complexes also yield values of approximately 3000 M^{-1} cm^{-1}.

The extraordinary decrease of the LMCT absorption energy from >24 000 cm^{-1} for imidazolate and related complexes[9b,11] of the $Cp(CO)_2Mn$ fragments to values below 12 000 cm^{-1} for the *p*-phenylenediamide(1−) complexes (Table II) may be rationalized by considering the simplified diagram in Figure 2. Increasing electron donation from ligand to metal corresponds to a strong destabilization of the occupied ligand π level and causes a less pronounced, indirect destabilization of the interacting metal orbital (ligand field effect).

Convergence of both levels in this model, which, among other factors, neglects Franck–Condon contributions, leads to a point of maximum orbital mixing and minimum excitation energy, from which on the transitions may be viewed as MLCT processes.[37] Convincing evidence for the LMCT character (IA,B) of the transitions summarized in Table II and against their formulation as $\pi^* \leftarrow d$ processes[13b] comes from a correlation between the absorption energies (in eV) and the ionization potentials of the protonated nitrogen ligands;[4,38] both processes involve the loss of one electron from the highest occupied π level of the ligand (Figure 3).

There is a reasonable correlation between both sets of data, justifying the use of the simple orbital scheme (IA,B). The deviation of the slope from unity can be attributed to the ligand field effect on the half-filled metal level in the case of the LMCT process (Figure 2). The absolute ligand field effect is by no means small as can be seen by the enormous cathodic shift in the oxidation potential of more than 2 V from complexes $Cp(CO)_3Mn$[39] to $[(C_5Me_5)(CO)_2(L)Mn]^-$, L = $-S$-*t*-Bu or $-NHC_6H_4Me$.[9b,26]

The *p*-phenylenediamide(1−) complexes do not show the pronounced solvatochromism that is often typical for charge-transfer transitions.[37b,40] The reason lies presumably in the considerably mixed metal/ligand character of the frontier orbitals (IA,B) so that external perturbations affect *both* levels and leave the difference little changed. This virtual insensitivity pertains also to the change from η-C_5H_4Me to η-C_5Me_5 coligands; in an MLCT situation there is a clear bathochromic shift on destabilization of the metal level by introducing methyl groups at the cyclopentadienyl ring.[36]

Summary. Despite preparative difficulties due to the intermediate nature of the species, we have succeeded in defining coordinatively simple, i.e. nonchelate, 1:1 complexes between the extremely σ- and π-electron-rich *p*-phenylenediamides(1−) and $[Cp(CO)_2Mn^{II}]^+$ fragments by EPR and electronic spectroscopy as systems with close-lying frontier orbitals of mixed metal/ligand character. These paramagnetic mononuclear species may be viewed as intermediates in reactions leading to diamagnetic binuclear *p*-quinone diimine or nitrene complexes. Notable metal-to-ligand spin transfer in the ground state as evidenced by reduced metal hyperfine splitting and detectable ligand superhyperfine splitting suggests the further use of the *p*-phenylenediamides(1−) as potentially noninnocent ligands in the fascinating intermediate area between paramagnetic transition-metal-centered species and genuine "radical" complexes, i.e., in the synthesis of truly delocalized open-shell coordination compounds. If a second oxidative deprotonation and binucleation can be avoided, e.g. by steric measures, the *p*-phenylenediamides(1−) may be considered as very suitable monodentate ligands for the stabilization of metals in high formal oxidation states.

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Registry No. 1, 99-98-9; 2, 110116-27-3; 3, 110095-89-1; 4, 110095-90-4; [Mn](THF), 86155-78-4; $(\eta^5$-$C_5H_4Me)(CO)_2Mn(THF)$, 51922-84-0; [Mn](PhNH), 110095-91-5; $(\eta^5$-$C_5H_4Me)(CO)_2(PhNH)Mn$, 110095-92-6; $[Mn](4$-$CH_3C_6H_4NH)$, 98104-74-6; $[Mn](4$-$NH_2C_6H_4NH)$, 110095-93-7; $[Mn](4$-$NMe_2C_6H_4NH)$, 110095-94-8; $(\eta^5$-$C_5H_4Me)(CO)_2(4$-$NMe_2C_6H_4NH)Mn$, 98104-73-5; $Cp(CO)_2(THF)Mn$, 12093-26-4; $Cp(CO)_2(Im)Mn$, 110116-28-4; $Cp(CO)_2(PhNH)Mn$, 97695-95-9; 4-$NH_2C_6H_4NH_2$, 106-50-3; $PhNH_2$, 62-53-3; 4-$MeC_6H_4NH_2$, 106-49-0.

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Kinetics of Acid-Catalyzed Dissociation of Copper(II) Diamino Diamide Complexes

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The dissociation kinetics of the copper(II) complexes of 4,7-diazadecanediamide (L-2,2,2), 5-methyl-4,7-diazadecanediamide (5-Me-L-2,2,2), 4,8-diazaundecanediamide (L-2,3,2), and 6-hydroxy-4,8-diazaundecanediamide (6-OH-L-2,3,2) have been studied at 25.0 °C and μ = 4.0 M ($NaClO_4$ + $HClO_4$) by the stopped-flow method. These reactions are specific-acid catalyzed; however, the rate constants of these reactions do not depend on the concentrations of acetic, chloroacetic, and dichloroacetic acids. At pH values below 1.4 both the proton-assisted and the direct protonation pathways make contributions to the rates. The ratios of the rate constant of dissociation by the direct protonation pathway to the rate constant by the proton-assisted pathway for the complexes with the 6,5,6-membered ring system are larger than those for the complexes with the 6,6,6-membered ring system. The reactions exhibit associative character.

Introduction

The kinetics of the reactions of copper(II) polyamine complexes are receiving considerable attention at present.[1] The earlier studies have been reviewed,[2] and recent work has focused on the acid-catalyzed dissociation of copper(II) polyamine complexes[3-12] and

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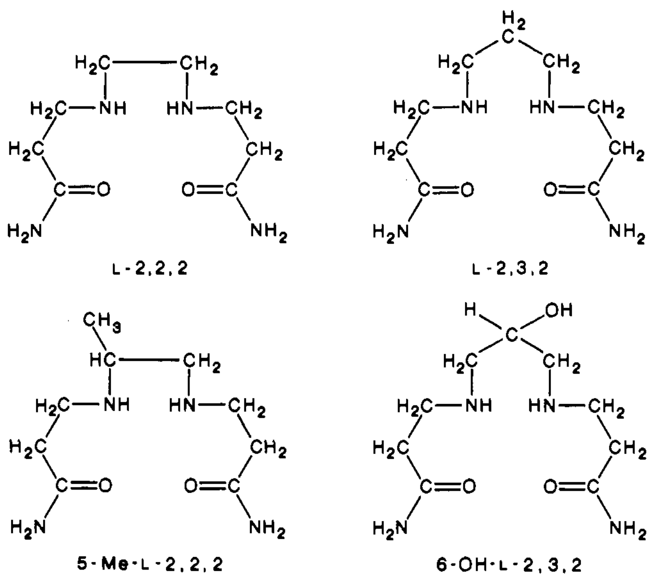
0020-1669/87/1326-3600$01.50/0

Chart I



the formation and isomerization reactions of copper(II) with cyclic tetraamines.[13-17]

Previously we have reported the protonation constants of the four closely related diamino diamides depicted in Chart I, the stability constants of copper(II) complexes of these ligands, and the complexation kinetics of these copper(II) complexes.[18] The purpose of this study is to investigate the specific- and general-acid dependences of the dissociation reactions of these four copper(II) diamino diamide complexes at low pH (eq 1).

$$CuL^{2+} + 2H^+ \rightarrow Cu^{2+} + H_2L^{2+} \qquad (1)$$

Experimental Section

Reagents. The complexes, Cu(L-2,2,2)$(ClO_4)_2$, Cu(5-Me-L-2,2,2)$(ClO_4)_2$, Cu(L-2,3,2)$(ClO_4)_2$, and Cu(6-OH-L-2,3,2)$(ClO_4)_2$, were the same as those reported previously.[19-24] All other chemicals used were of GR grade from Merck or Fluka.

Kinetic Measurements. The kinetics of the acid-catalyzed dissociation reactions of the copper complexes were followed at 25.0 ± 0.1 °C with the use of a Union Giken RA-401 stopped-flow spectrtophotometer equipped with a Union RA-415 rapid-scan attachment. Absorbance vs. time data were collected at 645, 645, 658, and 658 nm for the dissociation reactions of Cu(L-2,2,2)$^{2+}$, Cu(5-Me-L-2,2,2)$^{2+}$, Cu(L-2,3,2)$^{2+}$, and Cu(6-OH-L-2,3,2)$^{2+}$, respectively. Pseudo-first-order conditions were maintained by using at least a 10-fold excess of acid in each run. Good first-order kinetics were observed in all cases. The rate constants were obtained by a linear least-squares fit for the data by using the CDC Cyber-172 computer. Recrystallized $NaClO_4$ was used to maintain constant ionic strength at μ = 4.0 M in all solutions. The concentration of complexes employed for the kinetic work is 5.00×10^{-3} M. The concentrations of acid are in the range 0.05–2.00 M.

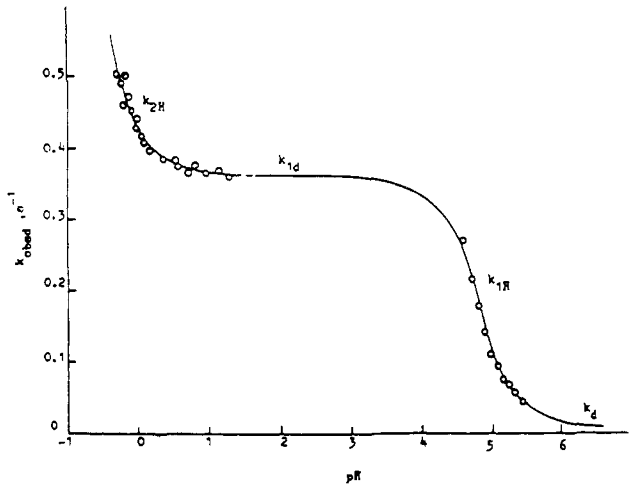


Figure 1. pH dependence for the dissociation of Cu(L-2,3,2)$^{2+}$ at 25.0 ± 0.1 °C.

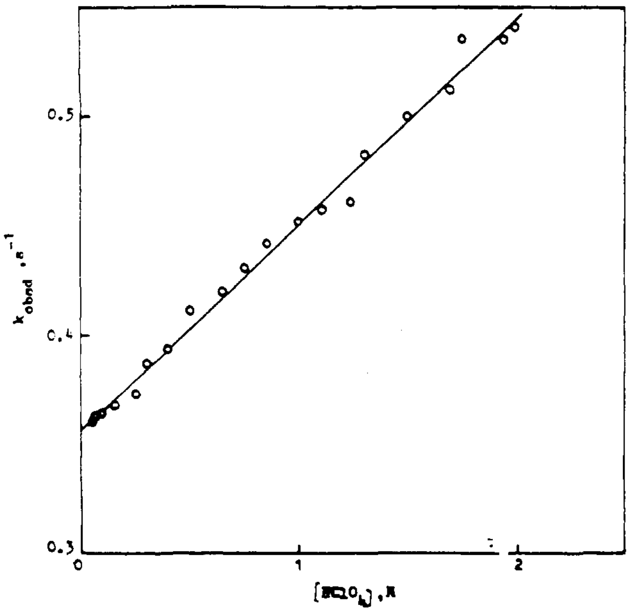


Figure 2. Plot of k_{obsd} vs. [H$^+$] for the dissociation of Cu(L-2,3,2)$^{2+}$ at 25.0 ± 0.1 °C and μ = 4.0 M ($NaClO_4$ + $HClO_4$).

Results

The kinetics of the dissociation reactions of these copper(II) diamino diamide complexes were studied at 25.0 °C, with μ = 4.0 M ($HClO_4$ + $NaClO_4$), and in 0.05–2.00 M $HClO_4$. Under these conditions, the dissociation reactions of these complexes were found to proceed to completion, and the observed pseudo-first-order rate constants are given in Table I. The pH dependence for the dissociation reaction of Cu(L-2,3,2)$^{2+}$ is shown in Figure 1.

The symbols of the rate constants k_d, k_{1H}, k_{1d}, and k_{2H} in this figure are the same as those used by Read and Margerum.[25] Plots of k_{obsd} vs. [H$^+$] give straight lines according to eq 2.

$$k_{obsd} = k_{1d} + k_{2H}[H^+] \qquad (2)$$

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Table I. Kinetic Data for the Dissociation of Copper(II) Diamino Diamide Complexes in Acid at 25.0 ± 0.1 °C and μ = 4.0 M ($NaClO_4$ + $HClO_4$)

complex	acid	$[HB]_T$, M	$[H^+]$, M	k_{obsd}, s^{-1}	complex	acid	$[HB]_T$, M	$[H^+]$, M	k_{obsd}, s^{-1}
$Cu(L\text{-}2,2,2)^{2+}$ [a]	H_3O^+		0.050	0.268 ± 0.002	$Cu(L\text{-}2,3,2)^{2+}$ [c]	H_3O^+		0.050	0.361 ± 0.002
			0.075	0.271 ± 0.002				0.075	0.363 ± 0.003
			0.10	0.274 ± 0.002				0.10	0.365 ± 0.002
			0.15	0.282 ± 0.003				0.15	0.368 ± 0.003
			0.25	0.290 ± 0.003				0.25	0.374 ± 0.004
			0.35	0.295 ± 0.004				0.35	0.386 ± 0.004
			0.40	0.302 ± 0.003				0.40	0.394 ± 0.003
			0.50	0.311 ± 0.004				0.50	0.412 ± 0.003
			0.65	0.320 ± 0.003				0.65	0.424 ± 0.003
			0.75	0.332 ± 0.003				0.75	0.431 ± 0.002
			0.85	0.346 ± 0.004				0.85	0.442 ± 0.004
			1.00	0.360 ± 0.002				1.00	0.452 ± 0.003
			1.10	0.365 ± 0.003				1.10	0.456 ± 0.003
			1.25	0.371 ± 0.004				1.25	0.461 ± 0.004
			1.40	0.386 ± 0.004				1.40	0.483 ± 0.004
			1.50	0.411 ± 0.003				1.50	0.501 ± 0.003
			1.65	0.426 ± 0.004				1.65	0.526 ± 0.004
			1.75	0.440 ± 0.005				1.75	0.534 ± 0.003
			1.85	0.445 ± 0.003				1.85	0.537 ± 0.003
			2.00	0.451 ± 0.004				2.00	0.541 ± 0.004
	CH_3COOH	0.0971	1.00	0.373 ± 0.003		CH_3COOH	0.0971	1.00	0.435 ± 0.004
		0.243	1.00	0.368 ± 0.002			0.243	1.00	0.426 ± 0.005
		0.586	1.00	0.358 ± 0.004			0.586	1.00	0.438 ± 0.003
		0.998	1.00	0.341 ± 0.005			0.998	1.00	0.422 ± 0.004
	$CH_2ClCOOH$	0.1921	1.00	0.368 ± 0.003		$CH_2ClCOOH$	0.1921	1.00	0.443 ± 0.003
		0.9603	1.00	0.351 ± 0.004			0.9603	1.00	0.435 ± 0.004
		1.509	1.00	0.342 ± 0.004			1.509	1.00	0.421 ± 0.004
		2.003	1.00	0.346 ± 0.005			2.003	1.00	0.430 ± 0.005
	$CHCl_2COOH$	0.1941	1.00	0.371 ± 0.004		$CHCl_2COOH$	0.1941	1.00	0.436 ± 0.003
		0.9708	1.00	0.362 ± 0.003			0.9708	1.00	0.431 ± 0.004
		1.402	1.00	0.353 ± 0.003			1.402	1.00	0.426 ± 0.004
		1.726	1.00	0.341 ± 0.005			1.726	1.00	0.402 ± 0.003
$Cu(5\text{-}Me\text{-}L\text{-}2,2,2)^{2+}$ [b]	H_3O^+		0.050	0.125 ± 0.002	$Cu(6\text{-}OH\text{-}L\text{-}2,3,2)^{2+}$ [d]	H_3O^+		0.050	3.14 ± 0.03
			0.075	0.126 ± 0.002				0.075	3.16 ± 0.03
			0.10	0.127 ± 0.002				0.10	3.20 ± 0.04
			0.15	0.132 ± 0.003				0.15	3.27 ± 0.03
			0.25	0.136 ± 0.003				0.25	3.35 ± 0.02
			0.35	0.138 ± 0.004				0.35	3.40 ± 0.04
			0.40	0.140 ± 0.003				0.40	3.43 ± 0.03
			0.50	0.145 ± 0.004				0.50	3.54 ± 0.04
			0.65	0.150 ± 0.003				0.65	3.59 ± 0.03
			0.75	0.154 ± 0.003				0.75	3.62 ± 0.04
			0.85	0.161 ± 0.003				0.85	3.80 ± 0.03
			1.00	0.167 ± 0.004				1.00	3.92 ± 0.04
			1.10	0.169 ± 0.003				1.10	3.96 ± 0.03
			1.25	0.172 ± 0.004				1.25	4.05 ± 0.03
			1.40	0.183 ± 0.004				1.40	4.18 ± 0.04
			1.50	0.190 ± 0.003				1.50	4.31 ± 0.04
			1.65	0.192 ± 0.003				1.65	4.36 ± 0.03
			1.75	0.194 ± 0.003				1.75	4.41 ± 0.03
			1.85	0.203 ± 0.004				1.85	4.56 ± 0.03
			2.00	0.213 ± 0.004				2.00	4.65 ± 0.04
	CH_3COOH	0.0971	1.00	0.169 ± 0.004		CH_3COOH	0.0971	1.00	4.02 ± 0.03
		0.243	1.00	0.162 ± 0.003			0.243	1.00	3.95 ± 0.04
		0.586	1.00	0.158 ± 0.004			0.586	1.00	4.03 ± 0.05
		0.998	1.00	0.160 ± 0.003			0.998	1.00	3.92 ± 0.03
	$CH_2ClCOOH$	0.1921	1.00	0.172 ± 0.003		$CH_2ClCOOH$	0.1921	1.00	4.05 ± 0.03
		0.9603	1.00	0.165 ± 0.004			0.9603	1.00	4.01 ± 0.04
		1.509	1.00	0.169 ± 0.003			1.509	1.00	4.02 ± 0.03
		2.003	1.00	0.158 ± 0.004			2.003	1.00	3.96 ± 0.04
	$CHCl_2COOH$	0.1941	1.00	0.168 ± 0.003		$CHCl_2COOH$	0.1941	1.00	4.04 ± 0.03
		0.9708	1.00	0.153 ± 0.002			0.9708	1.00	4.00 ± 0.04
		1.402	1.00	0.158 ± 0.003			1.402	1.00	3.98 ± 0.03
		1.726	1.00	0.155 ± 0.004			1.726	1.00	3.92 ± 0.04

[a] $[Cu(L\text{-}2,2,2)^{2+}]$ = 5.00 × 10^{-3} M; λ = 645 nm. [b] $[Cu(5\text{-}Me\text{-}L\text{-}2,2,2)^{2+}]$ = 5.00 × 10^{-3} M; λ = 645 nm. [c] $[Cu(L\text{-}2,3,2)^{2+}]$ = 5.00 × 10^{-3} M; λ = 658 nm. [d] $[Cu(6\text{-}OH\text{-}L\text{-}2,3,2)^{2+}]$ = 5.00 × 10^{-3} M; λ = 658 nm.

The plot for the dissociation reaction of $Cu(L\text{-}2,3,2)^{2+}$ is shown in Figure 2; the other complexes show a similar behavior. The values of k_{1d} and k_{2H} obtained in these plots are listed in Table II together with the values of k_d and k_{1H} for these copper(II) complexes reported previously.[18] In contrast with the behavior of $Ni(en)^{2+}$,[25] results given in Table I indicate that the rates of the dissociation reactions of these copper(II) complexes do not depend on the concentrations of acetic, chloroacetic, and dichloroacetic acids.

Discussion

The acid dissociation reactions of metal polyamine complexes have been studied extensively.[2] These reactions are catalyzed by specific and general acids, and the results have been explained

Table II. Summary of Measured Rate Constants Defined in Terms of the Rate Constants for Individual Steps in the Dissociation of Cu(II) Diamino Diamide Complexes at 25.0 °C

measd rate const	mechanistic rate const	Cu(L-2,2,2)$^{2+}$	Cu(L-2,3,2)$^{2+}$	Cu(5-Me-L-2,2,2)$^{2+}$	Cu(6-OH-L-2,3,2)$^{2+}$
k_d, s^{-1} [a]	$(k_1k_2/k_{-1}k_{-2})k_3$	8.81×10^{-5}	7.94×10^{-3}	5.35×10^{-5}	6.64×10^{-2}
k_{1d}, s^{-1} [b]	$(k_1/k_{-1})k_2$	0.263	0.355	0.123	3.13
k_{1H}, M^{-1} s^{-1} [a]	$(k_1k_2/k_{-1}k_{-2})k_4$	7.56	8.21×10^3	6.24	1.38×10^4
k_{2H}, M^{-1} s^{-1} [b]	$(k_5/k_{-5})k_6$	0.0957	0.0968	0.0426	0.758
k_{2H}/k_{1d}, M^{-1}		0.364	0.273	0.346	0.242
k_{1d}/k_d	k_{-2}/k_3	2.98×10^3	4.47×10^1	2.30×10^3	4.71×10^1
k_{1d}/k_{1H}, M	k_{-2}/k_4	3.48×10^{-2}	4.32×10^{-5}	1.97×10^{-2}	2.27×10^{-4}
k_{1H}/k_d, M^{-1}	k_4/k_3	8.58×10^4	1.03×10^6	1.17×10^5	2.08×10^5

[a] μ = 0.1 M ($NaClO_4$). [b] μ = 4.0 M ($NaClO_4$ + $HClO_4$).

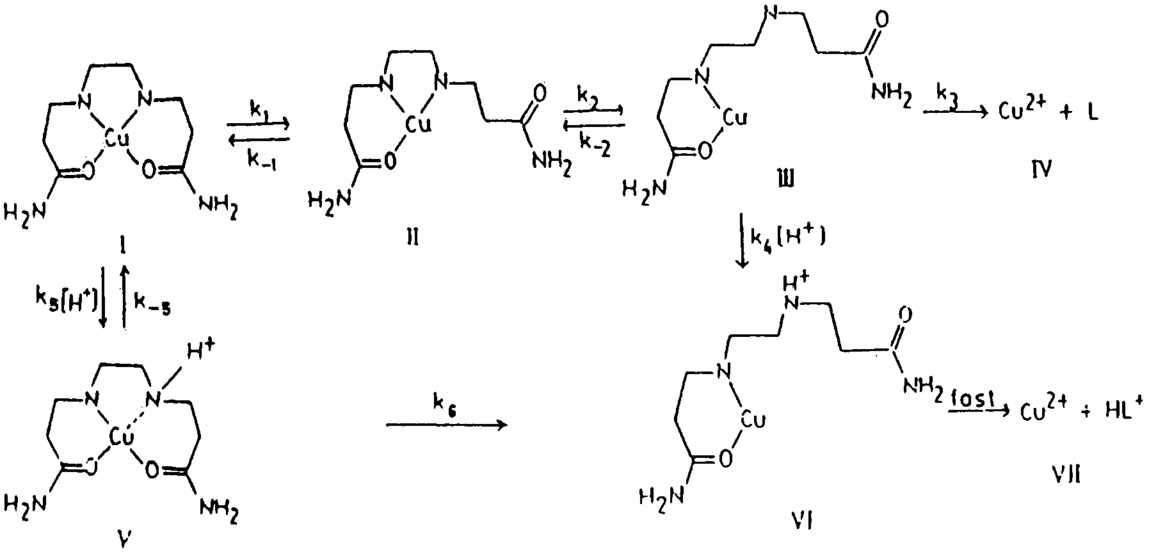

Figure 3. Proposed mechanism for the dissociation reactions of copper(II) diamino diamide complexes.

by a general mechanism proposed by Margerum and co-workers.[2,25] Unlike the reactions of metal polyamine complexes, the dissociation reactions of the copper diamino diamide complexes are not catalyzed by general acids. As shown in Table I, the values of the dissociation rate constants do not increase with the concentrations of acetic, chloroacetic and dichloroacetic acids. A modification of the mechanism proposed by Margerum and co-workers[2,25] to explain these results is shown in Figure 3. The symbols of rate constants are the same as those used by Margerum and co-workers in the dissociation reactions of nickel(II) polyamine complexes.[25] The measured rate constants for these dissociation reactions are summarized in Table II and are defined in terms of the mechanistic rate constants shown in Figure 3.

Without the assistance of acid (pH >6), the water dissociation reactions of these complexes are very slow, and the main pathway is represented by the sequence I → II → III → IV, where the rate-determining step is the breakage of the second copper–nitrogen bond (III → IV), and the overall rate constant for this solvent dissociation pathway, k_d, corresponds to $k_1k_2k_3/k_{-1}k_{-2}$. Individual steps in the unwrapping of damino diamide from copper(II) are not slow, but unless the reaction is assisted by acid, the successive equilibria leading up to the cleavage of the second copper–nitrogen bond are very unfavorable and a slow dissociation rate results.

Between pH 3.8 and 6, where acid helps to speed the dissociation reaction by protonation of the released amine group (III → VI), the main pathway is the proton-assisted pathway (I → II → III → VI → VII). At pH >3.8, $k_4[H^+] < k_{-2}$, the rate-determining step for this proton-assisted pathway is the protonation of the released amino group (III → VI), and the overall rate constant, k_{1H}, corresponds to $k_1k_2k_4/k_{-1}k_{-2}$. At pH <3.8, $k_4[H^+] > k_{-2}$ and the breakage of the first copper–nitrogen bond (II → III) becomes rate-determining for this pathway with the limiting rate constant k_{1d}, which corresponds to k_1k_2/k_{-1}.

At very low pH (pH <1.4), both the proton-assisted pathway (I → II → III → VI → VII) and the direct protonation pathway (I → V → VI → VII) make contributions to the rates of these reactions. For the direct protonation pathway, the rate-determining step is V → VI and the overall rate constant, k_{2H}, corresponds to k_5k_6/k_{-5}.

At high acid concentrations, the values of the rate constants of these dissociation reactions depend solely on the hydrogen ion concentration and not at all on the amount of acetic, chloroacetic and dichloroacetic acids present in the solution (Table I). The direct protonation pathway of these specific-acid-catalyzed reactions involves a rapid equilibration of the copper complexes with hydrogen ion to form a protonated species, V, which then in a slow, rate-determining step reacts to give VI. The last step of this pathway (VI → VII) is fast.

The rate constants k_d and k_{1H} for these complexes depend heavily on the nature of the diamino diamide, the leaving group, and vary over some 3 orders of magnitude. In contrast, the rate constants k_{1d} and k_{2H} are very insensitive to the nature of the leaving group. These constants span less than a factor of 26. These results suggest that in the step II → III and the step V → VI the Cu–N and Cu–O bonds only partially break in the transition states. If the cleavages of the Cu–N and Cu–O bonds were complete in these transition states, the steric constraints among linked consecutive chelate rings would be relieved, and the rate constants for the complexes with the 6,6,6-membered ring system should be much larger than those for the complexes with the 6,5,6-membered ring system. Thus the results listed in Table II indicate the degree of bond breaking in each of these steps is small, and these reactions are probably of associative activation. In addition, the fact that the measured rate constants for Cu(5-Me-L-2,2,2)$^{2+}$ are smaller than those for Cu(L-2,2,2)$^{2+}$ also indicate these reactions exhibit associative character.

The ratio k_{2H}/k_{1d} represents the relative rate of dissociation at high acid concentration by the direct protonation and the proton-assisted pathways. The results tabulated in Table II indicate that the ratios for the complexes with the 6,5,6-membered ring system are larger than those with the 6,6,6-membered ring system. As pointed out by Read and Margerum,[25] if the donor is unrestricted and able to move easily out of the first coordination sphere, the presence of acid has little effect. However, if the movement of the donor away from the metal ion is hindered in some way, acid can enhance the rate of dissociation. The restrictions holding the donor in the first coordination sphere imposed by the 6,5,6-membered chelate rings are larger than those imposed by the 6,6,6-membered chelate rings. Consequently, ring opening is easier for the 6,6,6-membered rings, making the direct protonation pathway less important.

For copper(II) complexes of macrocyclic tetraamines, the restrictions imposed by the macrocyclic ligand hold the donor atoms strongly in the first coordination sphere. Consequently, the direct protonation pathway becomes very important for the dissociation reactions of these complexes; therefore, the ratio of the rate constant of dissociation by the direct protonation pathway to the rate constant by the proton-assisted pathway for the macrocyclic ligand complex in planar coordination is extremely large.[3,5]

The results tabulated in Table II indicate that the ratios of k_4/k_3 for the complexes with the 6,6,6-membered ring system are slightly larger than those with the 6,5,6-membered ring system. This is attributed to the difference in the distance between the uncoordinated amino group and the metal ion in III (Figure 3). The additional methylene group in the complex with the 6,6,6-membered ring system increases the distance between the released amino group and the metal ion; thus, protonation of the released amino group (III → VI) is faster for the complex with the 6,6,6-membered ring system.

The values of the ratios k_{-2}/k_3 and k_{-2}/k_4 tabulated in Table II indicate that these ratios for the complexes with the 6,5,6-membered ring system are much larger than those with the 6,6,6-membered ring system. This is related to two factors: (1) the ring strain in linked consecutive rings and (2) the proximity effect. The ring strains in linked consecutive 6-membered rings are very large;[29] thus, the formation of the second Cu-N bond (III → V in Figure 3) for the complex with a center 6-membered ring is much slower than that with a 5-membered ring. In addition, the proximity effect also favors the formation of the center 5-membered chelate ring.[2] Consequently, the ratios k_{-2}/k_3 and k_{-2}/k_4 for the complexes with the 6,5,6-membered ring system are much larger than those with the 6,6,6-membered ring system.

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Electrochemical Oxidation of Hydroxide Ion in Acetonitrile and Its Facilitation by Transition-Metal Complexes

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The oxidation of hydroxide ion and phenoxide ion in acetonitrile has been characterized by cyclic voltammetry at glassy-carbon electrodes. In the presence of transition-metal complexes $M^{II}L^{2+}$ [M = Mn, Fe, Co, Ni; L = $(OPPh_3)_4$, $(2,2'\text{-bipyridine})_3$] and metalloporphyrins M(por) [M = Mn(III), Fe(III), Co(II); por = 5,10,15,20-tetraphenylporphinato(2−), 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphinato(2−)] the oxidation potentials for ^-OH and PhO^- are shifted to less positive potentials. This is due to the stabilization of the oxy radical products ($^{\bullet}OH$ and $PhO^{\bullet}$) via formation of a d-p ($d^n{-}^{\bullet}OR$) covalent bond. With excess ^-OH relative to the metal complex, oxidation of ^-OH is facilitated by an ECE mechanism [$ML(^-OH) \xrightarrow{-e^-} ML(^{\bullet}OH) \xrightarrow{^-OH} ML(O^{\bullet -})(OH_2) \xrightarrow{-e^-} ML(O^{2\bullet})(OH_2)$].

The electrochemical oxidation of ^-OH in aqueous[1] and aprotic[2-4] solvents along with the chemical reactivity of ^-OH with various substrates (e.g., CCl_4,[5] anthraquinone,[6] and $Fe^{III}(TPP)^+$ in pyridine[7]) indicates that ^-OH is an effective one-electron reductant. Other investigations have shown that the oxidations of metal-catechol[8-10] and metal-dithiolate[11] complexes are ligand-centered rather than metal-centered. In the latter investigation ligand oxidation is facilitated via formation of a d-p covalent bond (from an unpaired p electron of oxidized ligand and an unpaired d electron of the transition-metal center).

These observations have prompted us to examine the electrochemical oxidation of ^-OH and the effect of transition-metal complexes upon the electron-transfer potential. A specific goal has been to establish that the activated iron-oxygen intermediates of cytochrome P-450, peroxidase, and catalase involve 0-valent and −1-valent oxygen rather than iron(IV) or porphyrin radical (on the basis of their respective redox thermodynamics).

Experimental Section

Equipment. Cyclic voltammetry and controlled-potential electrolysis were accomplished with a Bioanalytical Systems Model CV-27 and a Houston Instruments Model 200 XY recorder. The electrochemical measurements were made with a microcell assembly (10-mL capacity) that was adapted to use a glassy-carbon working electrode, a platinum-wire auxiliary electrode (contained in a glass tube with a medium-porosity glass frit and filled with a concentrated solution of supporting electrolyte), and a Ag/AgCl reference electrode (filled with aqueous tetramethylammonium chloride solution and adjusted to 0.000 V vs SCE)[12] with a solution junction via a glass tube closed with a cracked-glass bead that was contained in a luggin capillary. A platinum-mesh working electrode and a platinum-wire auxiliary electrode were used for the controlled-potential electrolysis experiments.

Chemicals and Reagents. Acetonitrile (MeCN), "distilled-in-glass" grade (0.004% H_2O) from Burdick and Jackson, was used without further purification. Tetraethylammonium perchlorate (TEAP) was vacu-

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