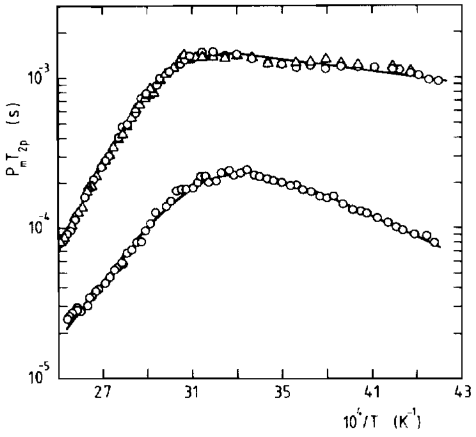

Fig. 1. Variable temperature ^{1}H relaxation data for the formyl resonance of bulk def. The upper data set refers to [Co(Me$_6$tren)def]$^{2+}$ where data points denoted ○ and △ refer to solutions for which P_m = 0.0085 and 0.0125. The solid curve represents the non-linear regression fit of both data sets simultaneously to $(P_mT_{2p})^{-1} = \tau_m^{-1} + T_{2o}^{-1}$. The lower data set refers to a [Cu(Me$_6$tren)def]$^{2+}$ solution for which P_m = 0.00808 and the solid curve represents a non-linear regression fit of these data to $(P_mT_{2p})^{-1} = \tau_m^{-1} + T_{2o}^{-1}$.

High pressure NMR study of [Co(Me$_6$tren)def]$^{2+}$ was carried out at 365.6 K and 364.5 K and that of [Cu(Me$_6$tren)def]$^{2+}$ at 365.4 K, at which temperatures eqn. 3 reduced to $P_mT_{2p} = \tau_m$ for both systems. The variation of τ_m with pressure was reversible for both systems. The pressure dependence of the ratios of k_{ex} at ambient pressure (k_0) and under an applied pressure (k_p) are shown in Fig. 2

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

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

M	Co	Co^b	Cu	Cu^b
solvent	def	dmf	def	dmf
k_{ex} (298.2 K) s^{-1}	26.3 ± 2.2	51.4 ± 4.2	980 ± 70	555 ± 39
$\Delta H^{\ddagger}$ kJ mol^{-1}	58.3 ± 1.7	52.4 ± 1.1	36.3 ± 0.9	43.3 ± 1.1
$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	−22.2 ± 4.6	−36.5 ± 3.0	−65.9 ± 2.5	−47.0 ± 3.1
$\Delta V^{\ddagger}$ cm^3 mol^{-1}	−1.3 ± 0.2	−2.7 ± 0.2	5.3 ± 0.3	6.5 ± 0.2
A_o s^{-1}	123 ± 15	28.6 ± 4.2	14.0 ± 3.4	17.0 ± 3.0
E_o kJ mol^{-1}	4.2 ± 0.3	7.3 ± 0.3	13.6 ± 0.5	12.5 ± 0.4

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

M	Co^c	Co^d	Cu	Cu
solvent	def	dmf	def	dmf
k_{ex} (298.2 K) s^{-1}	1.2×10^5	3.9×10^5	$\geqslant 10^7$	$\geqslant 10^7$
$\Delta H^{\ddagger}$ kJ mol^{-1}	51.4 ± 2.0	56.9 ± 2.1	–	–
$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	24.8 ± 7.0	52.7 ± 8.4	–	–
$\Delta V^{\ddagger}$ cm^3 mol^{-1}	–	6.7 ± 0.3	–	–

^{a}Errors represent one standard deviation determined through regression fits of the data to the appropriate equations as described in the text. ^{b}Data from ref. 3. ^{c}Data from ref. 7. ^{d}Data from ref. 8.

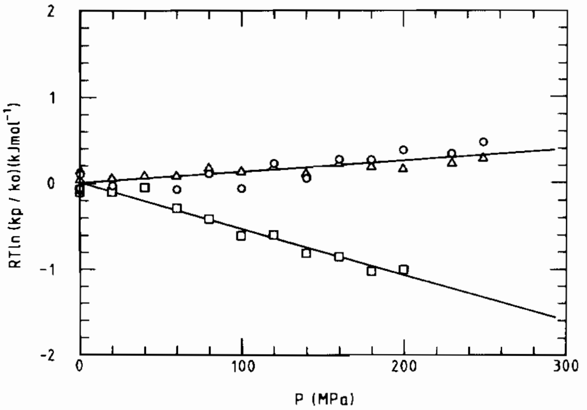

Fig. 2. The variation of the ratio of k_{ex} at ambient (k_0) and applied (k_p) pressure with pressure for [Co(Me$_6$tren)-def]$^{2+}$ (○, P_m = 0.0087, 365.6 K; △, P_m = 0.0133, 364.5 K) where the solid line represents the linear regression fit of both data sets simultaneously to eqn. 5; and for [Cu(Me$_6$-tren)def]$^{2+}$ (□, P_m = 0.0083, 365.4 K) where the solid line represents a linear regression fit of the data to eqn. 5.

from which it is seen that the behaviour of the two systems is quite different. The negative and positive $\Delta V^{\ddagger}$ [9] values derived through eqn. 5 for [Co(Me$_6$tren)def]$^{2+}$ and its copper(II) analogue are given in Table I. Fits of the data to the quadratic eqn. 6 showed the activation

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

compressibility $\Delta\beta^{\ddagger}$ to be indistinguishable from zero and accordingly only

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

$\Delta V^{\ddagger}$ data derived through eqn. 5 are discussed.

Discussion

The k_{ex} (298.2 K) data in Table I show that the lability of [Co(Me$_6$tren)def]$^{2+}$ is substantially decreased by comparison to that of [Co(def)$_6$]$^{2+}$ [7] and to an extent similar to that observed for the analogous dmf systems. It is known that solvent lability in trigonal bipyramidal [Co(tren)solvent]$^{2+}$ [10] is substantially increased over that in [Co(solvent)$_6$]$^{2+}$ and thus the decreased lability of [Co(Me$_6$tren)solvent]$^{2+}$ must be largely attributed to the steric hindrance to solvent exchange posed by the six methyl groups. The k_{ex} (298.2 K) characterising [Cu(def)$_6$]$^{2+}$ is not available but from data on other [Cu(solvent)$_6$]$^{2+}$ systems [11] it is expected to be $\geqslant 10^7$ s^{-1} on which basis the lability of def in [Cu(Me$_6$tren)def]$^{2+}$ is also seen to be much decreased. In this case the decreased lability of [Cu(Me$_6$tren)def]$^{2+}$ arises from both the steric hindrance posed by Me$_6$tren to def exchange and the removal of the Jahn–Teller effect which produces the tetragonal distortion in [Cu(solvent)$_6$]$^{2+}$ and its consequent high lability [1, 11].

The negative and positive $\Delta V^{\ddagger}$ values observed (Table I) for [Co(Me$_6$tren)def]$^{2+}$ and its copper(II) analogue are consistent with the operation of **a** and **d** activation modes respectively as has been previously demonstrated for the [Co(Me$_6$tren)dmf]$^{2+}$ and its copper(II) analogue which also are characterised by negative and positive $\Delta V^{\ddagger}$ values [3]; and which in addition exhibit substantial selectivity and little selectivity respectively for substitution of dmf by other ligands as expected for **a** and **d** activation modes [2, 12]. Estimation of the magnitudes of $\Delta V^{\ddagger}$ expected for A, I$_a$, I$_d$ and D mechanisms for def exchange on [M(Me$_6$tren)def]$^{2+}$ is not a simple matter due to the potential conformational changes in Me$_6$tren and the large size of def. However the small size of $\Delta V^{\ddagger}$ observed for [Co-Me$_6$tren)def]$^{2+}$ suggests the operation of an I$_a$ mechanism, and it is probable that [Cu(Me$_6$tren)-def]$^{2+}$ undergoes def exchange through an I$_d$ mechanism. The difference in activation mode between the d^7 and d^9 system suggests that the progressive electronic filling of the d_{xy}, d_{xz} and d_{yz} orbitals (for a trigonal bipyramidal structure with the equatorial ligands in the equatorial plane the sequence of orbital energies is: $d_{z^2} > d_{x^2-y^2} = d_{xy} > d_{xz} = d_{yz}$ [13]) increasingly electrostatically hinders the approach of a second def to any of the three faces of the trigonal bipyramid immediately adjacent to the coordinated def. This argument is similar to that proposed for [M-(solvent)$_6$]$^{2+}$ where the progressive electronic filling of the d_{xy}, d_{xz} and d_{yz} orbitals is considered to be a major cause of the decreasing associative character Mn > Fe > Co > Ni observed for solvent exchange [9].

It is apparent from the data in Table I that the increase in size of def over dmf does not generate significant differences between the mechanisms of exchange of these two solvents on [M(Me$_6$tren)-solvent]$^{2+}$. The changes in solvent lability are small with the decreased k_{ex} (298.2 K) for [Co(Me$_6$-tren)def]$^{2+}$ resulting from an increase in $\Delta H^{\ddagger}$ and conversely the increased k_{ex} (298.2 K) for [Cu(Me$_6$-tren)def]$^{2+}$ resulting from a decrease in $\Delta H^{\ddagger}$. These changes and the accompanying changes in $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ may indicate the differing effects of variation of the size of the exchanging solvent molecule on **a** and **d** activation modes, but are of insufficient magnitude to warrant extended discussion. It appears that the substitution of the methyl groups of dmf by the ethyl groups of def does not introduce steric changes sufficiently close to the metal centre to produce a significant mechanistic variation. Accordingly an attempt was made to study the effect of introducing steric crowding closer to the metal centre in N,N-dimethylacetamide solvent. Unfortunately the magnitudes of T_2 and $\Delta\omega$ (see eqns. 1 and 4) determined by proton NMR were insufficient to permit quantitative data analysis. In the future, it is planned to investigate further dma exchange on $[M(M_6tren)dma]^{2+}$.

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