ometry. The observed $\alpha \rightarrow \beta$ photoisomerization seems to require that the two non-tren ligands (Br and H_2O) simply exchange positions (Scheme I). Intramolecular exchange seems unlikely, but the mechanism for this photoisomerization is not known.

Photolysis of α-$[Rh(tren)(H_2O)Br]^{2+}$ may cause labilization of the coordinated water at site Y; photoinduced water exchanges at Rh(III) centers are known[42] and have been shown to occur with isomerization.[40] Loss of H_2O would lead to a square-pyramid $\{[Rh(tren)Br]^{3+}\}^*$ excited state, and rapid distortion of this species toward a C_{3v} geometry before attack of solvent water would lead to β-$[Rh(tren)(H_2O)Br]^{2+}$.

Photolabilization of the ligand at site Y conflicts with the tren-directed-photochemistry model proposed earlier, but electronic factors may favor H_2O photolabilization over Br^- loss in these complexes. Photolysis of the *cis*-$[Rh(N_4)(H_2O)Br]^{2+}$ ions efficiently generates *trans*-$[Rh(N_4)(H_2O)Br]^{2+}$ for $N_4 = (NH_3)_4$ ($\phi = 0.50$),[36b,c] $(en)_2$ ($\phi = 0.95$),[33b] and bis(1,3-diaminopropane) ($\phi = 0.55$).[37] These reactions presumably involve water exchange, so a photoinduced isomerization of α-$[Rh(tren)(H_2O)Br]^{2+}$ to the β form could also involve a water-exchange step. It is interesting to note that while the *cis*-$[Rh(N_4)(H_2O)Cl]^{2+}$ analogues (N_4 = $(NH_3)_4$,[36b,c] $(en)_2$,[33b] bis(1,3-diaminopropane)[37]) also photoisomerize (presumably via water exchange), photolysis of α-$[Rh(tren)(H_2O)Cl]^{2+}$ causes chloride labilization.[12]

To maintain the tren-directed-photochemistry model, one is forced to propose a reaction path in which photoinduced Br^- labilization (generating $[Rh(tren)(H_2O)_2]^{3+}$ and Br^-) is followed by *rapid* Br^- anation of the nascent diaquo ion. Bromide anation of independently prepared $[Rh(tren)(H_2O)_2]^{3+}$ does lead to β-$[Rh(tren)(H_2O)Br]^{2+}$, but the reaction requires several hours at 50 °C; photoisomerization of α-$[Rh(tren)(H_2O)Br]^{2+}$ proceeds quickly, with isosbestics, at room temperature and below. Seeking spectroscopic evidence for a diaquo intermediate, we attempted to slow the anation by photolyzing α-$[Rh(tren)(H_2O)Br]^{2+}$ solutions at 2 °C; apart from the expected narrowing of electronic transitions, the photoinduced spectral changes are indistinguishable from those observed at room temperature. Isosbestics are maintained even at 2 °C. If this two-step mechanism is operating, photolabilized Br^- would have to remain tightly bonded to the newly formed $\{[Rh(tren)(H_2O)_2]^{3+}\}^*$, presumably as part of an ion pair. Such rapid recombination within a solvent cage have been invoked for radical-pair recombinations[41,42] and for nonradical processes,[40,43] but further work would be needed to determine if such a process is important here.

Acknowledgment. The generous support of the Cottrell Grants Program of the Research Corp. and from the Colgate University Research Council is gratefully acknowledged.

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Thermal and Photochemical Reactions of d^9 Metal Complexes: The Silver(II) Macrocycles

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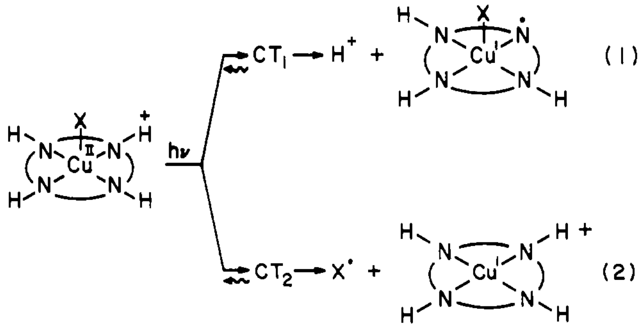
Rate constants for electron-transfer reactions of d^9 metal (Cu(II), Ni(I), and Ag(II)) macrocyclic complexes have been determined by pulse radiolysis. The self-exchange rate constants reveal slow exchanges for $d^{9/10}$ couples (values between 10^3 and 10^{-2} M^{-1} s^{-1}) and fast ones for $d^{8/9}$ couples (values between 10^4 and 10^9 M^{-1} s^{-1}). The photochemical oxidation of the macrocyclic ligand in $Ag([14]aneN_4)^{2+}$ takes place with larger quantum yields than in the corresponding Cu(II) complex (10^{-1} vs 10^{-3}). No photooxidation of axially coordinated ligands has been detected with Ag(II) complexes. The thermal and photochemical reactivities are discussed in terms of the differences in the electronic levels and nuclear configurations between these d^9 metal complexes.

Introduction

The thermal and photochemical redox reactivities of amino complexes of copper(II) have been studied in some detail.[1-3] The self-exchange electron transfer in Cu(II)/Cu(I) complexes is slow with most of the reported rate constants having values close to 10^2 M^{-1} s^{-1}.[4,5] The self-exchange in d^8/d^9 couples, e.g., Cu(III)/Cu(II), has been investigated with a rather limited number of compounds that have rate constants on the order of 10^6–10^{-4} M^{-1} s^{-1}.[1,3] From the standpoint of the photochemical reactivity, the Cu(II) complexes of the $[14]aneN_4$ macrocycle exhibit a meager photochemistry in the UV region (quantum yields below 10^{-2} for $\lambda_{exc} > 230$ nm), which can be described in terms of two primary processes,[6] i.e. the photooxidations of the macrocycle (eq 1) and the axial ligand (eq 2). Not much is known about the redox chemistry of complexes with other d^9 metal ions, in particular Ag(II) and Ni(I), because most of these compounds are regarded as too unstable for these studies.[7,8] We report here the



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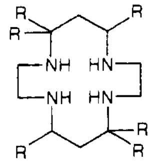
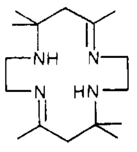
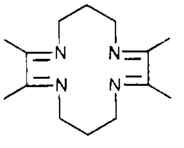
results of some studies where the redox reactivity of Ag(II) and Ni(I) complexes of macrocycles I–VII is compared to that of similar compounds of Cu(II).



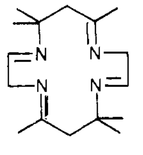
I, R = H: [14]aneN$_4$
II, R = CH$_3$: Me$_6$[14]aneN$_4$



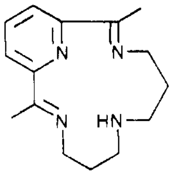
III: Me$_6$[14]-4,11-dieneN$_4$



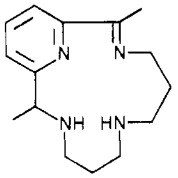
IV: Me$_4$[14]-1,3,8,10-tetraeneN$_4$



V: Me$_6$[14]-1,4,8,11-tetraeneN$_4$



VI: Me$_2$pyo[14]trieneN$_4$



VII: Me$_2$pyo[14]eneN$_4$

Experimental Section

Photochemical Procedures. The apparatus used for flash irradiations was previously described.[9] Two FP-8-100C Xenon Corp. lamps were fired in series at energies adjusted to values between 250 and 40 J/pulse. A lifetime of 30 μs was measured for the flash pulse under these conditions. Hence, points for either kinetic or spectral determination were regarded as significant for times equal to or longer than 50 μs. The waveform recorder, Biomation 805, was interfaced to a Digital computer, PDP 11/55, for the data analysis. Solutions were irradiated at preselected wavelengths by using appropriate cutoff filters. Continuous-wave irradiations were carried out with a 500-W high-pressure Hg–Xe lamp coupled with a high-intensity monochromator, collimating lenses, and IR filter. Relative values of the light intensity were determined with a photocell–microvoltmeter. Absolute values of the intensity were measured with tris(oxalato)ferrate(III).[10] The concentrations of the photolyte were adjusted for absorbing more than 99.99% of the incident light. Streams of ultrapure N$_2$ were used for the deaeration of the solutions prior to the irradiations. The homogeneity of the reaction medium was maintained by stirring the solutions with magnetic bars, and the concentration of Ag(I) ions, Ag$^+_{solv}$, was determined with a calibrated ion-selective electrode.

Pulse Radiochemical Procedures. The procedures and apparatus used for pulse radiolysis have been described elsewhere.[11,12] The reactions under investigation were initiated by reducing a given complex with solvated electrons and intercepting the OH radicals with alcohols. In each of these studies, a number of tests were required for establishing that reactions of the alcohol radical did not interfere with our measurements. The rate of the reaction between the reduced complex and either the Ni(II), Ag(II), or Cu(II) macrocycle was investigated at various concentrations of the macrocyclic complexes. In some experiments, the electron was intercepted with macrocyclic complexes and the reactions of the reduced species with given oxidants were followed at longer times. In this work, the electron-transfer reactions were investigated in aqueous solutions deaerated with streams of N$_2$ or N$_2$O.

Electrochemical Procedures. Cyclic voltammetry measurements were carried out on a BAS CV-1B apparatus with a glassy-carbon working electrode, a Pt wire as auxiliary electrode, and Ag/AgCl in acetonitrile as reference. Acetonitrile, dried over molecular sieves, was used as solvent and 0.1 M tetraethylammonium perchlorate as support electrolyte. The solutions were deaerated with streams of ultrapure N$_2$. Calibrations were carried out with ferrocene and results of these calibrations compared with literature reports.[13]

Table I. Rate Constants for Outer-Sphere Electron-Transfer Reactions Involving d^8 and d^9 Metal Ion Complexes

reactants	k, M^{-1} s^{-1}	I,^{a} M
Ni(Me$_6$[14]aneN$_4$)$^+$ + Ru(NH$_3$)$_6{}^{3+}$	(6.9 ± 0.2) × 10^8	
Ni(Me$_6$[14]dieneN$_4$)$^+$ + Ru(NH$_3$)$_6{}^{3+\,b}$	(4.5 ± 0.3) × 10^8	
Ni(Me$_6$[14]dieneN$_4$)$^+$ + Cr(bpy)$_3{}^{3+\,b}$	(3.1 ± 0.1) × 10^8	
Ni(Me$_6$[14]dieneN$_4$)$^+$ + Co(en)$_3{}^{3+\,b}$	(1.1 ± 0.1) × 10^6	
Ni(Me$_6$[14]dieneN$_4$)$^+$ + Co(Me$_4$[14]-1,4,8,11-tetraeneN$_4$)-(OH$_2$)$_2{}^{3+\,b}$	(4.0 ± 0.2) × 10^7	
Ni(Me$_6$[14]dieneN$_4$)$^+$ + Ni(Me$_2$pyo[14]trieneN$_4$)$^{2+}$	(2.1 ± 0.2) × 10^7	
Ni(Me$_6$[14]dieneN$_4$)$^+$ + Cu(Me$_2$pyo[14]trieneN$_4$)$^{2+}$	(1.0 ± 0.2) × 10^8	
Ni(Me$_6$[14]-1,4,8,11-tetraeneN$_4$)$^+$ + Ru(NH$_3$)$_6{}^{3+}$	(3.0 ± 0.2) × 10^8	
Ni(Me$_6$[14]-1,4,8,11-tetraeneN$_4$)$^+$ + Cr(bpy)$_3{}^{3+}$	(8.0 ± 0.5) × 10^8	
Ni(Me$_2\dot{p}$yo[14]trieneN$_4$)$^+$ + Ru(NH$_3$)$_6{}^{3+}$	(2.3 ± 0.2) × 10^8	
Ni(Me$_2$pyo[14]trieneN$_4$)$^+$ + Cr(bpy)$_3{}^{3+}$	(5.1 ± 0.2) × 10^8	
Cu(Me$_6$[14]dieneN$_4$)$^+$ + Ru(NH$_3$)$_6{}^{3+}$	(7.2 ± 0.3) × 10^4	
Cu(Me$_6$[14]dieneN$_4$)$^+$ + Cr(bpy)$_3{}^{3+}$	(3.7 ± 0.1) × 10^6	
Cu(Me$_4$[14]-1,3,8,10-tetraeneN$_4$)$^+$ + Co(bpy)$_3{}^{3+}$	(5.6 ± 0.2) × 10^6	
Cu(Me$_4$[14]-1,3,8,10-tetraeneN$_4$)$^+$ + Ru(NH$_3$)$_6{}^{3+}$	(1.2 ± 0.1) × 10^5	
Cu(Me$_4$[14]-1,3,8,10-tetraeneN$_4$)$^+$ + Co(en)$_3{}^{3+}$	3.3 ± 0.3^c	
Cu(Me$_2\dot{p}$yo[14]trieneN$_4$)$^+$ + Ru(NH$_3$)$_6{}^{3+}$	(1.5 ± 0.2) × 10^6	
Cu(Me$_4\dot{p}$yo[14]trieneN$_4$)$^+$ + Co(bpy)$_3{}^{3+}$	(2.5 ± 0.2) × 10^7	
Cu(Me$_2\dot{p}$yo[14]trieneN$_4$)$^+$ + Rh(bpy)$_3{}^{2+}$	(1.3 ± 0.2) × 10^7	7.0 × 10^{-1}
Ag([14]aneN$_4$)$^{2+}$ + Cr(bpy)$_3{}^{2+}$	(1.3 ± 0.1) × 10^8	3.0 × 10^{-2}
Ag([14]aneN$_4$)$^{2+}$ + Rh(bpy)$_3{}^{2+}$	(1.3 ± 0.2) × 10^8	4.0 × 10^{-2}
Ag([14]aneN$_4$)$^{2+}$ + Ni(Me$_6$[14]dieneN$_4$)$^+$	(5.7 ± 0.3) × 10^8	3.0 × 10^{-2}
Ag([14]aneN$_4$)$^{2+}$ + Ni(Me$_6$[14]dieneN$_4$)Cl$_2{}^+$	(4.8 ± 0.2) × 10^8	1.0 × 10^{-1}
Ag(bpy)$_3{}^{2+}$ + Cr(bpy)$_3{}^{2+}$	(3.7 ± 0.1) × 10^8	1.0 × 10^{-1}

^{a}Ionic strength adjusted to 10^{-2} M and pH 4 unless stated. ^{b}This work and ref 20. ^{c}pH 6.

Theoretical Calculations. The semiempirical MO and LF methods used in this work have been described elsewhere.[12,14] The extended Hückel calculations were carried out with a Forticon 8 program, QCPE Program No. 344, based on Hoffmann's work.[15,16] The program for a least-squares Gaussian fit of optical spectra was made available to us by Dr. J. Bentley.

Materials. The Ag(II) macrocycles, (Ag([14]aneN$_4$))(ClO$_4$)$_2$ and (Ag(*dl*-Me$_6$[14]aneN$_4$))(ClO$_4$)$_2$, were prepared and purified by literature procedures.[8,17] The Ni(II) and Cu(II) macrocycles were available from previous work and used without further purifications.[6,11,12,18] Other materials were reagent grade and used without further purification.

Results

Thermal Redox Reactions. Rates of fast redox reactions (Table I) involving Ni(II)/Ni(I) or Cu(II)/Cu(I) couples were determined by pulse radiolysis.[19,20] In such experiments, the macro-

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(19) A number of rate constants for cross-reactions of d^9 metal complexes have been reported elsewhere.[20] Insofar as determination of the constants was carried out under ill-defined experimental conditions and/or under competition with other reactions, their values were of little use for the calculation of self-exchange rate constants.

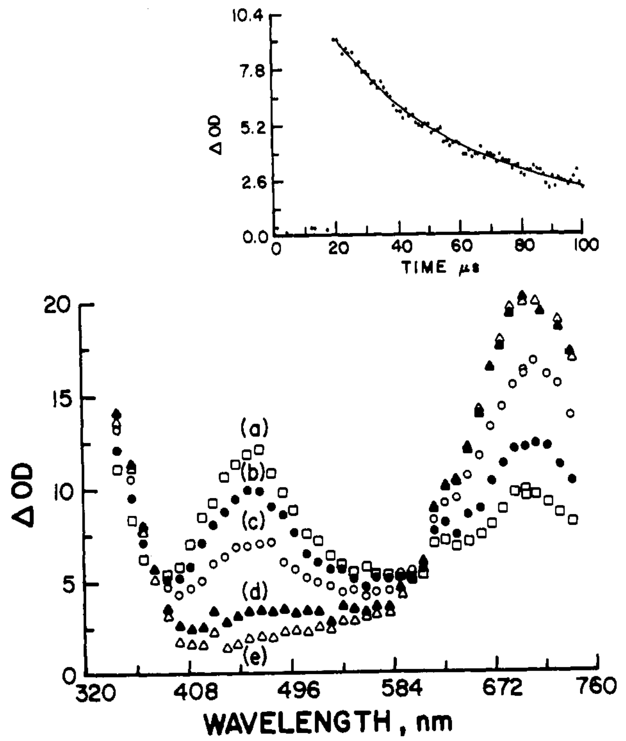

Figure 1. Spectral changes recorded in a pulse radiolytic study of the reaction $Ni(Me_6[14]\text{-}4,11\text{-}dieneN_4)^+ + Cu(Me_4[14]\text{-}1,4,8,11\text{-}tetraeneN_4)^{2+} \rightarrow Ni(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+} + Cu(Me_4[14]\text{-}1,3,8,10\text{-}tetraeneN_4)^+$. The reaction was investigated with deaerated solutions containing 10^{-2} M Ni(II) complex and 10^{-3} M Cu(II) complex at pH 6. Spectra were recorded at (a) 2, (b) 7, (c) 16, (d) 61, and (e) 92 μs. The inset shows a typical trace ($\lambda_{ob} \sim 450$ nm) with first-order-kinetics fitting (solid line). Vertical scales are in arbitrary units.

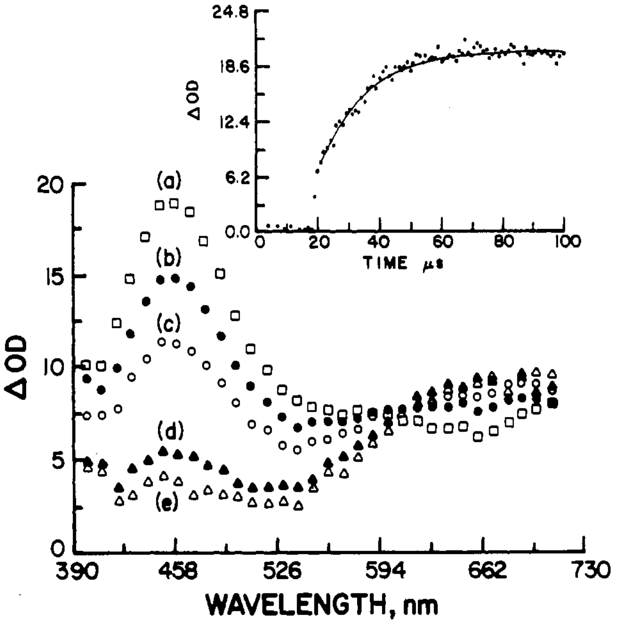

Figure 2. Spectral changes observed in a pulse radiolytic study of the reaction $Ni(Me_6[14]\text{-}4,11\text{-}dieneN_4)^+ + Cu(Me_2pyo[14]trieneN_4)^{2+} \rightarrow Ni(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+} + Cu(Me_2pyo[14]trieneN_4)^+$. The reaction was investigated with deaerated solutions containing 2×10^{-2} M Ni(II) and 2×10^{-4} M Cu(II) complexes at pH 6. Spectra were recorded at (a) 3, (b) 13, (c) 23, (d) 53, and (e) 73 μs. The inset shows a trace ($\lambda_{ob} \sim 650$ nm) with first-order-kinetics fitting (solid line). Vertical scales are in arbitrary units.

Table II. Electron-Transfer Self-Exchange Rate Constants for the Oxidation and Reduction of d⁹ Metal Ion Complexes in Aqueous Solutions

complex	k_{ex}, $M^{-1}\ s^{-1}$ [a,b]
$d^{8/9}$ Couples	
$Ni(Me_6[14]aneN_4)^{2+/+}$	1.0×10^4
$Ni(Me_6[14]dieneN_4)^{2+/+}$	2.3×10^6
$Ni(Me_2pyo[14]trieneN_4)^{2+/+}$	4.7×10^7 [c]
$Ni(Me_6[14]\text{-}1,4,8,11\text{-}tetraeneN_4)^{2+/+}$	1.5×10^8
$Ag([14]aneN_4)^{3+/2+}$	2.0×10^9
$d^{9/10}$ Couples	
$Cu(Me_6[14]dieneN_4)^{2+/+}$	2.3×10
$Cu(Me_4[14]\text{-}1,3,8,10\text{-}tetraeneN_4)^{2+/+}$	4.8×10^2
$Cu(Me_2pyo[14]trieneN_4)^{2+/+}$	2.7×10^3 [d]
$Cu(Me_2pyo[14]eneN_4)^{2+/+}$	~1
$Ag([14]aneN_4)^{2+/+}$	3.0×10^{-2}
$Ag(Me_6[14]aneN_4)^{2+/+}$	2.0×10^{-2}

[a] Values calculated for ionic strength $I = 0.1$ M. [b] The self-exchange rate constants reported in this table are averages (average deviation is less than or equal to 10%) of the values calculated for several reactions (Table I). Data for the calculations (redox potentials and self-exchange rate constants for the reactants of the cross-reaction) were extracted from: Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883. Ferraudi, G.; Endicott, J. F. *Inorg. Chim. Acta* **1979**, *37*, 219. Endicott, J. F.; Durham, B. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum: New York, 1979; Chapter 6. Also ref 1, 3, and 12. [c] A self-exchange rate constant, $k = 1.3 \times 10^4$ $M^{-1}\ s^{-1}$, has been calculated for $Ni^{II}L + Ni^{II}(L^{\bullet -}) \rightarrow Ni^{II}(L^{\bullet -}) + Ni^{II}L$. [d] A self-exchange rate constant, $k = 1.9 \times 10^4$ $M^{-1}\ s^{-1}$, has been calculated for $Cu^{II}L + Cu^{II}(L^{\bullet -}) \rightarrow Cu^{II}(L^{\bullet -}) + Cu^{II}L$.

cyclic complexes were reduced with the solvated electron and the reactions of the reduced complexes were followed at appropriate wavelengths corresponding to either the disappearance of the reactants or the formation of the products. Moreover transient spectra (Figure 1 and 2) were determined (whenever it was possible) in order to establish with certainty that the optical changes corresponded to the correct reaction. Insofar as the electron transfers between the reduced complexes and oxidants were carried out under a pseudo-first-order regime with an excess of oxidant over the concentration of reductant, the rate constants were calculated from the slopes of k_{obsd} vs [oxidant] plots. Complexes of the ligands $[14]aneN_4$, $Me_6[14]aneN_4$, $Me_6[14]\text{-}4,11\text{-}dieneN_4$, $Me_6[14]\text{-}1,4,8,11\text{-}tetraeneN_4$, and $Me_4[14]\text{-}1,3,8,10\text{-}tetraeneN_4$ exhibited simple electron-transfer reactions. However, complexes of $Me_2pyo[14]trieneN_4$ gave complex reactions with more than one step. The spectral transformations in a microsecond time domain, i.e. during the first step, and the rates of reaction were in accord with those expected for complexes with a reduced ligand. This behavior has been related to a multiple-step reduction of the metal center when the reducing species, i.e. e_{aq}^-, has a reduction potential that allows the rapid macrocycle reduction (eq 3), a redox reactivity that we previously

$$M^{II}(Me_2pyo[14]trieneN_4)^{2+} + e_{aq}^- \rightarrow M^{II}(Me_2\dot{p}yo[14]trieneN_4)^+ \rightarrow M^{I}(Me_2pyo[14]trieneN_4)^+ \quad (3)$$

$$M = Cu, Ni$$

reported for metallophthalocyanines.[21] For the determination of rate constants of the electron-transfer reactions involving $d^{8/9}$ and $d^{9/10}$ complexes of $Me_2pyo[14]trieneN_4$ without the complications introduced by the formation of the ligand-radical species, Ni(II) or Cu(II) complexes were reacted with pulse radiolytically generated reductants, R, whose potentials were too small for the macrocycle reduction (Table I). Such electron-transfer reactions exhibited rates and resulted in spectral changes that were in agreement with single-step, metal-centered electron transfers (eq 4). Self-exchange rate constants (Table II) were calculated from

$$M^{II}(Me_2pyo[14]trieneN_4)^{2+} + R \rightarrow M^{I}(Me_2pyo[14]trieneN_4)^+ + \ldots \quad (4)$$

the rate constants reported in Table I by using Marcus's expression

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Table III. Quantum Yields for the Photodecomposition of Ag(II) Macrocyclic Complexes[a]

λ_{exc}, nm	$10^6 I_0$, einsteins/(dm^3 s)	ϕ_A[b]	ϕ_B[b]
	Ag([14]aneN$_4$)$^{2+}$		
254	1.8 ± 0.1	0.16	0.13
313	1.9 ± 0.1		0.14
350	0.37 ± 0.02		0.12
370	4.5 ± 0.2	0.16	0.13
410	1.4 ± 0.1		0.14
	Ag(*dl*-Me$_6$[14]aneN$_4$)$^{2+}$		
254			0.17
313			0.18
350			0.18
370		0.17	0.17
410			0.18

[a] Quantum yields were calculated from the concentration of Ag_{solv}^+, ϕ_A, and the bleach of the 347-nm optical density, ϕ_B, measured as a function of the irradiation (Figure 3). All the experiments were carried out in deaerated CH_3CN with concentrations of the Ag(II) complexes adjusted for more than a 99.9% absorption of the incident light. [b] Experimental errors less than or equal to 10%.

for the cross-reaction rate constant.[3,22-25] In this regard, the required equilibrium constants were calculated from the corresponding redox potentials. Although most of the potentials were available from literature reports, reduction potentials for Ag(II)/Ag(I) couples were investigated by cyclic voltammetry. In accord with the reported stability of the Ag(I) macrocycles in dry acetonitrile, one-electron reversible waves were recorded for these complexes instead of the two-electron irreversible reductions reported for aqueous solutions. For Ag([14]aneN$_4$)$^{2+}$, the reversible oxidation to Ag(III) was observed at 1.048 V vs NHE and the reduction to Ag(I) at 0.350 V vs NHE. Thermochemical corrections, based on the theory of ionic solutions, were applied to these values in order to have potentials for the corresponding redox processes in aqueous solutions.[26,27]

Photochemical Reactivity. The Ag([14]aneN$_4$)$^{2+}$ ion exhibited considerable photoreactivity for continuous monochromatic irradiations at wavelengths of the violet–UV absorption bands. Photolyses of the complex in aqueous acidic solutions ($10^{-2} > [H^+] > 10^{-3}$ M in either $HClO_4$ or H_2SO_4) lead to the formation of metallic silver. The formation of Ag(0) was not observed, however, when photolyses were carried out in dry, deaerated acetonitrile. In these experiments, the spectrum of the Ag(II) complex was irreversibly bleached and Ag(I) ions, Ag^+_{solv}, were formed in the reaction as expected for the redox-induced opening of the macrocycle. Flash photolysis shows that the bleach of the spectrum associated with the reduction of the metal center takes place within the length of the irradiation, ca. 30 μs.

In continuous photolysis, the rates of Ag^+_{solv} formation and bleach of the Ag([14]aneN$_4$)$^{2+}$ spectrum exhibited dependences on the concentration of Ag(II) complex and on the percentage of conversion to products (Figure 3), which are indicative of a secondary photolysis. Moreover a slow postirradiation process resulted in the complete decomposition of unphotolyzed Ag([14]aneN$_4$)$^{2+}$. Such a process has been assigned to redox reactions of the Ag(II) macrocycle with organic compounds, e.g. amines, formed during the photolysis and later in the ensuing thermal decomposition of the complex.[28] In these contexts, quantum yields (Table III) were determined at complex concentrations that minimized the effects of secondary photolysis and corrected (if necessary) for contributions from the postirradiation process.

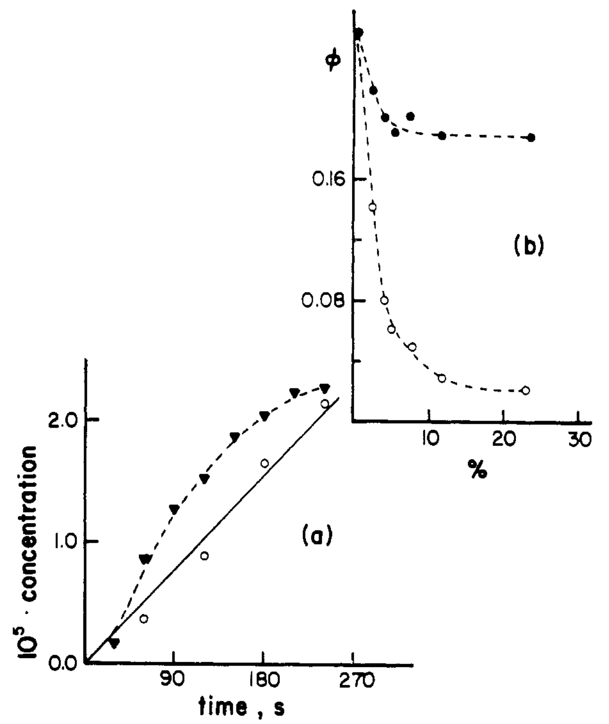

Figure 3. Nonlinear effects on the continuous photolysis (λ_{exc} = 370 nm, $I_0 = 4.5 \times 10^{-6}$ einstein/(dm^3 min)) of Ag([14]aneN$_4$)$^{2+}$ in deaerated CH_3CN. (a) Curves show the concentration of Ag(II) complex decomposed at given irradiation times for two initial concentrations of complex: (○) 2.7×10^{-3} M; (▼) 1.4×10^{-3} M. (b) Curves show the dependence of the quantum yields, (●) for the disappearance of the Ag(II) complex and (○) the formation of Ag^+_{solv}, as a function of the percentage of complex converted to products.

Discussion

Metal-Centered and Charge-Transfer Transitions in d^9 Complexes. The absorption spectra of planar Cu(II) macrocyclic complexes of the [14]aneN$_4$ and [14]dieneN$_4$ ligands exhibit absorption bands that can be easily assigned to charge-transfer or ligand-field electronic transitions. Comparison of the Cu(II), Ni(I), and Ag(II) spectra (Figure 4) reveals that intense transitions in the spectra of Ag(II) complexes are placed at lower energies than in those of the corresponding copper(II) complexes. Insofar as CT transitions in second-row transition-metal compounds are expected to be UV-shifted with respect to those of isoelectronic first-row metal complexes, the low energies of the absorptions in Ag([14]aneN$_4$)$^{2+}$ suggest differences in the electronic structures of the isoelectronic Cu(II) and Ag(II) complexes.[29,30-32] In terms

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(22) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21.

(23) Most of the reactions considered in this work (Tables I and II) involve species with various charges and sizes. Therefore, the Marcus equation for the rate constant of the cross-reaction was corrected by an exponential factor, $\exp(-\Delta W/RT)$, incorporating differences, ΔW, in the Coulombic activation energies of the cross-reaction and self-exchange reaction. The calculation of such energies has been discussed in literature reports.[24,25]

(24) Gordon, B. M.; Williams, L. L.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 2061.

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(27) Lewis, G. N.; Randall, M. In *Thermodynamics* (revised by K. Pitzer and L. Brewer); McGraw-Hill: New York, 1961.

(28) Formation of amines follows the photooxidation of the macrocycle as in the case of Cu(II) complexes.[1,2,6]

(29) Notice that Jørgensen's equation[30,31]

$$\bar{\nu}_{max} = 30(\chi_L - \chi_M) + 10Dq + \delta(SP) + ...$$

gives the maximum of a charge-transfer band in terms of the optical electronegativities, χ_L and χ_M, ligand field orbital splitting parameters, Dq, and differences in spin-pairing energies, δ(SP), of the ground and excited states. It has been shown that optical electronegativities of isoelectronic metal ions experience little variations within a family, while $10Dq$ values for transition-metal ions in the second row are ca. 30% larger than those in the first row.[32] Therefore, the equation predicts bathochromic shifts for the maxima of similar charge-transfer transitions when one moves from the first to the second row of transition-metal ions.

(30) Schmidthe, H. H. In *Physical Methods in Advanced Inorganic Chemistry*; Hill, H. A. O., Day, P., Eds.; Wiley-Interscience: New York, 1968; Chapter 4.

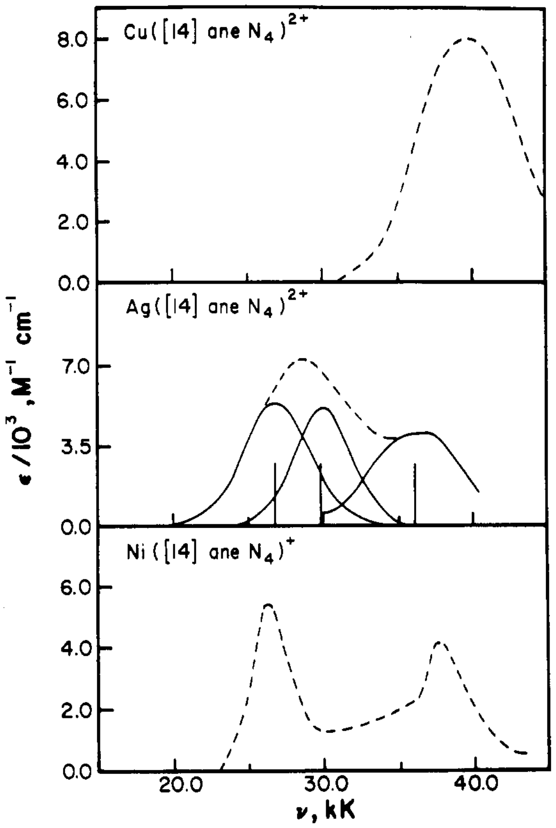


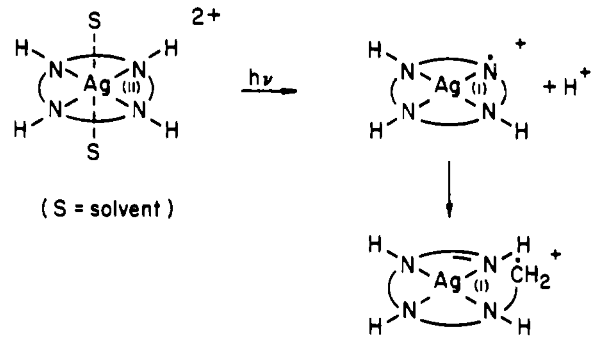
Figure 4. UV spectra of M([14]aneN$_4$)$^{z+}$ (M = Cu(II), Ag(II), Ni(I); z = 2, 1) in acetonitrile.[7,26] The Gaussians superimposed on the spectrum of Ag([14]aneN$_4$)$^{2+}$ (solid lines) are the solutions of a Gaussian–Least-squares fitting of the experimental spectrum (dashed line).[26] The vertical lines give the energies of three CT$_{N\rightarrow Ag}$ levels calculated by a semiempirical MO method.

of the ligand-field model,[33,34] values of 10*Dq* = 14.7 × 10^3 cm^{-1} and 10*Dt* = 17.2 × 10^3 are obtained from the positions of the dd and CT transitions in the spectrum of Cu([14]aneN$_4$)$^{2+}$. Our values, 10*Dq* = 19.2 × 10^3 cm^{-1} and 10*Dt* = 12.8 × 10^3 cm^{-1}, correspond to a more octahedral field around the Ag(II) ion; a condition that can only be fulfilled if there are intense metal–axial ligand interactions. In order to verify this conclusion, we have carried out a more quantitative analysis of the d^9 metal ion spectra by using MO calculations of the electronic levels and relevant electronic transitions. Results of these calculations are in agreement with our LF estimates, i.e. within 15% of the values reported above, and with the spectral properties of the Cu(II) and Ag(II) complexes. For example, Figure 4 gives a graphical account of the agreement between calculated energies of electronic transitions and the positions of maxima for charge-transfer bands of Ag([14]aneN$_4$)$^{2+}$. Such agreement suggests that the best description of the Ag^{II}([14]aneN$_4$)$^{2+}$ macrocycles in solution must be close to those provided by crystallographic and ESR studies.[8,35,36] In this regard the Ag(II) complex is expected to have solvent molecules coordinated in the axial position. This is not the case for the Cu(II) macrocycles, where the best agreement between calculations and experimental data suggests that Cu(II)–axial ligand interactions must be weaker than similar interactions in Ag(II) complexes.

Electron-Transfer Reactivity of d$^{8/9}$ and d$^{9/10}$ Couples. The previously reported data on self-exchange electron-transfer reactions of d$^{8/9}$ macrocyclic complexes, in general Cu(III)/Cu(II) complexes, have been interpreted in terms of a Franck–Condon activation energy receiving its major contribution from appreciable changes in the length of equatorial and axial metal–ligand bonds. Endicott et al. were able to obtain a good estimate of the self-exchange rate constant for d$^{8/9}$ macrocycles, $k \sim 10^6$ M^{-1} s^{-1}, by considering the reorganization of equatorial bonds as the only contribution to the inner-sphere reorganization energy.[3] Inspection of the values in Table II reveals that these arguments must also be approximately valid for the Ni(II)/Ni(I) macrocycles. Moreover, it is possible to see that the d$^{8/9}$ self-exchange rate constant increases in parallel with the rigidity of the macrocyclic ligand, as one could expect if such a rigidity reduces the reorganizational energy associated with equatorial bonds, i.e. by narrowing the differences between the nuclear configurations of the d^8 and d^9 metal complexes. In accord with this proposition, the self-exchange rate constants of the d$^{9/10}$ metal ion complexes show the expected dependence on the macrocycle rigidity.

Comparison of the Ag(III)/Ag(II) and Ag(II)/Ag(I) complexes to the corresponding d$^{8/9}$ and d$^{9/10}$ couples in Table II reveals that the silver rate constants are well above and below the values determined for other d^9 metal compounds, i.e. smaller and larger reorganizational energies, respectively, than in isoelectronic couples of Ni and Cu complexes. A possible reason for such behavior is that in the reduction of Ag(III) to Ag(II) the contribution to the reorganizational energy from changes in the metal–axial ligand interaction is smaller than in isoelectronic Ni(II)/Ni(I) complexes. Indeed, combined effects of charge and size in Ag (with respect to Ni) must have a compensatory effect on the Jahn–Teller distortions of a d^9 configuration.[37] In the reduction of Ag(II) to Ag(I), the interaction of Ag(II) with axial ligands is stronger than the Cu(II) interaction. Therefore, the reduction to a d^{10} configuration in Ag is expected to take place with a larger contribution from the metal–axial ligand reorganization to the reorganization energy than in the case of Cu.

Photochemistry of the d^9 Macrocycles. The photochemical reactivity of Ag(II) complexes with saturated macrocyclic ligands can be described in terms of a single primary photoprocess involving the reduction of the metal center and the oxidation of the macrocycle. The opening of the macrocycle (eq 5) follows the ligand photooxidation, a photoprocess already reported for Cu(II) macrocycles.[6] By contrast, the quantum yields for macrocycle



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(31) Jørgensen, C. K. *Orbitals in Atoms and Molecules*; Academic: New York, 1962.

(32) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984.

(33) Ligand-field parameters for Cu(II) complexes were calculated by applying the hole–electron equivalence, which relates the electronic levels of a d^{10-n} configuration to those of a d^n—a method of calculation whose application to various metal ions has been discussed in literature reports.[14,32] The spectra of the macrocyclic complexes required for such calculations have been reported elsewhere.[1,34] The results reported elsewhere in the text are in good agreement with other values reported for tetragonal Cu(II) complexes.[14,30,32] Calculations of the ligand-field parameters for Ag(II) were based on Jørgensen's equation for the position of a CT band maximum adapted to a tetragonal symmetry, namely by introducing in it the tetragonal contribution of the field *Dt*. In the application of Jørgensen's equation to our problem, the optical electronegativities of Cu(II) and Ag(II) are considered to be nearly the same.[32]

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(36) The spectrum of the Ni(I) complex was adapted from ref 7: Gaussians with maxima of 26.8 × 10^3, 29.8 × 10^3, and 36.1 × 10^3 cm^{-1} and widths of 6.6 × 10^3, 5.4 × 10^3, and 7.8 × 10^3 cm^{-1}, respectively.

(37) The point can be illustrated by considering that Ag ions have much larger ionic potentials (charge divided by effective ionic radius) than Ni ions, e.g. 3.8 for Ag(III) vs 2.9 for Ni(II).

photooxidation in Cu(II) macrocycles are smaller than those determined for similar Ag(II) compounds. These Cu(II) complexes also undergo a significant photooxidation of axial ligands that we have not detected with Ag(II) homologues. Quantum yields, calculated from changes in the optical spectrum and from the concentration of free Ag(I), give an upper limit, $\phi \leq 10^{-2}$, for the axial ligand photooxidation, i.e. less than 1% of the total photochemical transformation, in spite of the existence of (axial ligand to metal) charge-transfer states at low energies. Insofar as flash photolysis shows the absence of slow back-electron-transfer reactions where Ag(I) macrocycles are reoxidized, the low value of the quantum yield must reflect rapid reoxidation within the solvent cage and/or a fast relaxation of the charge-transfer excited state. Consideration of the respective self-exchange rate constants of Cu(II)/Cu(I) and Ag(II)/Ag(I) complexes of the [14]aneN_4 macrocycle (Table II) casts doubt upon the first possibility, i.e. the reoxidation of Ag(I) in the solvent cage with a faster rate than in the case of Cu(I) complexes. Moreover, comparison of the wavelength-dependent low quantum yield photochemistry of the Cu(II) to the wavelength-independent high quantum yield photochemistry (relative to Cu(II)) of the Ag(II) complexes suggests that the $CTTM_{N\rightarrow Ag}$ reactive state or states in Ag(II) macrocycles are rapidly populated from states placed at higher energies including those involving charge transfers from axial ligands. Although the role of metal-centered states in depopulating the reactive CTTM must still be investigated, one can propose that such a radiationless crossing, faster for Cu(II) than for Ag(II), can explain some of our experimental observations.[1] Evidence about this mechanism will be the subject of further work on the photochemistry of Ag(II) complexes.

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Registry No. $Ni(Me_6[14]aneN_4)^{2+}$, 18444-38-7; $Ni(Me_6[14]aneN_4)^+$, 47105-34-0; $Ni(Me_6[14]dieneN_4)^{2+}$, 15079-51-3; $Ni(Me_6[14]dieneN_4)^+$, 115303-92-9; $Ni(Me_2pyo[14]trieneN_4)^{2+}$, 47023-95-0; $Ni(Me_2pyo[14]trieneN_4)^+$, 116025-30-0; $Ni(Me_6[14]\text{-}1,4,8,14\text{-}tetraeneN_4)^{2+}$, 18444-46-7; $Ni(Me_6[14]\text{-}1,4,8,11\text{-}tetraeneN_4)^+$, 75400-04-3; $Ag([14]aneN_4)^{3+}$, 48146-03-8; $Ag([14]aneN_4)^{2+}$, 48146-02-7; $Ag[14]aneN_4{}^+$, 116025-32-2; $Cu(Me_6[14]dieneN_4)^{2+}$, 33727-13-8; $Cu(Me_6[14]dieneN_4)^+$, 47105-27-1; $Cu(Me_4[14]\text{-}1,3,8,10\text{-}tetraeneN_4)^{2+}$, 71170-97-3; $Cu(Me_4[14]\text{-}1,3,8,10\text{-}tetraeneN_4)^+$, 80502-51-8; $Cu(Me_2pyo[14]trieneN_4)^{2+}$, 21780-13-2; $Cu(Me_2pyo[14]trieneN_4)^+$, 80502-45-0; $Cu(Me_2pyo[14]eneN_4)^{2+}$, 116301-16-7; $Cu(Me_2pyo[14]eneN_4)^+$, 116301-15-6; $Ag(Me_6[14]aneN_4)^{2+}$, 47105-14-6; $Ag(Me_6[14]aneN_4)^+$, 47105-13-5.

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Theoretical Study on the Difference in the Relative Strengths of Metal-Hydrogen and Metal-Methyl Bonds in Complexes of Early Transition Metals and Complexes of Middle to Late Transition Metals

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Molecular orbital calculations based on density-functional theory have been carried out on the homolytic metal-hydrogen and metal-methyl bond energies in Cp_2MR (M = Sc, V, Mn), CpNi(CO)R, $Co(CO)_4R$, $CpFe(CO)_2R$, $Mn(CO)_5R$, and $CpCr(CO)_3R$ for R = H and CH_3. The intrinsic M-H bond energies (the bond energies between H and the metal fragments ML_n of the same conformation as the ML_n framework in HML_n) are calculated to be remarkably similar (202-230 kJ mol^{-1}) for all the hydride complexes, irrespective of the vast differences in electronegativity between the metal centers. The calculated strengths of the metal-methyl bonds vary strongly from 220 kJ mol^{-1} for the early transition metal Sc to between 100 and 170 kJ mol^{-1} for the middle to late transition metals. It is shown that the electroneutral $M-CH_3$ bond in complexes of middle to late transition metals is weakened by repulsive interactions between occupied metal orbitals and the fully occupied (mainly) $2s_C$ orbital on CH_3, to the extent where the $M-CH_3$ bond becomes weaker than the corresponding M-H bond. The repulsive interaction between occupied metal orbitals and the fully occupied $2s_C$ orbital on CH_3 is reduced considerably in the polar $M-CH_3$ bond of $Cp_2Sc(CH_3)$, and it is found for the early transition metal scandium that the $M-CH_3$ bond is as strong as the M-H bond. An extension of our study to Cp_2MR (M = Y, La, Tc, and Re) reveals, among the 4d and 5d elements, the same change in the stability order from M-H $\sim$ $M-CH_3$ for the early transition metals to M-H > $M-CH_3$ for the middle transition metals. It is in addition found that the M-R bond energies increase on descending each of the two triads M = Sc, Y, La and M = Mn, Tc, Re. The increase is correlated to a corresponding increase in bonding overlaps.

Introduction

Thermochemical data on metal-ligand bonds constitute a much needed source of input in any estimate of the energetics for organometallic reaction steps. Of particular importance are data on the strength of M-R (R = H, alkyl) bonds, in view of the fact that M-R bond cleavage and M-R bond formation pervade most of the elementary reaction steps in organometallic chemistry. Nevertheless, the development of a thermochemistry for the metal-alkyl and metal-hydride bonds has been slow and painful.[1] The M-R bond strength (R = alkyl, H) has been studied in a number of ligand-free MR systems both experimentally[2] and theoretically.[3] Experimental[4] and theoretical[5] data on M-R bond strengths in RML_n alkyl and hydride complexes are, however, often insufficient for a rational approach to the synthesis of new organometallics based on quantitative estimates of reaction en-

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