CN Flipping. As mentioned in the preceding section, the final products of $[Co(NH_3)_6$ or $Co(H_2O)(NH_3)_5][Cr(CN)_6]$ were found to be $Co(CN)_6Cr$ but not $Co(NC)_6Cr$. This suggests that CN flipping takes place during the reaction. A similar CN flipping has been reported in the studies of the solid-state reaction of Prussian blue analogues such as $Co_3[Cr(CN)_6]_2$[24] and $Fe_3[Cr(CN)_6]_2$.[25]

Metal–Metal Interaction. The CN^- ion is rich in π electrons and capable of forming a M–NC–M′ bond (M and M′ are the same or different metal ions). The final products obtained in this study are therefore expected to have some extent of metal–metal interaction. The final products of the [Cr][Cr] reaction have a magnetic moment of 2.4–2.5 μ_B, which is remarkably low as compared with that expected from the spin-only value of the Cr(III) ion. Such subnormal magnetic moments are indicative of the presence of appreciable metal–metal interaction. As for the other complexes, a similar situation might be expected, but unfortunately we have insufficient evidence to bear out the expectation.

Registry No. $[Cr(NH_3)_6][Cr(CN)_6]$, 23540-70-7; $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$, 75058-08-1; $[Cr(NH_3)_6][Co(CN)_6]$, 39963-01-4; $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$, 62534-93-4; $[Co(NH_3)_6][Cr(CN)_6]$, 38670-48-3; $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$, 60897-44-1; $[Co(NH_3)_6][Co(CN)_6]$, 15556-03-3; $[Co(H_2O)(NH_3)_5][Co(CN)_6]$, 22622-91-9; *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$, 49732-16-3; $[Cr(NH_3)_6](NO_3)_3$, 15363-28-7; $[Co(NH_3)_6]Cl_3$, 10534-89-1; $[Cr(H_2O)(NH_3)_5](NO_3)_3$, 19683-62-6; $[Co(H_2O)(NH_3)_5]Cl_3$, 13820-80-9; $K_3[Cr(CN)_6]$, 13601-11-1; $K_3[Co(CN)_6]$, 13963-58-1; *cis*-$[Co(H_2O)_2(NH_3)_4]Cl_3$, 21264-85-7; $Co^{II}_3[Co(CN)_6]_2$, 14123-08-1; $Co^{II}_3[Cr(CN)_6]_2$, 14049-80-0; $Cr(NC)_6Co$, 26248-18-0; $Cr(NC)_6Cr$, 41751-48-8; $(H_2O)(NH_3)Cr(NC)_4Cr(CN)_2$, 86688-57-5; $(NH_3)_2Co^{II}(NC)_4Co(CN)_2$, 86688-58-6; $(NH_3)_5Co(NC)Co(CN)_5$, 86709-24-2; $(NH_3)_4Co(NC)_2Co(CN)_4$, 86688-60-0.

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Solvent Exchange and Anation on Five-Coordinate (*N*,*N*-Dimethylformamide)(2,2′,2″-tris(dimethylamino)triethylamine)copper(II)

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Proton NMR studies show that *N*,*N*-dimethylformamide exchange on five-coordinate $[Cu(Me_6tren)dmf]^{2+}$ (where Me_6tren = 2,2′,2″-tris(dimethylamino)triethylamine) is characterized by $k_{ex}(298.2\ K) = 555 \pm 39\ s^{-1}$, $\Delta H^* = 43.3 \pm 1.1\ kJ\ mol^{-1}$, $\Delta S^* = -47.0 \pm 3.1\ J\ K^{-1}\ mol^{-1}$, and $\Delta V^*(365\ K) = 6.1 \pm 0.1\ cm^3\ mol^{-1}$. These data suggest a dissociative (d) activation mode for dmf exchange. Anation of $[Cu(Me_6tren)dmf]^{2+}$ by NCS^-, N_3^-, and Br^- is characterized by kinetic data consistent with the operation of a dissociative interchange (I_d) mechanism.

Introduction

The coordination of the tetradentate ligand 2,2′,2″-tris(dimethylamino)triethylamine (Me_6tren) to copper(II) produces a five-coordinate copper(II) species in which solvent in the fifth cordination site exhibits a $\sim 10^5$ reduction in lability by comparison to that exhibited by hexakis(solvent)copper(II) species.[1–6] In consequence of this it is found that in *N*,*N*-dimethylformamide (dmf) $[Cu(Me_6tren)dmf]^{2+}$ undergoes solvent exchange and anation reactions at rates that fall conveniently into the NMR and stopped-flow spectrophotometric time scales. This facilitates a detailed kinetic characterization of simple ligand substitution processes on this example of five-coordinate copper(II)—a state that for copper(II) in particular and metal ions in general has not been subjected to the intensive mechanistic scrutiny afforded six-coordinate species.[3]

Experimental Section

Materials. *N*,*N*-Dimethylformamide was distilled under vacuum from anhydrous copper sulfate and was dried and stored over Linde 4A molecule sieves under nitrogen. Cyclohexane used as a reference was distilled at atmospheric pressure and was dried and stored as for dmf.

The 2,2′,2″-tris(dimethylamino)triethylamine (Me_6tren) ligand was prepared as previously described, as was the complex $[Cu(Me_6tren)ClO_4]ClO_4$.[5] This complex (3.7 g) was dissolved in dmf (10 cm^3) at 340 K, 13.4 g of triethyl orthoformate was added, and heating at 340 K was continued for 1 h. On cooling the blue crystalline $[Cu(Me_6tren)dmf](ClO_4)_2$ precipitated, and a further crop was obtained on addition of ether. The combined products were filtered off and washed with ether under dry nitrogen prior to pumping down under vacuum for 6 h. Anal. Calcd for $[Cu(Me_6tren)dmf](ClO_4)_2$: Cu, 11.2. Found: Cu, 11.2. $[Zn(Me_6tren)dmf](ClO_4)_2$ was similarly prepared. Anal. Calcd for $[Zn(Me_6tren)dmf](ClO_4)_2$: Zn, 11.5. Found: Zn, 11.6. Sodium azide, bromide, perchlorate, and thiocyanate were recrystallized from water prior to drying at 355 K for 5 days prior to pumping under vacuum for 1 day. The infrared spectra of these salts exhibited no water bands after this treatment. All chemicals used were from BDH.

Perchlorate salts of metal complexes may be explosive under some circumstances and should be handled with caution. No explosion hazard was encountered under the conditions of this study.

All solution preparations were carried out in a dry nitrogen atmosphere. Solutions for equilibrium studies by Job's method of continuous variations[7] and general spectrophotometric studies were contained in tightly stoppered quartz spectrophotometric cells. The solutions for stopped-flow spectrophotometric studies were transferred to storage syringes under dry nitrogen. Solutions for NMR studies were sealed under vacuum in 2-mm diameter NMR tubes, which were positioned concentrically in 5-mm diameter NMR tubes containing CD_3NO_2 or $(CD_3)_2SO$ (Stohler), depending on the temperature range studied.

Spectrophotometric Studies. The stoichiometry of the complex formed between $[Cu(Me_6tren)dmf]^{2+}$ and X^- (Br^-, N_3^-, or NCS^-) was investigated by Job's method of continuous variations in the $[[Cu(Me_6tren)dmf]^{2+}]$ and $[X^-]$ ranges of 2.8×10^{-5}–4.2×10^{-3} and 2.9×10^{-5}–4.0×10^{-3} mol dm^{-3}, respectively, at 298.2 K. The wavelengths employed were 315 and 330, 410, and 700 nm, respectively, for Br^-, N_3^-, and NCS^- at which substantial differences in molar

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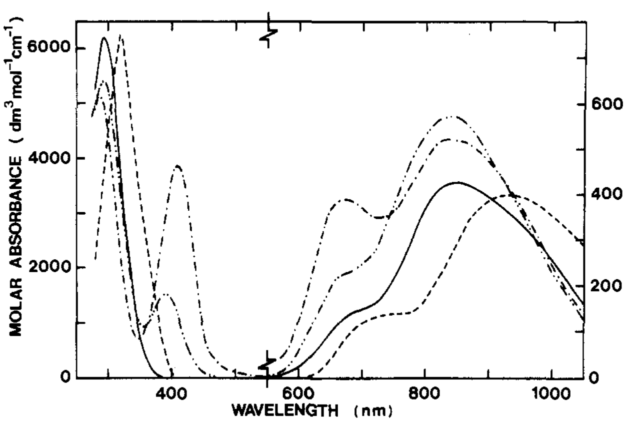

Figure 1. Ultraviolet/visible absorption spectra of $[Cu(Me_6tren)dmf]^{2+}$ (—) and $[Cu(Me_6tren)X]^+$ (X = Br (- - -), N_3 (-··-), and NCS (-···-)) in dmf.

absorptivity occur as seen from Figure 1. Ideally the reactants should have no absorbance at the wavelengths selected for the application of Job's method. In this study this condition was not always met, and appropriate allowances were made when reactant species absorbed. Spectrophotometric measurements were made with a Zeiss DMR-10 spectrophotometer equipped with a thermostatted (±0.05 K) cell block.

Stopped-flow spectrophotometric studies were carried out on equipment of conventional design at 315 and 330, 300 and 410, and 390 and 700 nm when $X^- = Br^-$, N_3^-, and NCS^-, respectively. Kinetic traces (5–10 for each solution) were digitized by using a Datalab DL905 transient recorder, transferred to floppy disks, and signal averaged and analyzed through a Computer Data Products LSI-11 minicomputer. The initial concentrations of $[Cu(Me_6tren)dmf]^{2+}$ varied in the range 5.0×10^{-5}–8.5×10^{-4} mol dm^{-3} and in all cases never exceeded 10% of the excess anion concentrations, which varied in the range 5.0×10^{-4}–2.5×10^{-2} mol dm^{-3}.

Proton NMR Studies. Measurements were carried out at 90 MHz on a Bruker HX90E spectrometer in PFT mode using quadrature detection and locked on the deuterium frequency. Depending on the width of the bulk dmf formyl resonance at half-maximum amplitude, $\nu_{1/2}$, between 50 and 400 transients were collected as 4 K real data points prior to Fourier transformation. Typically the delay time was 2 s between each 3 μs pulse, and the sweep width was 2 kHz. The computer-applied line broadening of 0.5 Hz was allowed for in all line-width determinations used in calculating the formyl proton transverse relaxation time $T_2 = 1/(\pi\nu_{1/2})$. For each solution of $[Cu(Me_6tren)dmf]^{2+}$ studied measurements were made under identical conditions on $[Zn(Me_6tren)dmf]^{2+}$ reference solutions of the same concentration. All solutions contained 2% cyclohexane that acted both as a shift reference and as an additional resonance to monitor field homogeneity. Sample temperature control was ±0.3 K, and the thermostat was calibrated against a copper constantan thermocouple. The fitting of the line-width data to the appropriate relaxation equation given in the Results and Discussion sections was carried out on a Cyber 173 computer using a nonlinear least-squares program.

Results

Species in Solution. Spectrophotometric studies of dmf solutions of $[Cu(Me_6tren)dmf](ClO_4)_2$ (ionic strength adjusted to 0.5 mol dm^{-3} with sodium perchlorate) using Job's method of continuous variations[7] show the formation of single 1:1 species, $[Cu(Me_6tren)X]^+$, characterized by stability constants $\sim 10^5$ dm^3 mol^{-1} in the reaction of $[Cu(Me_6tren)dmf]^{2+}$ with $X^- = Br^-$, N_3^-, and NCS^-. The visible spectra of $[Cu(Me_6tren)dmf]^{2+}$ and $[Cu(Me_6tren)X]^+$ (Figure 1) are characterized by bands in the 600–1100-nm region consistent with at least two absorptions that in the case of trigonal-bipyramidal geometry may be assigned to the $^2E'' \leftarrow {}^2A_1'$ and $^2E' \leftarrow {}^2A_1'$ transitions.[8] An X-ray structural study[5] of $[Cu(Me_6tren)Br]Br$ shows copper(II) to be five-coordinate with approximate trigonal-bipyramidal geometry, and similar

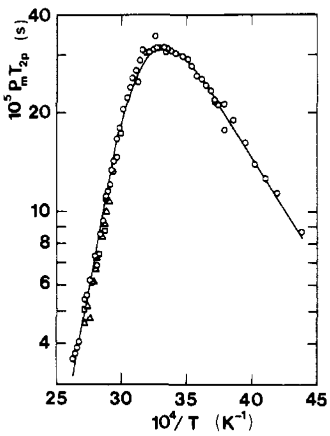

Figure 2. Temperature variation of P_mT_{2p} for the bulk dmf formyl proton characterizing dmf exchange on $[Cu(Me_6tren)dmf]^{2+}$. Circles, triangles, and squares represent data for solutions i–iii, respectively. The solid curve represents the best fit of the data for solution i to eq 3.

stereochemistries are assumed to characterize $[Cu(Me_6tren)dmf]^{2+}$ and $[Cu(Me_6tren)X]^+$ in dmf solution. In the closely related five-coordinate $[Cu(tren)NCS]^+$ species (where tren = 2,2′,2″-triaminotriethylamine), an X-ray study has shown the NCS^- ligand to be nitrogen bonded, and it is probable that similar bonding characterizes $[Cu(Me_6tren)NCS]^+$ in dmf.

Proton NMR Studies. The relaxation parameter T_{2p} is related to the transverse relaxation times of the formyl proton of bulk dmf in the $[Cu(Me_6tren)dmf]^{2+}$ solutions, T_2, and that of the reference solution, T_{2ref}, through eq 1. The variation

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

of the magnitude of T_{2p} was studied over the temperature range 225–380 K for solutions i–iii, which were 0.164, 0.0547, and 0.0912 mol dm^{-3} in $[Cu(Me_6tren)dmf]^{2+}$, respectively. The ionic strength of solution iii was adjusted to 0.5 mol dm^{-3} with sodium perchlorate. According to Swift and Connick,[10] the form of T_{2p} is given by eq 2, where P_m is the mole fraction

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

of coordinated dmf, τ_m is the mean lifetime of coordinated dmf, T_{2m} is the transverse relaxation time of coordinated dmf, $\Delta\omega_m$ is the chemical shift between coordinated and bulk dmf, and T_{2o} is the contribution to T_{2p} arising from outside the first coordination sphere. For dmf exchange on $[Cu(Me_6tren)dmf]^{2+}$, eq 2 reduces to eq 3 where $\tau_m^{-1} = k_{ex}$, the rate constant

$$(P_mT_{2p})^{-1} = \tau_m^{-1} + T_{2o}^{-1} = (K_BT/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R} + A_0e^{-E_0/RT} \tag{3}$$

for dmf exchange on $[Cu(Me_6tren)dmf]^{2+}$, and the dmf exchange rate = k_{ex} $[Cu(Me_6tren)dmf]^{2+}$.[10] The best fit of the T_{2p} data for solution i is shown in Figure 2, and is is seen that the data for solutions ii and iii show no significant deviations from this best fit curve. The derived parameters are given in Table I, and the raw T_{2p} data are available as supplementary material. Direct determinations of T_{1e} and the tumbling time τ_r of $[Cu(Me_6tren)dmf]^{2+}$ are not available, but it is reasonable to assume that they will be similar to those for six-coordinate copper(II) species, i.e., $\sim 10^{-9}$ and 10^{-11} s, respectively, at 298.2 K.[1] Thus, it is probable that τ_r dominates the relaxation of

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Table I. Parameters[a] for dmf Exchange and Anation by X^- in the $[Cu(Me_6tren)dmf]^{2+}$ Species in dmf Solution

dmf Exchange

k_{ex}, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	A_0, s^{-1}	E_0, kJ mol^{-1}
555 ± 39 (298.2 K)	43.3 ± 1.1	−47.0 ± 3.1	6.1 ± 0.1 (365 K)[b]	17.0 ± 3.0	12.5 ± 0.4
298 ± 21 (288.2 K)			6.8 ± 0.2 (350 K)[b]		
150 ± 10 (278.2 K)					

Anation

X^-	k_i-(298.2 K),[c] s^{-1}	k_i-(288.2 K),[c] s^{-1}	k_i-(278.2 K),[c] s^{-1}	K_o-(298.2 K),[c] dm^3 mol^{-1}
NCS^-	545 ± 38 (529 ± 32)	220 ± 11 (235 ± 10)	107 ± 6 (99 ± 5)	157 ± 16 (175 ± 15)
N_3^-	451 ± 13 (435 ± 19)	294 ± 11 (263 ± 12)	180 ± 13 (157 ± 7)	403 ± 43 (464 ± 15)
Br^-	563 ± 27			52 ± 3

[a] All errors quoted represent 1 standard deviation from the best fit of the data to the appropriate equation. [b] Merbach, A. E., private communication. [c] The first value is derived from data at a single temperature, and the value in parentheses is derived from a simultaneous fit of data at three temperatures to eq 6.

dmf outside the first coordination sphere of $[Cu(Me_6tren)dmf]^{2+}$.

A variation of the chemical shift of bulk dmf, $\Delta\omega$, with temperature according to eq 4 and consistent with the interpretation of the T_{2p} data was also observed over the experimental temperature range. These data are also available as supplementary material.

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

Anation Reactions. The variation of k_{obsd} with excess $[X^-]$ as typified by NCS^- in Figure 3 for the anation reaction given by eq 5 where X^- = NCS^-, N_3^-, and Br^-, is consistent with

$$[Cu(Me_6tren)dmf]^{2+} + X^- \xrightarrow{k_{obsd}} [Cu(Me_6tren)X]^+ + dmf \qquad (5)$$

eq 6 which typifies an interchange (I) mechanism[11] proceeding

$$k_{obsd} = k_i K_o [X^-]/(1 + K_o[X^-]) \qquad (6)$$

through the two steps shown in eq 7. (The rate constant

$$[Cu(Me_6tren)dmf]^{2+} + X^- \underset{fast}{\overset{K_o}{\rightleftharpoons}} [Cu(Me_6tren)dmf]^{2+}\cdots X^- \underset{slow}{\overset{k_i}{\rightleftharpoons}} [Cu(Me_6tren)X]^+ + dmf \qquad (7)$$

characterizing the dissociation of X^- from $[Cu(Me_6tren)X]^+$ is too small to be distinguished from the experimental error in k_{obsd}.) The rapid formation of the encounter complex in which X^- resides in the second coordination sphere of $[Cu(Me_6tren)dmf]^{2+}$ is characterized by K_o, and the subsequent rate-determining interchange of X^- between the second and first coordination spheres is characterized by k_i. The derivation of k_i was achieved through a nonlinear least-squares fit of k_{obsd} to eq 6 separately at the three temperatures studied or simultaneously for all three temperatures after substitution of k_i and K_o by their temperature-dependent formulations (X^- = NCS^-, N_3^-). The best fit lines for both fitting procedures are shwon in Figure 3, and the derived parameters appear in Table I from which it is seen that both procedures yield similar k_i values. (For X^- = Br^-, data obtained at 298.2 K only are considered.) As the variation of k_{obsd} with $[X^-]$ is not fully developed over the $[X^-]$ range studied (particularly when X^- = Br^-) and because there is probable internal compensation between $\Delta G°$ (for K_o) and $\Delta H^{\ddagger}_i$ and $\Delta S^{\ddagger}_i$, the latter activation parameters are unlikely to be reliable and hence are not considered in subsequent mechanistic discussion (the raw k_{obsd} data are available as supplementary material).

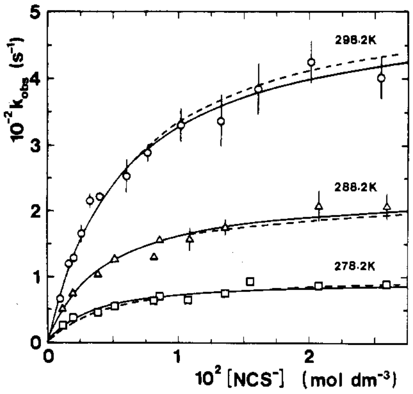

Figure 3. Variation of k_{obsd} for the anation of $[Cu(Me_6tren)dmf]^{2+}$ by NCS^- with temperature and excess $[NCS^-]$. Solid curves represent the simultaneous best fit of the data at 298.2, 288.2, and 278.2 K to eq 6, whereas broken lines represent the best fits of the data to eq 6 obtained separately at each temperature.

Discussion

The k_{ex} and k_i values (Table I) characterizing $[Cu(Me_6tren)dmf]^{2+}$ indicate a $\sim 10^5$-fold reduction in the lability of this species toward solvent exchange and ligand substitution by comparison to $[Cu(dmf)_6]^{2+}$. The exchange of dmf and other solvents on $[Cu(solvent)_6]^{2+}$ is characterized by k_{ex} (298.2 K) > 10^7 s^{-1}, and ligand substitution on this species occurs with similar rapidity.[1-4] The lability of $[Cu(solvent)_6]^{2+}$ is greater than that expected for bivalent first-row transition-metal ions, and this is attributed to a tetragonal distortion (Jahn–Teller effect) that alternates rapidly over all three axes and produces a pairwise labilization of all six solvent molecules.[1,2] This source of labilization is not available to $[Cu(Me_6tren)dmf]^{2+}$ as the Jahn–Teller effect is inoperative in d^9 systems of C_{3v} symmetry. It is improbable that this alone accounts for the reduction of the lability of this species below that anticipated for a bivalent first-row transition-metal ion however, and it appears that structural effects are also important. On the basis of the solid-state structure of $[Cu(Me_6tren)Br]^+$, it is seen that the dmf coordination site in $[Cu(Me_6tren)dmf]^{2+}$ is in an annulus formed by the three NMe_2 groups of Me_6tren and is sterically shielded from interaction with an entering ligand. In addition to this effect, it is probable that the tripod Me_6tren ligand substantially reduces the degree of flexibility available in forming the transition state by comparison to that available to $[Cu(solvent)_6]^{2+}$. [It has been observed that the labilities of six-coordinate cobalt(II) and nickel(II) species usually exhibit substantial increases on coordination of amine groups.[3] The fact that such labilization is not observed for $[Cu(Me_6tren)dmf]^{2+}$ indicates in this case the greater importance of the factors reducing lability and emphasizes the complexity of the summation of factors controlling lability.]

There is persuasive evidence that positive and negative $\Delta V^{\ddagger}$ values are diagnostic of dissociative (d) and associative (a) activation modes, respectively,[12-14] as exemplified for dmf

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exchange on $[Cr(dmf)_6]^{3+}$ ($\Delta V^\ddagger = -6.3$ cm^3 mol^{-1})[15] and $[Ni(dmf)_6]^{2+}$ ($\Delta V^\ddagger = +9.1$ cm^3 mol^{-1}).[16] As these two species are of similar size to $[Cu(Me_6tren)dmf]^{2+}$ ($\Delta V^\ddagger = +6.1 \pm 0.1$ cm^3 mol^{-1}), characterizing this species is interpreted in terms of a d activation mode. Although it appears to be possible to discriminate between dissociative (D) and dissociative interchange (i_d) mechanisms from the magnitude of $\Delta V^\ddagger$ for water exchange, such does not appear to be the case for the more complicated dmf molecule.[13] Nevertheless, as $\Delta V^\ddagger$ observed for $[Ni(dmf)_6]^{2+}$ is larger than that for $[Cu(Me_6tren)dmf]^{2+}$, it is probable that the latter species is characterized by an I_d mechanism for dmf exchange. The negative $\Delta S^\ddagger$ value is at first sight unexpected for a d activated mechanism, but if solvent rearrangements outside the first coordination sphere and vibrational and rotational changes within the first coordination sphere together or separately make significant contributions to this parameter, then its sign becomes of dubious value in mechanistic interpretations.[17,18]

The general similarity of k_i characterizing anation by NCS^-, N_3^-, and Br^- to k_{ex} (Table I) suggests that dissociation of dmf from $[Cu(Me_6tren)dmf]^{2+}$ is the major rate-determining factor in the anation reaction. In view of this and the variation of k_{obsd} according to eq 6 it is probable that an I_d mechanism characterizes the anation of $[Cu(Me_6tren)dmf]^{2+}$. (A D mechanism would also be characterized by a rate law of similar form to eq 6, but as the opposite charges of $[Cu(Me_6tren)dmf]^{2+}$ and X^- render the formation of encounter complexes inevitable under the conditions of this study, experimental distinction between the D and I_d mechanisms is virtually impossible.) By contrast the anation of $[Cr(dmf)_6]^{3+}$ by X^-, which appears to be a classic example of the operation of an associative interchange (I_a) mechanism, is characterized by $k_i/k_{ex} = 0.088$, 1.03, 2.35, and 57.5 at 344.5 K when $X^- = Br^-$, Cl^-, NCS^-, and N_3^-, respectively.[19]

Acknowledgment. We thank the Australian Research Grants Committee for supporting this research and Professor A. E. Merbach of the University of Lausanne for making data available prior to publication.

Registry No. $[Cu(Me_6tren)dmf](ClO_4)_2$, 86632-76-0; NCS^-, 302-04-5; N_3^-, 14343-69-2; Br^-, 24959-67-9; dmf, 68-12-2.

Supplementary Material Available: P_mT_{2p} and $\Delta\omega$ values for dmf exchange on $[Cu(Me_6tren)dmf]^{2+}$ (Tables S1 and S2, respectively) and anation k_{obsd} values (Table S3) (6 pages). Ordering information is given on any current masthead page.

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Solvation and Ionic Association of Bis(2,4-pentanedionato)(diamine)cobalt(III) Complexes in Nitrobenzene and 1,2-Dichloroethane

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The conductances of 11 bis(2,4-pentanedionato)(diamine)cobalt(III) complexes ($[Co(acac)_2(diamine)]X$ where diamine = en (ethylenediamine), pn (1,2-propanediamine), *N,N*-dmen (*N,N*-dimethylethylenediamine), *N,N'*-dmen (*N,N'*-dimethylethylenediamine), *N,N,N'*-trimen (*N,N,N'*-trimethylethylenediamine), *N,N,N',N'*-tmen (*N,N,N',N'*-tetramethylethylenediamine), 2-ampy (2-(aminomethyl)pyridine), and bpy (2,2'-bipyridine) and where $X^- = ClO_4^-$ and I^-) were measured in nitrobenzene ($PhNO_2$) and 1,2-dichloroethane (1,2-DCE) at 25 °C. It was found that the mobilities of $[Co(acac)_2(diamine)]^+$ in $PhNO_2$ increase with the introduction of the *N*-methyl groups, whereas those in 1,2-DCE are approximately constant. The mobility of $[Co(acac)_2(bpy)]^+$ in $PhNO_2$ is more retarded than that in 1,2-DCE. The association constants decrease with the decrease in the number of the NH protons in both solvents except for $[Co(acac)_2(N,N'\text{-dmen})]ClO_4$ in $PhNO_2$. These results were explained in terms of the specific ion–solvent interactions: (a) the change in hydrogen-bonding activity of the NH protons in the chelate cations due to both the solvation and the desolvation accompanying the introduction of the substituents and (b) the π–π interaction between nitrobenzene and $[Co(acac)_2(bpy)]^+$.

Introduction

Metal chelate electrolytes, in which a metal cation is surrounded by aromatic and aliphatic ligands, have recently been noted as unique electrolytes. The characteristics of their solute–solvent interactions, concerning charge, size, and chemical properties of ligands, have been elucidated by the studies of salting in,[1] ion-pair extraction,[2] electronic spectra,[3] racemization,[4] optical resolution,[5] viscosity and molal volume,[6] and conductivity.[7-13] Among these, the conductivity measurements are useful as an effective means to understand the nature of

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