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Slow Solvent Exchange on Five Coordinate (N,N-Dimethylformamide)2,2′,2″-tri(N,N-dimethylamino)triethylaminezinc(II), $[Zn(Me_6tren)dmf]^{2+}$

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Introduction

The effects of the non-exchanging ligand, X, on the lability of coordinated solvent in bivalent first row transition metal complexes of the type $[MX(solvent)_n]^{(2+x)+}$ (where n is the difference between the coordination number of M and the number of bonds formed between M and X, and x is the charge of X) have been the subject of considerable study [1, 2]. Inevitably effects arising from the incomplete filling of the d orbitals are superimposed on the lability patterns of these complexes and thus it is of interest to make comparisons with the effect of X in $[ZnX(solvent)_n]^{(2+x)+}$ in which the d orbitals are filled. Usually such comparisons have not been possible as the NMR methods which permit direct determinations of solvent exchange rate constants up to $\sim 10^7$ s^{-1} for the paramagnetic $[MX(solvent)_n]^{(2+x)+}$ complexes are not applicable to the diamagnetic zinc(II) analogues for which rate constants $> 10^3$ s^{-1} cannot be measured by conventional NMR methods [3]. However some of the five coordinate first row transition metal $[M(Me_6tren)solvent]^{2+}$ complexes (where Me_6tren is 2,2′,2″-tri(N,N-dimethylamino)triethylamine) are unusual in exhibiting a decreased lability towards solvent exchange [4–6] by comparison to $[M(solvent)_6]^{2+}$ and thereby provide an opportunity to make direct comparisons with solvent lability in $[Zn(Me_6tren)solvent]^{2+}$. The solvent chosen for this preliminary study is N,N-dimethylformamide (dmf) as the substantial shift of the formyl proton resonances of dmf from those of Me_6tren permits an unhindered observation of the resonance coalescence accompanying dmf exchange.

Experimental

The ligand 2,2′,2″-triaminotriethylamine(tren) was obtained from its hydrochloride (Strem) by standard procedures and was used in the preparation of 2,2′,2″-tri(N,N-dimethylamino)triethylamine (Me_6tren) as previously described [7]. $[Zn(tren)dmf](ClO_4)_2$ and $[Zn(Me_6tren)dmf](ClO_4)_2$ were prepared by heating $[Zn(OH_2)_6](ClO_4)_2$ (3.9 g) in triethylorthoformate (33 cm^3) with stirring at 325 K for 1 h after which tren (1.6 g) or Me_6tren (2.6 g) in dmf (15 cm^3) was added dropwise at room temperature. The white crystalline complexes were washed with ether under dry nitrogen and dried under vacuum. (Yield 90%). Excellent elemental analyses were obtained for C, H, N, and Zn.

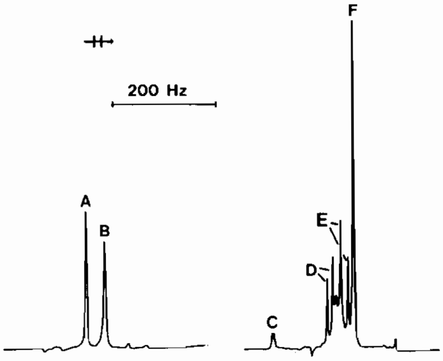

Fig. 1. Proton NMR (90 MHz) spectrum of a CD_3NO_2 solution of $[Zn(Me_6tren)dmf]^{2+}$ (0.576 mol dm^{-3}) and dmf (0.685 mol dm^{-3}) at 260 K. The origins of the resonances are as follows: A and B, the formyl protons of coordinated and free dmf respectively, C, the proton impurity in CD_3NO_2; D and E, the methyl protons of coordinated and free dmf respectively; F, the methyl protons of Me_6tren. The other resonances in the vicinity of D, E, and F arise from the ethylenic protons of Me_6tren. The left hand side of the spectrum is presented at eight times the amplitude of the right hand side.

Solutions for NMR study were prepared under dry nitrogen and were degassed and sealed in 5 mm NMR tubes under vacuum. Redistilled dmf (Unilab) and CD_3NO_2 (Stohler) were dried over Linde 4A molecular sieves (BDH). Variable temperature 90 MHz ^1H NMR studies were carried out on a Bruker HX90E spectrometer in FT mode locked on the CD_3NO_2 deuterium frequency. Between 50 and 200 transients were collected as 4 K real data points at each experimental temperature prior to Fourier transformation. Sample temperature control was ±0.3 K, and the thermostat was calibrated against a copper constantan thermocouple. Line shape analysis was carried out using previously described methods [3].

Results and Discussion

Solutions of $[Zn(Me_6tren)dmf](ClO_4)_2$ and dmf in the non-coordinating medium CD_3NO_2 exhibit

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TABLE I. Solution Compositions.

Solution	$[Zn(Me_6tren)dmf^{2+}]$ (mol dm^{-3})	$[dmf]_{free}$ (mol dm^{-3})	$[CD_3NO_2]$ (mol dm^{-3})
A	0.165	0.196	17.2
B	0.306	0.363	15.8
C	0.576	0.685	13.3
D	0.464	1.19	12.7

proton NMR spectra characterised by separate resonances for coordinated and free dmf (Fig. 1). Integrations of the formyl resonances show $[Zn(Me_6tren)dmf]^{2+}$ to be the only detectable zinc(II) species in solutions A–D (Table I). The mean site lifetime of coordinated dmf, τ_c, was determined from the coalescence of the formyl resonances of coordinated and free dmf in the temperature range 273–350 K using complete line shape analysis methods [3]. The variation of τ_c with the free dmf concentration, [dmf], and temperature (Fig. 2) is consistent with eqn. 1

$$1/\tau_c = k_2[\mathrm{dmf}] = \mathrm{dmf\ exchange\ rate}/[\mathrm{Zn(Me_6tren)dmf^{2+}}] \qquad (1)$$
$$= (k_BT[\mathrm{dmf}]/h)\exp(-\Delta H^{\#}/RT)\exp(\Delta S^{\#}/R)$$

in which k_2 is a second order rate constant and the other symbols have their usual meaning. A regression analysis of the data in Fig. 2 according to eqn. 1 yields: k_2 (298.2 K) = 85.7 ± 1.5 dm^3 mol^{-1} s^{-1}, $\Delta H^{\#}$ = 54.3 ± 0.6 kJ mol^{-1} and $\Delta S^{\#} = -25.8$ ± 1.9 JK^{-1} mol^{-1} where the errors represent one standard deviation for the data fit to eqn. 1. (A pseudo first order rate constant = 1100 s^{-1} may be calculated from k_2 at the pure dmf concentration = 12.9 mol dm^{-3}).

Solvent exchange on $[Zn(solvent)_6]^{2+}$ in water [8], methanol [9], and dimethyl sulphoxide [10] is characterised by rate constants in the range 10^4–10^7 s^{-1} at 298.2 K as estimated from indirect and direct methods, and NMR studies of $[Zn(dmf)_6]^{2+}$ are consistent with this species exhibiting a similar lability [11]. By comparison dmf in $[Zn(Me_6tren)dmf]^{2+}$ exhibits a decreased lability. However dmf exchange on $[Zn(tren)dmf]^{2+}$ in CD_3NO_2 medium over a similar concentration range to that in Table I was found to be in the fast exchange limit of the NMR time scale down to the lowest liquid temperature (245 K) of the solutions studied consistent with $1/\tau_c \geqslant 10^3$ s^{-1} at 245 K. This demonstrates that the slowness of dmf exchange in $[Zn(Me_6tren)dmf]^{2+}$ is a consequence of the steric hindrance caused by the six methyl groups of the tripod Me_6tren ligand. It is assumed that both $[Zn(tren)dmf]^{2+}$ and $[Zn(Me_6tren)dmf]^{2+}$ exhibit the same trigonal bipyramidal structures with dmf in an apical position which characterises the analogous thiocyanato [12] and bromo [7] complexes in the solid state. On this basis it is seen that dmf in $[Zn(Me_6tren)dmf]^{2+}$ is at the centre of an annulus formed by six methyl groups which substantially restricts access to the dmf coordination site whereas such access is far less restricted in $[Zn(tren)dmf]^{2+}$. The second order dmf exchange rate law observed for $[Zn(Me_6tren)dmf]^{2+}$ (eqn. 1) is consistent with the operation of an associative (A) mechanism [13] in which the entering dmf molecule is substantially involved in the formation of the transition state. Alternatively eqn. 1 is consistent with the operation of an interchange (I) mechanism [13] in which encounter complex formation is slight. (Here $k_2 = k_iK_o$ where k_i characterises interchange of dmf between the first and second coordination sphere of the encounter complex characterised by a formation constant K_o.) The I mechanism, which may be either associatively or dissociatively activated, involves the entering dmf molecule in the transition state to a lesser extent than does the A mechanism, but for both mechanisms steric hindrance from the annulus of methyl groups is expected to decrease the rate of dmf exchange at the zinc(II) centre.

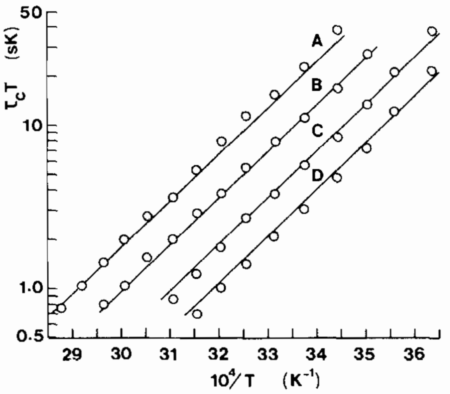

Fig. 2. The variation of τ_cT with temperature. The data point sets labelled A–D arise from solutions A–D and the solid curves represent the simultaneous best fit of these data to eqn. 1 through a regression analysis.

The observation that $[Zn(dmf)_6]^{2+}$ and $Zn(tren)dmf]^{2+}$ are considerably more labile than $[Zn(Me_6tren)dmf]^{2+}$ is consistent with similar observations made on the analogous cobalt(II), nickel(II), and copper(II) complexes when acetonitrile and dmf are the coordinating solvents [4–6]. Solid state X-ray diffraction studies of $[M(Me_6tren)Br]^+$ show that the theoretical tendency for bond distances to decrease as M varies from Mn to Zn has superimposed on it the effects of d orbital occupancy and Me_6-tren steric constraints which cause variations in the bond distances of the overall trigonal bipyramidal geometry [14]. Such structural effects probably affect the relative labilities and exchange mechanism of $[M(Me_6tren)solvent]^{2+}$ complexes to some extent but the previous postulation that the steric effect of Me_6tren is the predominant factor producing the greatly decreased labilities observed when M = Co, Ni, and Cu [4–6] is substantially reinforced by these new observations of the d_{10} zinc(II) system.

Acknowledgements

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