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Solvent Exchange on Hexakis(methanol)copper(II) Ion. ^{17}O NMR Variable-Temperature, -Pressure, and -Frequency Study

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A variable-pressure, -temperature, and -frequency ^{17}O FT NMR study of methanol exchange on $[Cu(MeOH)_6]^{2+}$ yields k_{ex}(298.2 K) = $(3.1 \pm 0.5) \times 10^7$ s^{-1}, $\Delta H^\ddagger = 17.2 \pm 0.8$ kJ mol^{-1}, $\Delta S^\ddagger = -44.0 \pm 4.0$ J K^{-1} mol^{-1}, and $\Delta V^\ddagger = +8.3 \pm 0.4$ cm^3 mol^{-1}. This $\Delta V^\ddagger$ value is the first reported for a solvent-exchange reaction on copper(II), and its positive value is consistent with the operation of a dissociative activation mode. These data are discussed in conjunction with the results for the analogous Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} systems.

Introduction

The high lability of the hexakis(solvent)copper(II) ion is considered to be a consequence of the tetragonal distortion arising from the operation of the Jahn–Teller effect in d^9 configurations.[2] In a combined ESR and NMR study Poupko and Luz[3] have shown that the tetragonal distortion of $[Cu(MeOH)_6]^{2+}$ alternates about the x, y, and z axes such that the mean lifetime of a particular tetragonal distortion is 1.2×10^{-11} s, while the mean lifetime of a particular methanol in $[Cu(MeOH)_6]^{2+}$ is 1.35×10^{-8} s at 298.2 K. Thus a given methanol in $[Cu(MeOH)_6]^{2+}$ experiences all orientations of the tetragonal distortion of the first coordination sphere many times prior to undergoing exchange with bulk methanol such that the six coordinated methanols are kinetically indistinguishable. It is reasonable to assume that the longer axial bonds in $[Cu(MeOH)_6]^{2+}$ should facilitate methanol exchange through a d-activation mode; however, because of their high lability $[Cu(solvent)_6]^{2+}$ species have been the subject of few mechanistic studies. The activation volume for solvent exchange, $\Delta V^\ddagger$, has proved to be particularly diagnostic of activation mode for solvent exchange on first-row transition-metal $[M(solvent)_6]^{2+}$ species,[4,5] but there has been no such reported study of a copper(II) or other tetragonally distorted species. Thus to gain further insight into the mechanism of solvent exchange on copper(II) a variable-pressure and -temperature ^{17}O NMR study of methanol exchange (during the course of which it was coincidentally found that the ^{17}O NMR transverse relaxation in this system was markedly frequency dependent) has been undertaken.

Experimental Section

Hydrated copper(II) triflate was prepared by the dropwise addition with stirring of 8.3 g of CF_3SO_3H (Fluka, 98%) to 2.2 g of CuO in 10 cm^3 of water. After subsidence of the vigorous reaction, residual CuO was filtered off and pale blue crystalline hydrated copper(II) triflate was obtained in ca. 90% yield after ca. 70% reduction of the filtrate volume. Tetrakis(methanol)copper(II) triflate was prepared by heating hydrated copper(II) triflate (2 g) with trimethyl orthoformate (6 g) with stirring at 315 K for 1 h in a round-bottomed flask fitted with a reflux condenser and silica gel guard tube. On cooling, the reaction mixture was transferred to a dry, nitrogen-flushed glovebox and the pale blue crystals were filtered off, washed with a 1:4 anhydrous ethanol/ether solution (20 cm^3) followed by an anhydrous ether solution, and dried on a vacuum line for 2 h (yield 54%). Anal. Calcd for $C_6H_{16}O_{10}S_2F_6Cu$: C, 14.71; H, 3.30; S, 12.93; F, 23.27; Cu, 12.97. Found: C, 14.60; H, 3.21; S, 12.93; F, 23.23; Cu, 12.88. Analysis for Cu was carried out by EDTA titration and analyses for other elements were by Analytische Laboratorien, Engelskirchen, FRG. ^{17}O-enriched (7.5%) methanol was prepared by a literature method[6] and was distilled from magnesium turnings and stored over Linde 3-Å molecular sieves prior to use. For the NMR study, a reference methanol solution and a sample methanol solution 3.37×10^{-3} mol kg^{-1} in copper(II), both containing 2×10^{-4} mol kg^{-1} CF_3SO_3H, were prepared by weight.

The temperature variation of the ^{17}O line width was determined at three different frequencies on Bruker FT NMR spectrometers: 8.13 (WP-60), 27.11 (CXP-200), and 48.80 MHz (WH-360). The sample was thermostated by using a Bruker VT-1000 thermostat, and temperature was measured with a Pt-100 resistance thermometer using a substitution technique.[7] The variation of the ^{17}O line width with pressure was determined on the CXP-200 instrument by using previously described high-pressure equipment.[8] The low temperatures were achieved by pumping methanol, thermostated with a LAUDA UK 80 DW cryostat, through the pressure vessel. The temperature stability was ±0.2 K. Depending on the temperature and pressure, up to 2000 transients were accumulated to achieve a good signal-to-noise ratio in the transformed spectra from which the line widths were determined.

Results

The temperature variation of the ^{17}O resonance of bulk MeOH arising from MeOH exchange on $[Cu(MeOH)_6]^{2+}$ was analyzed through eq 1,[9] in which P_m is the mole fraction of bound methanol,

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left(\frac{1}{T_2} - \frac{1}{T_{2A}}\right) = \frac{1}{\tau_m}\left[\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + (\Delta\omega_m)^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + (\Delta\omega_m)^2}\right] \quad (1)$$

$1/T_2$ and $1/T_{2A}$ are the half-widths at half-height of the ^{17}O resonance of bulk methanol in the $[Cu(MeOH)_6]^{2+}$ solution and the reference solution, respectively, T_{2m} is the transverse relaxation time of coordinated methanol, $\Delta\omega_m$ is the chemical shift between coordinated and bulk methanol in the absence of chemical exchange, and τ_m (= $1/k_{ex}$) is the residence time of a coordinated MeOH on $[Cu(MeOH)_6]^{2+}$ such that the rate of exchange = $6k_{ex}[Cu(MeOH)_6{}^{2+}]$. The ^{17}O spectrum of pure methanol is a doublet as a consequence of spin–spin coupling ($J(^{17}O–^{1}H) = 85.5$ Hz)[10] but in the reference sample (2×10^{-4} mol kg^{-1} in CF_3SO_3H) employed herein this doublet collapsed to a singlet as a result of rapid proton exchange. The temperature dependence of $1/T_{2A}$ may be described as the sum of two exponential functions.[11] No frequency dependence of $1/T_{2A}$ was found as expected for pure quadrupole-induced relaxation in small molecules. The normalized ^{17}O relaxation induced by $[Cu(MeOH)_6]^{2+}$, $1/T_{2r}$, was calculated

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(1) (a) Université de Lausanne. (b) University of Adelaide.

(2) West, R. J.; Lincoln, S. F. *J. Chem. Soc., Dalton Trans.* **1974**, 281–284.

(3) Poupko, R.; Luz, Z. *J. Chem. Phys.* **1972**, *57*, 3311–3318.

(4) Meyer, F. K.; Newman, K. E.; Merbach, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 5588–5592.

(5) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479–1493.

(6) Sawyer, C. B. *J. Org. Chem.* **1972**, *37*, 4225–4226.

(7) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319–321.

(8) Pisaniello, D. L.; Helm, L.; Meier, P.; Merbach, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 4528–4536.

(9) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307–320; **1964**, *41*, 2553–2554.

(10) Versmold, H.; Yoon, C. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 1164–1168.

(11) From the fit of our data to

$$1/T_{2A} = A_1 \exp(B_1/RT) + A_2 \exp(B_2/RT)$$

$A_1 = 34.2 \pm 29.8$ s^{-1}, $A_2 = 1.45 \pm 0.10$ s^{-1}, $B_1 = 1.37 \pm 2.57$ kJ mol^{-1}, and $B_2 = 11.15 \pm 0.56$ kJ mol^{-1}.

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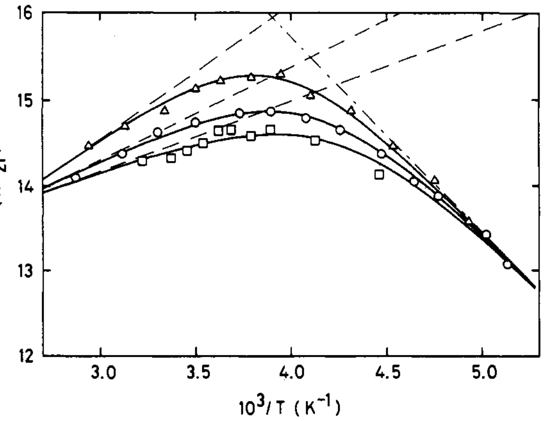

Figure 1. Variation of ln $(1/T_{2r})$ with temperature and frequency. Data obtained at 8.13, 27.11, and 48.80 MHz are shown as triangles, circles, and squares, respectively, and the solid curves represent the best fit of these data to eq 1.

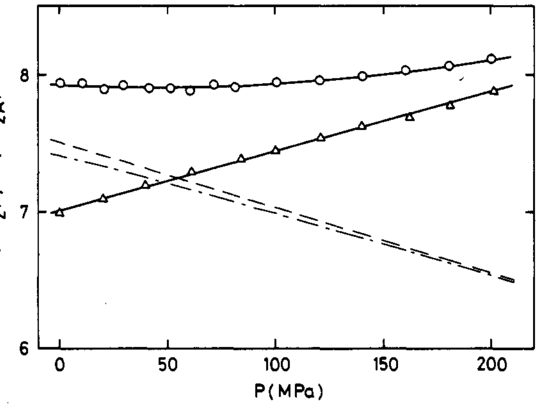

Figure 2. Variation of ln $(1/T_2)$ and ln $(1/T_{2A})$ shown as circles and triangles, respectively, with applied pressure at 210.6 K and 27.11 MHz. The solid curves drawn through the data points represent the simultaneous best fit of the data to eq 7 and 8. The dashed curves represent ln $(P_m/(\tau_m + T_{2m}))$ (--) and ln (P_m/k_{ex}) (---) calculated from this data fit.

through eq 1 and is plotted as a function of temperature in Figure 1. The curves drawn are derived through nonlinear least-squares fits of the $1/T_{2r}$ data to eq 1 in which k_{ex} is replaced by eq 2, $1/T_{2m}$ by eq 3[12] for scalar relaxation, and $\Delta\omega_m$ by eq 4[13] where $1/\tau_{e1}$

$$k_{ex} = (k_BT/h)\exp(\Delta S^{*}/R - \Delta H^{*}/RT) \qquad (2)$$

$$1/T_{2m} = \tfrac{1}{3}S(S+1)(2\pi A/h)^2\left(\tau_{e1} + \frac{\tau_{e2}}{1+\tau_{e2}^{2}\omega_s^{2}}\right) \qquad (3)$$

$$\Delta\omega_m = -\omega_I\frac{S(S+1)\gamma_e A}{\gamma_I(3kT)} \qquad (4)$$

$= 1/k_{ex} + 1/T_{1e}$ and $1/\tau_{e2} = 1/k_{ex} + 1/T_{2e}$, T_{1e} and T_{2e} are electron spin relaxation times, and all other symbols have their usual significance.[14] For copper(II) eq 3 approximates to eq 5.[3]

$$1/T_{2m} = \tfrac{1}{3}S(S+1)(2\pi A/h)^2T_{1e} \qquad (5)$$

Herein the simple exponential function 6 is used to describe the

$$T_{1e} = T_{1e}^{298}\exp[E_e/R(1/T - 1/298.2)] \qquad (6)$$

temperature dependence of T_{1e}. Because the frequency dependence of T_{1e} is not known, different values of E_e and T_{1e}^{298} were used to fit the ^{17}O data determined at the three frequencies. The reported[3] $A/h = 2.9 \times 10^7$ s^{-1} value was used in the data fitting.

The derived kinetic parameters for methanol exchange on $[Cu(MeOH)_6]^{2+}$ are $k_{ex}(298.2\ K) = (3.09 \pm 0.46) \times 10^7$ s^{-1}, $\Delta H^{*} = 17.16 \pm 0.81$ kJ mol^{-1} and $\Delta S^{*} = -43.96 \pm 3.95$ J K^{-1} mol^{-1}, which compare with $k_{ex}(298.2\ K) = 7.4 \times 10^7$ s^{-1}, $\Delta H^{*} = 24.0$ kJ mol^{-1} and $\Delta S^{*} = -10.9$ J K^{-1} mol^{-1} obtained by Poupko and Luz.[3] The origin of the differences between the kinetic parameters derived in the two studies is not apparent, but both data sets demonstrate the great lability of $[Cu(MeOH)_6]^{2+}$ toward methanol exchange. The values of the electron spin relaxation parameters E_e (kJ mol^{-1}) and T_{1e}^{298} (ns) are 12.95 ± 1.16 and 43.1 ± 1.8 at 8.13 MHz, 8.95 ± 0.75 and 28.5 ± 1.0 at 27.11 MHz, and 6.74 ± 0.89 and 22.8 ± 0.8 at 48.80 MHz, which compare with values of ca. 12 and ca. 59 obtained from the data of Poupko and Luz[3] at 8.13 MHz.

The ^{17}O variable-pressure measurements were carried out at 210.6 K and 27.11 MHz. Under these conditions $\Delta\omega_m << 1/T_{2m}$, and eq 1 after rearrangement approximates to eq 7 where the

$$1/T_2 = P_m/(\tau_m + T_{2m}) + 1/T_{2r} \qquad (7)$$

pressure dependencies are given by eq 8a–c. Two series of

$$1/\tau_m = k_{ex} = k_0\exp(-\Delta V^{*}P/RT) \qquad (8a)$$

$$1/T_{2A} = 1/T_{2A_0}\exp(-\Delta V_A^{*}P/RT) \qquad (8b)$$

$$1/T_{2m} = 1/T_{2m_0}\exp(-\Delta V_m^{*}P/RT) \qquad (8c)$$

variable-pressure measurements were carried out to determine ΔV^{*}. The first series determined the pressure variation of $1/T_{2A}$ for the methanol reference solution and the second determined the pressure dependence of $1/T_2$ for a 0.0205 mol kg^{-1} $[Cu(MeOH)_6]^{2+}$ solution. The pressure variations of these two parameters are shown in Figure 2. While the contribution of $1/T_{2m}$ to $P_m/(\tau_m + T_{2m})$ at 210.6 K is only about 10% at ambient pressure, which corresponds to a 5% contribution to $1/T_2$, the pressure variation of $1/T_{2m}$ (ΔV_m^{*}) should be taken into account in the calculation of ΔV^{*}, as seen from eq 7 and 8. However, ΔV_m^{*} cannot be separately determined from the available data, and accordingly the approximation $\Delta V_m^{*} = \Delta V_A^{*} = -7.62 \pm 0.10$ cm^3 mol^{-1} (determined from the pressure dependence of $1/T_{2A}$) was used in the calculation through eq 7 of $\Delta V^{*} = +8.34 \pm 0.35$ cm^3 mol^{-1} from the pressure dependence of $1/T_2$. In this calculation $1/T_{2m_0}$ was set equal to the value derived from the ambient-pressure variable-temperature data. The rate constant for methanol exchange at ambient pressure at 210.6 K, k_0 (=0.96 × 10^6 s^{-1}), and the corresponding $1/T_{2A_0}$ (=1101 s^{-1}) value calculated from the variable-pressure data are in reasonable agreement with $k_{ex} = 1.22 \times 10^6$ s^{-1} and $1/T_{2A} = 975$ s^{-1} calculated from the ambient-pressure variable-temperature data. The effect of the $\Delta V_m^{*} = \Delta V_A^{*}$ approximation on the derivation of ΔV^{*} was tested by setting ΔV_m^{*} equal to zero, which resulted in the derived ΔV^{*} value decreasing to +7.5 ± 0.3 cm^3 mol^{-1}. As this major change in ΔV_m^{*} results in only a small change in ΔV^{*}, it is clear that any error induced through the $\Delta V_m^{*} = \Delta V_A^{*}$ approximation will be small and accordingly the value $\Delta V^{*} = +8.34 \pm 0.35$ cm^3 mol^{-1} is employed in the ensuing discussion.

Discussion

The kinetic parameters characterizing methanol exchange on $[M(MeOH)_6]^{2+}$, where M = Mn, Fe, Co, Ni, and Cu, are given in Table I, from which it is apparent that $[Cu(MeOH)_6]^{2+}$ is by far the more labile species (previously attributed to the labilizing effect of the tetragonal distortion, which alternates rapidly over the *x*, *y*, and *z* axes[2,3]) but is characterized by a ΔV^{*} similar in magnitude to that of its Co analogue. The $\Delta V^{*} = +8.34 \pm 0.35$ cm^3 mol^{-1} value obtained for $[Cu(MeOH)_6]^{2+}$ is consistent with the operation of a d-activation mode for methanol exchange. This in turn is consistent with the tendency for the mechanism of solvent exchange on the first-row bivalent transition-metal ions to become increasingly dissociative in nature with increase in d-orbital electronic occupancy; a tendency that has been largely attributed to the consequent increase in electronic repulsion between the entering ligand and the t_{2g} electrons of the metal center.[4,5] It seems unlikely that the tetragonal distortion of $[Cu(MeOH)_6]^{2+}$ will

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(12) Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon: Oxford, England, 1961.

(13) Bloembergen, N. *J. Chem. Phys.* **1957**, *27*, 595–596.

(14) Monnerat, A. R.; Newman, K. E.; Merbach, A. E.; Boubel, J.-C.; Delpuech, J.-J.; Mathis, G. *Mol. Phys.* **1982**, *45*, 373–384.

Table I. Parameters for Methanol Exchange on $[M(MeOH)_6]^{2+}$

param	M Mn	 Fe	 Co	 Ni	 Cu
$k(298.2\ K)/s^{-1}$	$3.7 \times 10^{5\,a}$	$5.0 \times 10^{4\,a}$	$1.8 \times 10^{4\,b}$	$1.0 \times 10^{3\,b}$	$3.09 \times 10^{7\,c}$ $(7.4 \times 10^{7})^{d}$
$\Delta H^{\ddagger}/kJ\ mol^{-1}$	25.9^{a}	50.2^{a}	57.7^{b}	66.1^{b}	17.2^{c} $(24.9)^{d}$
$\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1}$	-50.2^{a}	12.6^{a}	30.1^{b}	33.5^{b}	-44.0^{c} $(-10.8)^{c}$
$\Delta V^{\ddagger}/cm^{3}\ mol^{-1}$	-5.0^{e}	0.4^{e}	8.9^{f}	11.4^{f}	8.3^{c}
r^{g}/pm	83	78	74.5	69	73

[a] Breivogel, F. W. *J. Chem. Phys.* **1969**, *51*, 445–449. [b] Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1964**, *40*, 2686–2692. [c] This work. [d] Reference 3. [e] Meyer, F. K.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 2142–2148. [f] Reference 4. [g] Effective six-coordination ionic radii from ref 24.

significantly alter the importance of this electronic effect on the mechanism, but it is nevertheless appropriate to consider other consequences that may flow from this distortion.

There appears to be no published structure of $[Cu(MeOH)_6]^{2+}$ determined in solution or in the solid state and hence no direct measure of the magnitude of the tetragonal distortion of this d^9 species. However it is reasonable to assume that the Cu–O bond distances in this species will be similar to the Cu–O(equatorial) and Cu–O(axial) distances of 198 and 239 pm respectively determined for $[Cu(OH_2)_6]^{2+}$ in aqueous 3 mol dm^{-3} perchlorate solution by Magini[15] using X-ray diffraction methods. (Tetragonal distortions of similar magnitude are also observed for $[Cu(OH_2)_6]^{2+}$ in the solid state.[15]) These distances may be compared with the metal–oxygen distances of 205.3 and 209.5 pm, respectively, quoted for octahedral $[Ni(OH_2)_6]^{2+}$[16] and $[Zn(OH_2)_6]^{2+}$[17] from which it is apparent that the Cu–O(equatorial) and Cu–O(axial) distances respectively represent a ca. 5% contraction and a ca. 15% extension of the bond distances expected for $[Cu(OH_2)_6]^{2+}$ in the absence of a tetragonal distortion and a similar structure is assumed for $[Cu(MeOH)_6]^{2+}$. Thus it is envisaged that $[Cu(MeOH)_6]^{2+}$ undergoes rapidly alternating tetragonal distortions, which not only have a labilizing effect but also cause the axial methanols to penetrate into the second coordination sphere to a greater extent than is the case for first coordination sphere methanol in octahedral $[M(MeOH)_6]^{2+}$. It is also envisaged that methanol exchange occurs through the axial sites with the elongation of the Cu–O(axial) bond in the ground state (by comparison to that anticipated for regular octahedral geometry) being an important contribution factor to the small $\Delta H^{\ddagger}$ exhibited by $[Cu(MeOH)_6]^{2+}$ (Table I). The formation of the transition state probably involves a further lengthening of one axial bond and the contraction of the other (with coincidental and compensatory changes in the bond distances and angles of the axial methanols) to produce an incipient five-coordinated intermediate species. These bonding changes occurring during the formation of the transition state from the tetragonally distorted ground state may differ substantially in direction and magnitude from those anticipated[16-18] for the octahedral d-activated species in Table I. Such differences may partially account for the negative $\Delta S^{\ddagger}$ characterizing $[Cu(MeOH)_6]^{2+}$, which contrasts with the positive values obtained for the other d-activated species in Table I. However it is possible that some of this difference in $\Delta S^{\ddagger}$ may arise from the effect of the tetragonal distortion on the interactions between the first and second coordination spheres. Connick and Alder[19] have described a two-dimensional model of the solvent-exchange process that incorporates the individual motions of 89 solvent molecules disposed around a metal ion. They deduce that exchange occurs by a highly collective motion involving many small displacements of the solvent in the first and second coordination spheres and that the leaving and entering solvent molecules are disposed between the two coordination spheres in the transition state. This model indicates a substantial interaction between the first and second coordination spheres in the solvent-exchange process, and hence any directional bonding effect, such as the rapidly alternating tetragonal distortion of $[Cu(MeOH)_6]^{2+}$, which causes that interaction to differ from that in otherwise similar octahedral $[M(MeOH)_6]^{2+}$ species, may generate differences in the activation parameters characterizing the solvent exchange process.

The prediction of the magnitude of $\Delta V^{\ddagger}$ for solvent-exchange processes has been the subject of considerable discussion,[20,21] and recently Swaddle and Mak[22,23] have noted that for water exchange on $[M(OH_2)_6]^{2+}$ there exists an inverse correlation of $\Delta V^{\ddagger}$ with the absolute partial molar volume of the hydrated metal ion, $\bar{V}_{abs}{}^{0}$. From this it is predicted that $\Delta V^{\ddagger}$ for $[Cu(OH_2)_6]^{2+}$ should be significantly less than that for its Ni analogue and similar to that for its Co analog. No $\Delta V^{\ddagger}$ data is available for $[Cu(OH_2)_6]^{2+}$; however, the trends in $\Delta V^{\ddagger}$ for $[M(MeOH)_6]^{2+}$ (M = Mn, Fe, Co, Ni) are similar to those exhibited by the analogous aquo ion series[4] and $[Cu(MeOH)_6]^{2+}$ is characterized by a $\Delta V^{\ddagger}$ value significantly less than that of its Ni analogue and similar to that of its Co analogue (Table I). These observations together with the similarity of the six-coordinate effective ionic radii calculated by Shannon,[24] r, of Co^{2+} and Cu^{2+} (Table I) indicate that r is an important characteristic affecting the solvent-exchange mechanism and therefore the value of $\Delta V^{\ddagger}$[18] (A similar deduction has been drawn from a classical electrostatic model of the transition state for solvent exchange on six-coordinate bivalent metal ions.[17]) The observation that $\Delta V^{\ddagger}$ for $[Cu(MeOH)_6]^{2+}$ fits smoothly into the mechanistic trend established for the preceding $[M(MeOH)_6]^{2+}$ species suggests that the tetragonal distortion does not have a major impact on the activation mode for solvent exchange despite its substantial enhancement of lability and possible generation of a negative $\Delta S^{\ddagger}$. Overall it appears that for $[Cu(MeOH)_6]^{2+}$, as for the preceding $[M(MeOH)_6]^{2+}$, the dominant metal-center characteristics determining the mechanism of solvent exchange are (i) the electronic occupancy of the d orbitals and (ii) the effective ionic radius. The mechanistic aspects of characteristic i have been discussed above. Characteristic ii substantially reflects the magnitudes of the bonding interactions between the metal center and the solvent, the interactions between coordinated solvent molecules, and the variations of bond distances and angles, which produce the minimum-energy transition state. For $[Cu(MeOH)_6]^{2+}$, the positive $\Delta V^{\ddagger}$ value is consistent with the operation of a d activation. The tetragonal distortion of this species imposes different constraints on the bonding variations possible in the transition state (by comparison to those imposed on the preceding $[M(MeOH)_6]^{2+}$); the net consequence is an increase in lability and a negative $\Delta S^{\ddagger}$ value, which may arise from both first and second coordination sphere effects.

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Registry No. $[Cu(MeOH)_6]^{2+}$, 25544-93-8; MeOH, 67-56-1.

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(15) Magini, M. *Inorg. Chem.* **1982**, *21*, 1535–1538.

(16) Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1980**, *19*, 2481–2482.

(17) Newman, K. E.; Adamson-Sharpe, K. E. *Inorg. Chem.* **1984**, *23*, 3818–3822.

(18) Swaddle, T. W. *Inorg. Chem.* **1980**, *19*, 3203–3205.

(19) Connick, R. E.; Adler, B. J. *J. Phys. Chem.* **1983**, *87*, 2764–2771.

(20) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303–323.

(21) Kitamura, Y. *Inorg. Chem.* **1985**, *24*, 2–3.

(22) Swaddle, T. W.; Mak, M. K. S. *Can. J. Chem.* **1983**, *61*, 473–480.

(23) Swaddle, T. W. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 95–138.

(24) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.