Nitrogen-14 Magnetic Resonance Study of the Exchange of Acetonitrile on Copper(II) Complexes

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The kinetic parameters, determined by ^{14}N n.m.r., for the exchange of acetonitrile are: $Cu(MeCN)_6^{2+}$, k_{ex} (228 K) $\geqslant 1{\cdot}6 \times 10^7$ s^{-1}; $Cu(tren)(MeCN)^{2+}$, k_{ex} (228 K) = $(5{\cdot}1 \pm 0{\cdot}7) \times 10^3$ s^{-1}, $\Delta H^\ddagger = 45 \pm 4$ kJ mol^{-1}, and $\Delta S^\ddagger = 26 \pm 16$ J mol^{-1} K^{-1}; $Cu(trenol)(MeCN)_2^{2+}$, k_{ex} (228 K) = $(8{\cdot}0 \pm 2{\cdot}0) \times 10^4$ s^{-1}, $\Delta H^\ddagger = 26 \pm 8$ kJ mol^{-1}, and $\Delta S^\ddagger = -34 \pm 32$ J mol^{-1} K^{-1}; and $Cu(Me_6tren)(MeCN)^{2+}$, k_{ex} (228 K) $< 10^2$ s^{-1}, where in all cases k_{ex} refers to the exchange at a single site. The kinetic data are discussed in terms of a model whereby the rapidity of exchange on $Cu(MeCN)_6^{2+}$ is attributed at least partially to a dynamic Jahn–Teller effect, and the reduction in lability upon co-ordination of polydentate ligands is due to elimination of this exchange pathway.

THE rapidity of solvent exchange on copper(II) has been attributed [1,2] in part to a Jahn–Teller distortion of the first co-ordination sphere geometry. The interconversion time ($\tau_i = ca.\ 10^{-11}$ s) for the axial and equatorial sites in $Cu(H_2O)_6^{2+}$ and $Cu(MeOH)_6^{2+}$ is such that all six co-ordinated solvent molecules become equivalent on the time scale of the n.m.r. method used in the determination of solvent exchange rates on these species,[3] so it is not possible to determine whether the axial and equatorial co-ordinated solvent molecules exchange at different rates, or whether the rapid interconversion process provides the only significant path for solvent exchange. Polydentate ligands [4] increase τ_i and also appear to decrease the lability of co-ordinated solvent,[5,6] but so far only one direct solvent exchange study has been reported in which a chelating ligand has been shown to decrease solvent lability on copper(II).[7] In this study the effects of a number of polydentate ligands [2,2′,2″-triaminotriethylamine (tren); 2,2′,2″-tri-(*NN*-dimethylamino)triethylamine (Me_6tren); 2,2′,2″-trihydroxyethylamine (trenol); and 1,4,8,11-tetra-azacyclotetradecane (cyclam)] on the lability of acetonitrile co-ordinated to copper(II) are examined with the intention of gaining a better insight into solvent exchange processes on copper(II).

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RESULTS

Visible Absorption Spectra.—The visible spectra of the copper(II) species in acetonitrile are shown in Figure 1, from which it is seen that the spectrum of $[Cu(MeCN)_4](ClO_4)_2$ dissolved in acetonitrile ($\tilde{\nu}_{max.}$/cm^{-1} = 13 500; ε/dm^3 mol^{-1} cm^{-1} = 21·5) is similar to that reported by Hathaway and Underhill,[8] and is consistent with tetragonally distorted $Cu(MeCN)_6^{2+}$ (electronic transitions $^2B_{2g} \longleftarrow {}^2B_{1g}$, $^2E_g \longleftarrow {}^2B_{1g}$) predominating in solution.[9] The reflectance spectrum [10] of [Cu(tren)(NCS)]NCS, which possesses approximate trigonal bipyramidal stereochemistry [11] is very similar in band shape and position to those of acetonitrile solutions of $Cu(tren)(MeCN)^{2+}$ ($\nu_{max.}$ 12 400, ε 136) which are considered to arise from the transitions $^2E'' \longleftarrow {}^2A_1'$ and $^2E' \longleftarrow {}^2A_1'$; consistent with trigonal bipyramidal stereochemistry for the latter species. There is evidence for the existence of the five-co-ordinate species $Cu(tren)H_2O^{2+}$ and $Cu(tren)OH^+$ in aqueous solution.[7,12] The solid-state structure [13] of $[Cu(Me_6tren)Br]Br$ is approximately trigonal pyramidal, and consequently the spectrum observed ($\nu_{max.}$ 12 000, ε 498) upon dissolution of the perchlorate analogue in acetonitrile is considered to arise from the $Cu(Me_6tren)(MeCN)^{2+}$ species which exhibits a maximum [12] at a higher frequency than $Cu(Me_6tren)(ClO_4)^+$.

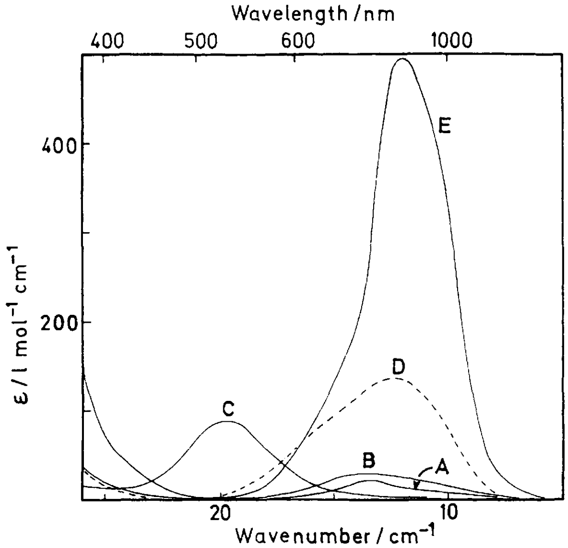

FIGURE 1 Visible absorption spectra of A, $Cu(MeCN)_6^{2+}$; B, $Cu(trenol)(MeCN)_2^{2+}$; C, $Cu(cyclam)^{2+}$; D, $Cu(tren)(MeCN)^{2+}$; and E, $Cu(Me_6tren)(MeCN)^{2+}$ in acetonitrile

The nitrogen atoms of the cyclic tetra-amine in the copper cyclam species most probably lie in the equatorial plane of the tetragonally distorted complex, as is the case for the nickel(II) analogue.[14] It does not appear possible to establish with any certainty the degree of tetragonal distortion of the species from its spectrum in acetonitrile ($\nu_{max.}$ 19 700, ε 88·9) which is similar to the spectrum of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclodecanecopper(II) perchlorate [15] in aqueous solution and also to that of bis(1,2-diaminoethane)copper(II) thiocyanate in the solid state.[16] In the latter compound the nearest thiocyanate atom (S) is 3·27 Å from copper(II) along the axis perpendicular to the plane of the four nitrogen atoms of the 1,2-diaminoethane ligands.[17] It appears probable that the copper(II)–acetonitrile interaction is likely to be weak in $Cu(cyclam)(MeCN)_2^{2+}$ and that the observed spectral envelope most probably arises from the transitions [16] $^2E_g \longleftarrow {}^2B_{1g}$, $^2B_{2g} \longleftarrow {}^2B_{1g}$, and $^2A_{1g} \longleftarrow {}^2B_{1g}$.

In aqueous solution the monomeric 2,2′,2″-trihydroxytriethylaminecopper(II) species predominates [18] and the spectral data for acetonitrile solutions are also consistent with the predominant formation of a 1 : 1 species. The visible spectrum ($\nu_{max.}$ 13 600, ε 30·8) most closely resembles that of $Cu(MeCN)_6^{2+}$ on which basis the six-co-ordinate formula $Cu(trenol)(MeCN)_2^{2+}$ appears to be the most appropriate, but such a method of species identification is somewhat equivocal. The main thrust of this study, which is an investigation of solvent-exchange processes, is not critically dependent upon a more positive identification of the stoicheiometry of the trenol complex, however, as is discussed later.

*Nitrogen-*14 *Magnetic Resonance.*—The relationship of bulk solvent nuclear relaxation to the rates of solvent exchange on paramagnetic metal ions in dilute solution has been discussed in detail [19,20] and hence only the major aspects of this relationship applicable to the copper(II)–acetonitrile systems under study are considered here. The relaxation of the ^{14}N nucleus of bulk acetonitrile by the copper(II) complexes may be expressed by equation (1)

$$T_{2p} = (1/T_2 - 1/T_{2A})^{-1} = 2\gamma^{-1}(W - W_A)^{-1} \quad (1)$$

where γ is the ^{14}N gyromagnetic ratio (1934 × 10^4 T^{-1} s^{-1}), W and W_A are the full widths (in T) at half maximum amplitude of the absorption signal of the bulk acetonitrile ^{14}N resonance in a copper(II)–acetonitrile solution and a pure acetonitrile reference solution respectively, and T_2 and T_{2A} are the associated transverse relaxation times.

The ^{14}N relaxation data for the copper(II)–acetonitrile systems are plotted as mT_{2p} [where m is the molality of copper(II) and hence the mole fraction of acetonitrile co-ordinated, P_M = relative molar mass of MeCN × number of MeCN molecules co-ordinated per copper(II) × m × 10^{-3}] in Figure 2. The temperature dependence of mT_{2p} for the $Cu(MeCN)_6^{2+}$ system is consistent with rapid acetonitrile exchange [3] such that $T_{2p} = T_{2M}P_M^{-1}$ where T_{2M} is the (averaged) ^{14}N transverse relaxation time in co-ordinated acetonitrile. The temperature dependence of the T_{2M} relaxation process is characterised by $E_{act} = -12{\cdot}6 \pm 0{\cdot}3$ kJ mol^{-1} which is similar to that observed for the copper(II)–methanol system.[3] No kinetic parameters can be directly derived from these relaxation data, but an upper limit may

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be set for τ_M, the mean residence time of an acetonitrile molecule on copper(II), by assuming that the two terms to

$$P_M T_{2p} = (T_{2M} + \tau_M) \qquad (2)$$

the right of equation (2) are equal at the low-temperature data extreme (228 K), such that $\tau_M^{-1} = k_{ex} = 1{\cdot}6 \times 10^7$ s^{-1} where the minimum rate of acetonitrile exchange is given by (3).

$$\text{Rate} = k_{ex}6[\text{Cu(MeCN)}_6{}^{2+}] \qquad (3)$$

A ^{14}N chemical shift, S, of -3×10^{-5} T was measured at four temperatures within the range 328—349 K for bulk acetonitrile in a $5{\cdot}89 \times 10^{-3}$m-Cu(MeCN)$_6{}^{2+}$ solution by use of pure acetonitrile as a reference. The error on these measurements is $\pm 30\%$, and meaningful measurements at lower temperatures were precluded as the bulk acetonitrile line became increasingly broad. A ^{14}N A/h value of $(6{\cdot}8 \pm 2{\cdot}0) \times 10^7$ Hz was calculated from equation (4),[21] which

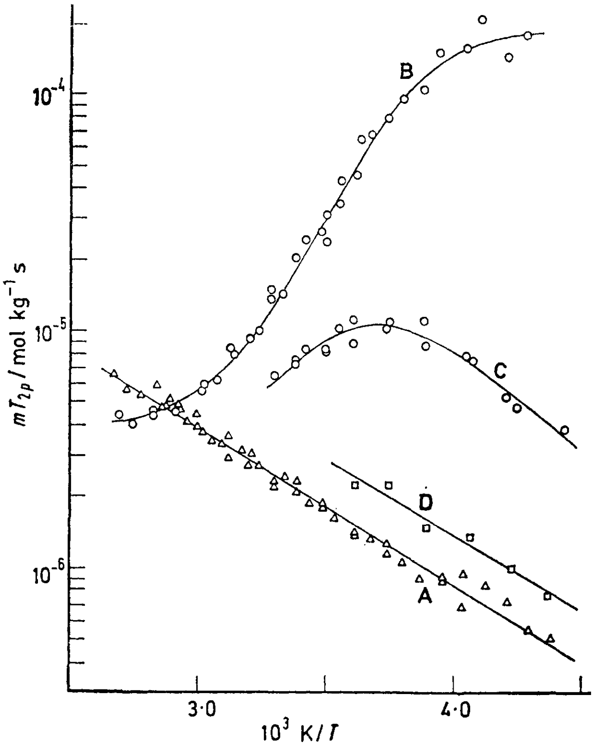

FIGURE 2 Nitrogen-14 relaxation for the bulk solvent acetonitrile resonance in the systems: A, Cu(MeCN)$_6{}^{2+}$; B, Cu(tren)(MeCN)$^{2+}$; C, Cu(trenol)(MeCN)$_2{}^{2+}$; and D, Cu(cyclam)$^{2+}$ [for the Cu(cyclam)$^{2+}$ system mT_{2p} is multiplied by 2×10^{-3}]. The solid curves represent computed best fits of the data to relaxation equations discussed in the text

$$-\frac{SP_M{}^{-1}}{\omega} = \frac{\Delta\omega_M}{\omega} = \frac{2\pi\mu_{eff}\beta(A/h)}{3kT\gamma}[S'(S'+1)]^{\frac{1}{2}} \qquad (4)$$

applies when complete environmental averaging between co-ordinated and bulk sites occurs, as is the case here, and where P_M is calculated for six co-ordination sites, $\Delta\omega_M$ in the chemical shift between co-ordinated and bulk acetonitrile, S' is the net electron spin for copper(II), $\mu_{eff} = 1{\cdot}63$ B.M. determined by Evans's method[22] with toluene as a reference signal, and the other symbols have their usual meaning. No measurable chemical shift was observed for the other systems.

The ^{14}N relaxation data for the Cu(tren)(MeCN)$^{2+}$ system is fitted to equation (5) where the term T_{2O} arises from

$$(P_M T_{2p})^{-1} = (T_{2M} + \tau_M)^{-1} + T_2{}^{-1} \qquad (5)$$

dipolar relaxation of acetonitrile outside the first co-ordination sphere. The τ_M term predominates from $10^3/T = 3{\cdot}0$ to $4{\cdot}0$ (Figure 2), but the contributions of T_{2M} and T_{2O} to the overall relaxation process are seen at the high and low temperature extremes respectively. For this system the exchange rate law is (6). Values of k_{ex} (298 K) $= (1{\cdot}7 \pm 0{\cdot}2) \times 10^6$ s^{-1}, $\Delta H^\ddagger = 45 \pm 4$ kJ mol^{-1}, and $\Delta S^\ddagger = 26 \pm 16$ J mol^{-1} K^{-1} for the acetonitrile exchange process and E_{act}

$$\text{Rate} = k_{ex}[\text{Cu(tren)(MeCN)}^{2+}] \qquad (6)$$

values of $-0{\cdot}4 \pm 5{\cdot}2$ and $-0{\cdot}2 \pm 5{\cdot}2$ kJ mol^{-1} for T_{2M} and T_{2O} respectively correspond to the best fit of equation (4) to the mT_{2p} data shown in Figure 2.

The best fit of equation (2) to the ^{14}N relaxation data from the Cu(trenol)(MeCN)$_2{}^{2+}$ system gave values of k_{ex} (298 K) $= (2{\cdot}6 \pm 0{\cdot}5) \times 10^6$ s^{-1}, $\Delta H^\ddagger = 26 \pm 8$ kJ mol^{-1}, $\Delta S^\ddagger = -34 \pm 32$ J mol^{-1} K^{-1}, and $E_{act} = -18 \pm 6$ kJ mol^{-1} for T_{2M} (if the predominant low temperature component of curve C is assigned to the T_{2M} relaxation region of a second and more labile site for acetonitrile exchange in the complex, otherwise E_{act} will pertain to a T_{2O} relaxation process). These parameters are calculated on the assumption that the observed ^{14}N relaxation arises from exchange at a single site, but if it arises from exchange at two sites the k_{ex} value must be halved and $\Delta S^\ddagger$ changes accordingly. It seems improbable, however, that the two non-equivalent sites in Cu(trenol)(MeCN)$_2{}^{2+}$ will be characterised by similar exchange parameters and thus it is concluded that either exchange at one site is too slow or fast to produce ^{14}N relaxation from which chemical parameters can be derived, or that the stoicheiometry Cu(trenol)(MeCN)$^{2+}$ pertains to the trenol species, in which case only a single site need be considered. In either case the major point is established that trenol considerably reduces the lability of co-ordinated acetonitrile (Table).

Rate parameters for the exchange of acetonitrile on bivalent metal complexes

Complex	k_{ex} (298 K)/s^{-1}	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$ J mol^{-1} K^{-1}	Ref.
Cu(MeCN)$_6{}^{2+}$	$\geqslant 1{\cdot}6 \times 10^7$ (228 K)	—	—	*d*
Cu(tren)(MeCN)$^{2+}$	$(1{\cdot}7 \pm 0{\cdot}2) \times 10^6$ $(5{\cdot}1 \pm 0{\cdot}7) \times 10^3$ (228 K)	45 ± 4	26 ± 16	*d*
Cu(trenol)(MeCN)$_2{}^{2+}$	$(2{\cdot}6 \pm 0{\cdot}5) \times 10^6$ $(8{\cdot}0 \pm 2{\cdot}0) \times 10^4$ (228 K)	26 ± 8	-34 ± 32	*d*
Cu(Me$_6$tren)(MeCN)$^+$	< 100[c]	—	—	*d*
Co(MeCN)$_6{}^{2+}$	$(3{\cdot}2 \pm 0{\cdot}3) \times 10^5$	48 ± 2	22 ± 8	23
Co(tren)(MeCN)$^{2+}$	$\geqslant 2 \times 10^6$	—	—	23
Ni(MeCN)$_6{}^{2+}$	$(2{\cdot}0 \pm 0{\cdot}3) \times 10^3$	69 ± 2	50 ± 8	23
[a] Ni(tren)(MeCN)$_2{}^{2+}$	$(16{\cdot}5 \pm 3{\cdot}5) \times 10^4$	45 ± 6	6 ± 21	23
[b] Ni(tren)(MeCN)$_2{}^{2+}$	$\geqslant 2 \times 10^6$	—	—	23

[a] MeCN *trans* to tertiary amine group. [b] MeCN *cis* to tertiary amine group. [c] At 350 K. [d] This work.

Above 320 K Cu(trenol)(MeCN)$_2{}^{2+}$ solutions slowly become colourless consistent with the formation of copper(I) in solution, so ^{14}N n.m.r. measurements were not made above 302 K.

The ^{14}N relaxation data for the Cu(cyclam)$^{2+}$ system is

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consistent with either a very rapid acetonitrile exchange process, or with relaxation arising from dipolar interaction of acetonitrile outside the first co-ordination sphere with the copper(II) species. The observation of no ^{14}N relaxation in the Cu(Me$_6$tren)(MeCN)$^{2+}$ system (0·494m solution) is consistent with slow exchange of acetonitrile ($\tau_M > 10^{-2}$ s over a range 228—349 K) at the single available site, and also with the dipolar interaction distance, r, being increased by the presence of the methyl groups such that this mechanism for ^{14}N relaxation outside the first co-ordination sphere (which has an r^{-3} dependence) is reduced in effectiveness.

DISCUSSION

The observation that acetonitrile is at least 3000 times more labile in Cu(MeCN)$_6$$^{2+}$ than is the case in Cu(tren)(MeCN)$^{2+}$ is in marked contrast to the observation that the co-ordination of tren considerably increases the lability of acetonitrile in the analogous nickel(II) and cobalt(II) systems.[23] * The labilisation of acetonitrile in the latter two systems has been attributed to a reduced $\Delta H^\ddagger$ for the exchange process resulting from electron donation to the metal ion by tren, but it appears that this is not a predominant factor determining the modification of acetonitrile lability upon co-ordination of tren to copper(II). If these variations of acetonitrile lability by tren are viewed as modifications of the exchange processes on the hexakis(acetonitrile)metal(II) species, it must be concluded that the exchange mechanism for the copper(II) species differs from that for the nickel(II) and cobalt(II) species. The most probable source of mechanistic difference is the dynamic Jahn–Teller effect in Cu(MeCN)$_6$$^{2+}$ which, by reference to the methanol and water analogues,[3] is expected to be characterised by an inversion time, τ_i, of *ca.* 10^{-11} s (298 K) and an associated activation energy ΔE_i of *ca.* 4 kJ mol^{-1}. The long axial Cu–N bonds are likely to be characterised by a low $\Delta H^\ddagger$ for exchange, compared with the $\Delta H^\ddagger$ values for the nickel(II) and cobalt(II) analogues, such that all six acetonitrile ligands are labilised through the very rapid inversion process in a predominantly dissociative acetonitrile exchange mechanism. Such a pathway does not appear to be operative in the exchange processes in Ni(MeCN)$_6$$^{2+}$ and Co(MeCN)$_6$$^{2+}$. The formation of Cu(tren)(MeCN)$^{2+}$ removes the Jahn–Teller pathway for acetonitrile exchange, and the electron-donating characteristics of tren are not sufficiently great to compensate for the consequent loss of lability, whereas in the case of the nickel(II) and cobalt(II) analogues the net effect is an increase in acetonitrile lability. The reduction of acetonitrile lability in Cu(trenol)(MeCN)$_2$$^{2+}$, and of water[7] lability in Cu(tren)H$_2$O^{2+} can be similarly rationalised.

The apparently greatly reduced lability of acetonitrile in Cu(Me$_6$tren)(MeCN)$^{2+}$ is consistent with the arguments presented in this paper, but also suggests that Me$_6$tren reduces transition-state flexibility as has been previously discussed for the nickel(II) and cobalt(II) analogues which also show greatly reduced lability.[23]

EXPERIMENTAL

Commercial acetonitrile, 2,2′,2″-triaminotriethylamine, and 2,2′,2″-trihydroxyethylamine were redistilled and dried and stored over Linde 4A molecular sieves. *Tetrakis(acetonitrile)copper*(II) *perchlorate* was prepared by using the triethyl orthoformate dehydration method used by Leeuwen and Groeneveld[24] in the preparaton of other acetonitrile complexes. All operations were performed under dry nitrogen {Found: Cu, 14·75. Calc. for [Cu(MeCN)$_4$](ClO$_4$)$_2$: Cu, 14·89%}. The method of Ciampolini and Nardi[12] was used in the preparation of perchlorato[2,2′,2″-tri(*NN*-dimethylamino)triethylamine]copper(II) perchlorate. All solutions for spectral studies were made up under dry nitrogen.

Nitrogen-14 n.m.r. measurements were performed as described[25] and spectrophotometric determinations were made on samples in air-tight silica cells with a Unicam SP 700 spectrophotometer.

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* In ref. 23 equation (3) should read

$$T_{2p}^{-1} = \left(\frac{\tau_M}{P_M}\left[\frac{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2}{T_{2M}^{-2} + (T_{2M}\tau_M)^{-1} + \Delta\omega_M^2}\right]\right)^{-1} + \left(\frac{T_{2M}'}{P_M'}\right)^{-1}$$

and the left-hand ordinate of figure 2 should be $\ln(T_{2p}m)$.

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