in the axial position. Structural studies completed on the related complexes $[Cu^{II}(tepa)X]^{z+}$ ($X = NO_3^-$,[11e] Me-Im[12]) show the same effect, where one Cu^{II}–N_{py} distance is ca. 0.18 Å longer than the others.

In contrast, the structure of $[Cu^{II}(tmpa)Cl]^+$ is very close to trigonal bipyramidal as indicated by the near equivalence of the Cu–N bond lengths and all related bond angles (Figure 2).[25] The analysis of important dihedral angles supports this description and contrasts greatly with that for the tepa complex.[26]

Physicochemical properties of **1** and **2** in solution are also consistent with the structural results and the differences described. $[Cu(tepa)Cl]PF_6$ shows a visible absorption band maximum at 665 nm (ϵ 200) with a low-energy shoulder (λ 967 nm, ϵ 48), while the spectrum of $[Cu(tmpa)Cl]PF_6$ has a reversed appearance with a band at 962 (ϵ 210) and a high-energy shoulder at 632 nm (ϵ 88) (CH_3CN solutions). These data are consistent with a square-pyramidal coordination for **1** and trigonal bipyramidal for **2**.[27] The electron spin resonance spectrum of frozen solutions of all pentacoordinate Cu(II) complexes of tepa exhibit typical axial spectra with well-resolved Cu hyperfine splittings in the parallel region.[28] On the other hand, **2** shows a reversal of parallel and perpendicular regions ($g_\parallel < g_\perp$) as expected for trigonal-bipyramidal Cu(II) compounds[29] and consistent with that observed in a number of Cu(II) complexes with tripod ligands.[13–15,27,30] Again, $[Cu^{II}(tmpa)X]^{z+}$ (z = 1, 2; X = Me-Im, N_3^-) exhibit analogous behavior.

There are also considerable differences in the redox behavior of **1** and **2**. Cyclic voltammetric experiments[31] indicate both chloride complexes are well-behaved and give quasi-reversible redox waves with $E_{1/2} = +0.17$ V for **1** and $E_{1/2} = -0.39$ V for **2**. The difference of 0.56 V in the reduction potential of these complexes could be explained in part by the expected relative instability of a Cu(I) analogoue of tmpa in which only five-membered chelate rings would be formed.[33] In a series of copper complexes containing tripod ligands, we have found that each change of a chelate ring from six to five membered results in a lowering of the Cu(II)–Cu(I) redox potential by ~0.2 V.[34]

In conclusion, Cu(II) complexes containing tripodal tetradentate ligands can have trigonal or tetragonal coordination environments depending on whether one or two methylene groups separate adjacent donor functions. These variations dictate differences in the electronic properties as manifested by the ESR and absorption spectra of these compounds. The complexes described thus provide a structural basis for variations observed in other studies of tripodal Cu(II) complexes.[13–15]

Continuing studies on these and related compounds will help to elucidate reactivity and structure–function relationships for the copper ion sites of redox-active proteins.

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Registry No. **1**, 82871-02-1; **2**, 82865-79-0.

Supplementary Material Available: Listings of positional and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, and bond angles (11 pages). Ordering information is given on any current masthead page.

(25) $[Cu(tmpa)Cl]PF_6$: orthorhombic space group *I2ab*; a = 14.924 (3), b = 16.632 (4), c = 17.346 (3) Å; V = 4305.6 (16) Å^3; Z = 8. An R value of 0.063 was obtained from refinement of 1793 independent reflections (Mo Kα, λ = 0.71069 Å).

(26) The shape determining angles e_1, e_2, and e_3 for **2** are 51.3, 53.0, and 52.6° compared to the values of $e_1 = e_2 = e_3 = 53.1°$ for an idealized trigonal-bipyramidal geometry. For **1**, e_1, e_2, and e_3 are 75.1, 71.8, and 11.6° compared to 75.7, 75.7, and 0.0° for an idealized square-based pyramid. See: Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

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(28) For **1**: $g_\parallel = 2.23$, $A_\parallel = 162 \times 10^{-4}$ cm^{-1} ($DMF-CHCl_3$).

(29) For **2**: $g_\parallel = 2.00$, $g_\perp = 2.19$, $A_\perp = 96 \times 10^{-4}$ cm^{-1}.

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(31) Dimethylformamide solvent; 0.11 M tetra-*n*-butylammonium hexafluorophosphate supporting electrolyte; glassy-carbon working electrode. Potentials are vs. NHE where ferrocene is used as calibrant.[32] Complex **2** is well-behaved with the peak current ratio i_a/i_c = 0.95 and cathodic to anodic peak separations approaching those of ferrocene. For **1**, a kinetic barrier to electron transfer is indicated by considerably larger peak separations that decrease with decreasing scan rate (180 mV at 50 mV/s) ($i_a/i_c \approx 0.8$).[34b]

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High-Pressure Temperature-Jump Evidence for an I_a Mechanism for Substitution Reactions of Manganese(II) in Aqueous Solution

Sir:

In a series of papers[1] Merbach and co-workers reported high-pressure NMR evidence for a gradual mechanistic changeover from I_a to I_d for solvent-exchange reactions on divalent octahedral first-row transition-metal ions. They reported[1–3] negative volumes of activation for the exchange of CH_3OH and H_2O on Mn(II) and positive values for the exchange of CH_3OH and H_2O on Fe(II) and for the exchange of CH_3OH, H_2O, CH_3CN, and DMF on Co(II) and Ni(II). These results were interpreted as evidence for I_a and I_d exchange mechanisms,[4] respectively, resulting in the mentioned gradual mechanistic changeover along the first-row transition-metal ions. The above series was recently extended to include the hexaaquated V(II) ion, for which a volume of activation of -4.1 ± 0.1 cm^3 mol^{-1} for the water-exchange process was reported.[5] This result further confirms the earlier observed tendency.[1]

Complex formation reactions of such solvated metal species are generally controlled by, or strongly related to, the solvent-exchange process. Only few pressure dependence studies of fast (T-jump) substitution reactions of divalent first-row

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Table I. Values of τ^{-1}, K, k_f, and k_d as Functions of Pressure at 21 °C[a]

pressure, bar	$10^{-2}\tau^{-1}$,[b] s^{-1}	$10^{-1}K$,[c] M	$10^{-5}k_f$, M^{-1} s^{-1}	$10^{-2}k_d$, s^{-1}
10	11.1 ± 0.8	53.1 ± 1.2	2.86 ± 0.18	5.39 ± 0.45
500	11.8 ± 1.2	48.2 ± 0.9	2.89 ± 0.27	6.01 ± 0.66
1000	12.5 ± 1.2	44.9 ± 0.9	2.96 ± 0.27	6.60 ± 0.67
1500	13.5 ± 1.6	43.0 ± 1.2	3.12 ± 0.28	7.27 ± 0.94
2000	13.7 ± 1.4	41.4 ± 1.5	3.11 ± 0.27	7.51 ± 0.90
$\Delta V^{\ddagger}$, cm^3 mol^{-1}		+3.0 ± 0.4[d]	−1.2 ± 0.2	−4.1 ± 0.4

[a] [Total Mn(II)] = 2×10^{-3} M; [total bpy] = 1×10^{-4} M; ionic strength = 0.3 M ($NaClO_4$); pH ~6.8. [b] Mean value of sixteen determinations. [c] Mean value of six determinations. [d] $\Delta \bar{V}$ value.

transition-metal ions have been reported to date.[6-10] These include typical complex formation reactions of Co(II) and Ni(II), for which a good correlation with the volume of activation for the solvent-exchange reaction was observed,[1] confirming the I_d character of the substitution process. Unfortunately, no pressure dependence study of complex formation reactions of Mn(II) has been reported to date to confirm the nature of such processes in comparison to the solvent-exchange results. In addition, such data would also indicate whether a similar changeover in mechanism is observed as in the case of solvent-exchange reactions. A thorough search and numerous preliminary measurements indicated that very few complex formation reactions of Mn(II) are indeed suitable for such a study.

One of these is the reaction with 2,2′-bipyridine (referred to as bpy hereafter) for which Hague and Martin[11] measured rate constants and activation parameters for the formation and dissociation of a 1:1 complex using the temperature-jump technique. We performed a pressure dependence study of this system using a recently constructed high-pressure temperature-jump instrument.[12] The overall reaction is given by

$$Mn(OH_2)_6^{2+} + bpy \underset{k_d}{\overset{k_f}{\rightleftharpoons}} Mn(bpy)(OH_2)_4^{2+} + 2H_2O$$

for which $\tau^{-1} = k_f([Mn(II)] + [bpy]) + k_d$, where [Mn(II)] and [bpy] represent the equilibrium concentrations of the free metal ion and free bpy, respectively. The relaxation time τ was measured as a function of pressure up to 2 kbar at constant [total Mn(II)] and [total bpy], for which the results are summarized in Table I. The error limits on τ^{-1} are higher than usually found in conventional high-pressure kinetics but are of the same order as generally observed for temperature-jump measurements at ambient pressure. The pressure dependence of the overall equilibrium constant K $(=k_f/k_d)$ was determined spectrophotometrically,[11,12] with a Zeiss DMR 10 spectrophotometer equipped with a conventional high-pressure cell,[13] and the results are included in Table I. The value of K at atmospheric pressure is slightly higher than that reported by Hague and Martin.[11] The pressure dependence of k_f (and therefore k_d) was estimated from the data in Table I by using the relationship

$$k_f = \tau^{-1}([Mn(II)] + [bpy] + K^{-1})^{-1}$$

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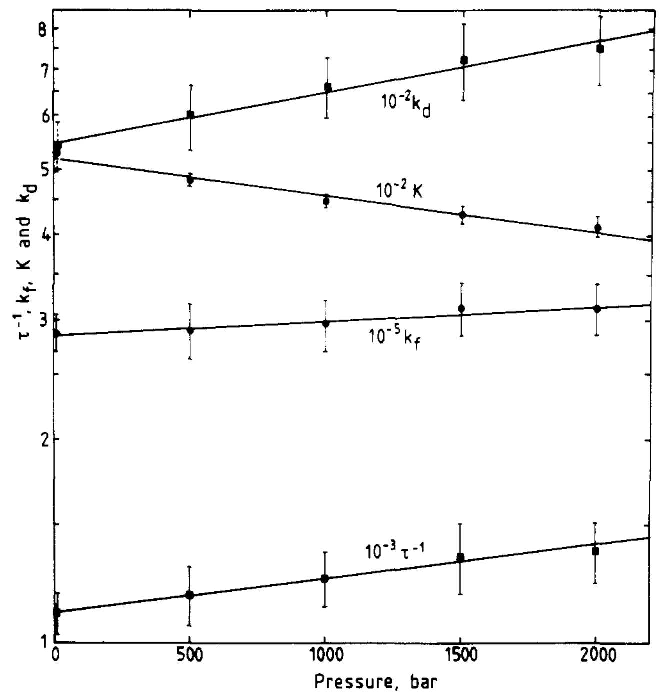

Figure 1. Plots of τ^{-1}, k_f, K, and k_d vs. pressure for the data in Table I.

The values of k_f and k_d at ambient pressure are in good agreement with those reported before.[11] Plots of ln (K, τ^{-1}, k_f, and k_d) vs. pressure (Figure 1) are linear within the experimental error limits, from which the reaction and activation volumes, respectively, were estimated in the usual way.

τ^{-1}, k_f, and k_d exhibit meaningful pressure dependences, and the corresponding volumes of activation (Table I) have relatively small error limits. Very significant is the negative sign of $\Delta V^{\ddagger}$ for k_f and k_d, which suggests the complex formation and reverse aquation process to be of the I_a type. In terms of such a mechanism[1] $k_f = K_{os}k$, where K_{os} is the outer-sphere complex formation constant and k the interchange rate constant, such that $\Delta V^{\ddagger}(k_f) = \Delta\bar{V}(K_{os}) + \Delta V^{\ddagger}(k)$. Fortunately, it can be assumed that $\Delta\bar{V}(K_{os})$ is negligible[1,14] for systems involving neutral ligands, such that $\Delta V^{\ddagger}(k_f)$ represents the volume of activation for the rate-determining interchange step. Although $\Delta V^{\ddagger}(k_f)$ is only a small value, it is significantly more negative than similar values reported[6] for complex formation reactions involving neutral ligands (NH_3 and pada) and Co(II) and Ni(II). This illustrates that the earlier observed changeover in mechanism from I_a to I_d for solvent-exchange reactions of first-row transition metal elements also occurs during complex formation (anation) reactions of such metal centers.

We are at present expanding these measurements to include complex formation reactions of Mn(II), Fe(II), Co(II), and Ni(II) with ligands such as 1,10-phenanthroline, bpy, and terpy (2,2′,2″-terpyridine).

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