The distinctive spectral characteristics of $Ru(phi)_3^{2+}$ might be understandable on the basis of a delocalized charge transfer onto the three ligands. The sequential lowering of the energy of the transition (150 nm change in wavelength)[20] with increasing substitution of phi ligands suggests such delocalization and stands in sharp contrast to spectral characteristics of the localized bipyridyl system, where the intensity rises but the energy of the charge-transfer band does not shift appreciably with increasing bpy substitution. This delocalization may also explain the intense low-energy transitions observed in other tris(α-diimine) complexes.[8,21] The delocalized framework may, finally, also account for the short excited-state lifetime of the complex, owing to large spin–orbit coupling that would be inherent in a completely delocalized system. Alternatively, the excited state is sufficiently low in energy that it may be rapidly deactivated by coupling to the ground state.

In summary, $Ru(phi)_3^{2+}$ displays intense, unusual transitions at low energies. On the basis of a comparison with a zinc analogue, the transitions may be described as charge transfer in character. By comparison with a mixed-ligand complex of phi, a delocalized charge-transfer transition is suggested. Finally the dependence of the transitions on hydrogen bonding in addition to the rich intensity at long wavelengths renders the complex useful as a biophysical probe.

(20) It is interesting that the transition centered at 510 nm in $Ru(phi)_3^{2+}$ is not at all apparent in mixed-ligand complexes containing the phi ligand. Instead, the 525-nm transition in $Ru(bpy)_2(phi)^{2+}$ (presumably a result of localized charge transfer onto phi) is centered between the two transitions observed for the tris-substituted $Ru(phi)_3^{2+}$ species. The visible spectrum of $Ru(bpy)(phi)_2^{2+}$ (data not shown) shows visible transitions centered at 472 and 572 nm, consistent with some degree of delocalization.

(21) A similar delocalization may explain the intense visible transition in the ruthenium cage complex recently prepared by Sargeson et al. (personal communication).

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Kinetic Study of Electron-Transfer Reactions of Sterically Constrained Bis(diimine) Complexes of Copper(II) and Copper(I) with Ruthenium Ammine Complexes

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Although correlation of rate data through the Marcus relations has been satisfactorily achieved for many Cu(I)–Cu(II) electron-transfer reactions,[2–7] attempts at determining Cu(I)–Cu(II)

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self-exchange electron-transfer rate constants in other instances have met with less success. For reactions involving the bis-(1,10-phenanthroline) and bis(2,2'-bipyridine) complexes of Cu(I) and Cu(II), in particular, where considerable structural differences exist between the two oxidation states, widely divergent estimates of the $Cu(phen)_2^{+/2+}$ and $Cu(bpy)_2^{+/2+}$ self-exchange rate constants have been obtained,[3,8] depending upon the oxidation state of the copper complex in the cross reaction and the redox partner involved. For the corresponding 2,9-dimethyl-1,10-phenanthroline (dmp) complexes, where steric constraints imposed by the methyl substituents force a closer match in the geometry of the copper centers, the Marcus relations have been able to provide more consistent self-exchange rate constants as well as successfully correlate rate constants with thermodynamic driving force for several series of reactions.[2,9,10] The weak driving-force dependence noted for the reduction of $Cu(dmp)_2^{2+}$ by Ru(II) reductants[5] and the finding[11] of saturation kinetics for the reactions of the sulfonyloxyphenyl substituted dmp complex $Cu(dpmp)_2^{2-}$ (dpmp = 2,9-dimethyl-4,7-bis((sulfonyloxy)phenyl)-1,10-phenanthroline) further illustrate the kinetic complexities that can result in labile Cu(I)–Cu(II) systems where changes in coordination number may accompany the activation process. We report here the kinetic redox behavior of two other sterically constrained bis(diimine) Cu(II) complexes. We have examined the reduction of the bis-(4,4',6,6'-tetramethyl-2,2'-bipyridine)copper(II) and bis(6,6'-dimethyl-2,2'-bipyridine)copper(II) complexes, $Cu(tmbp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$, by a series of Ru(II) complexes, as well as the oxidation of the Cu(I) complex $Cu(tmbp)_2^{+}$ by the Ru(III) oxidant cis-[Ru(NH₃)₄(isn)₂]³⁺.

Experimental Section

Chemicals and Solutions. The ruthenium complexes [Ru-(NH₃)₅py](ClO₄)₂ (py = pyridine), [Ru(NH₃)₅isn](ClO₄)₂ (isn = isonicotinamide), [Ru(NH₃)₄bpy](ClO₄)₂ (bpy = 2,2'-bipyridine), cis-[Ru(NH₃)₄(isn)₂](ClO₄)₂, and cis-[Ru(NH₃)₄(isn)₂](ClO₄)₃ were prepared by publishing procedures.[12,13] Spectra of the ammine complexes were in good agreement with literature values. The ligand tmbp was synthesized by the procedure of Linnell[14] and purified by vacuum sublimation (0.5 mm) and recrystallization from hexanes. The ligand dmbp was synthesized by the G. F. Smith Co. and recrystallized from hexanes prior to use. The purity and structure of the tmbp and dmbp ligands were confirmed by NMR. The complexes Cu(tmbp)₂(ClO₄)₂·2H₂O, Cu-(tmbp)₂(ClO₄)₂, and Cu(tmbp)₂ClO₄ were prepared by the reported methods.[15] Reactions were generally carried out in 20% methanol/80% water. Solutions of $Cu(tmbp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ were prepared by adding Cu(CH₃CO₂)₂·H₂O to a 20–100-fold excess of ligand dissolved in methanol. MES (2-morpholinoethanesulfonic acid) was used to buffer reaction solutions at operational "pH" values measured with respect to aqueous reference standards. The 20% methanol/80% water solutions, after adjustment of the ionic strength to 0.10 M with LiCF₃CO₂, were generally at "pH" 6.1. Such solutions were prepared immediately prior to their use in the kinetic experiments. The Cu(I) products showed an absorption maximum at 450 nm ($\epsilon = 6.5 \times 10^3$ M⁻¹ cm⁻¹) characteristic of sterically constrained bis(diimine)copper(I) complexes. Solutions of the Cu(II) complexes absorb negligibly below 700 nm.

The reaction of $Ru(NH_3)_4(isn)_2^{3+}$ with $Cu(tmbp)_2^{+}$ was followed at pH 6.1 in 20% methanol/80% water and 0.10 M LiCF₃CO₂ by mixing, in the stopped-flow apparatus, a solution of the Cu(I) reductant containing 0.010 M sodium 2-morpholinoethanesulfonate at pH 8.3 with the Ru(III) oxidant in 0.010 M free acid buffer, 2-morpholinoethanesulfonic acid, at pH 3.8. $Ru(NH_3)_4(isn)_2^{3+}$ was slowly reduced by the solvent ($t_{1/2}$ = 35 s) at pH 6.1.

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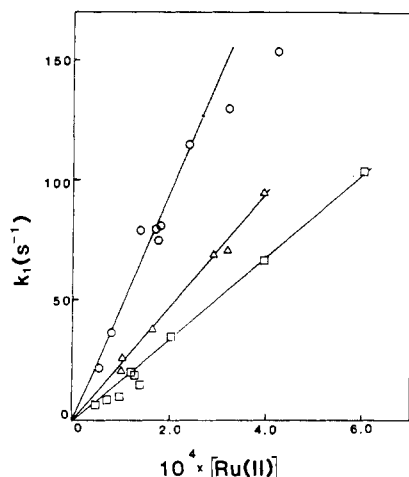
Figure 1. Variation of the first-order rate constant, k_1, with concentration of Ru(II) reductant for reduction of Cu(tmbp)$_2^{2+}$ at 25 °C and pH 6.1, in 0.10 M LiCF$_3$CO$_2$: (O) Ru(NH$_3$)$_5$py^{2+}; (△) Ru(NH$_3$)$_5$isn^{2+}; (□) Ru(NH$_3$)$_4$bpy^{2+}.

Electrochemical Measurements. A PAR Model 176 potentiostat-galvanostat coupled with a Houston Instruments Model 2000 X-Y recorder was used for cyclic voltammetry. Potentials were measured at a Pt electrode vs SCE at 25 °C in 0.10 M LiCF$_3$CO$_2$, with a Pt wire as auxiliary electrode.

Values of the formal reduction potentials for the Cu(II)/Cu(I) and Ru(III)/Ru(II) couples were determined as the arithmetic mean of anodic and cathodic peak potentials, which were separated by 75–85 mV in the cyclic voltammetric scans. Values measured in 20% methanol/80% water, under the conditions employed in the kinetic experiments, were 25–35 mV more positive than in aqueous media. Values of 600 and 592 mV (vs NHE) were obtained for the Cu(tmbp)$_2^{+/2+}$ and Cu(dmbp)$_2^{+/2+}$ couples. The Ru(II)/Ru(III) potentials measured in 20% methanol/80% water were 315, 394, 533, and 681 mV for Ru(NH$_3$)$_5$py$^{2+/3+}$, Ru-(NH$_3$)$_5$isn$^{2+/3+}$, Ru(NH$_3$)$_4$bpy$^{2+/3+}$, and *cis*-Ru(NH$_3$)$_4$(isn)$_2^{2+/3+}$, respectively.

Kinetic Measurements. Rate measurements were made with Ru(II) in excess ([Ru(II)] = 8.3 × 10^{-4}–5.4 × 10^{-5} M; [Cu(II)] = (1–2) × 10^{-5} M) by using a thermostated Aminco-Morrow stopped-flow spectrophotometer as described elsewhere.[7] Rate constants generally agreed to within ±8%, except for experiments at higher excess [Ru(II)], where the reproducibility was ±10–15%.

Results and Discussion

Rapid oxidation of the Ru(II) reductants by the Cu(II) complexes Cu(tmbp)$_2^{2+}$ and Cu(dmbp)$_2^{2+}$ was observed in all cases. Pseudo-first-order rate constants, k_1, generally showed a linear dependence on [Ru(II)] (Figure 1) and were independent of the excess ligand concentration ([tmbp]/[Cu(II)]$_T$ > 20). Data obtained at low excess ligand concentration ([tmbp] = 2.0 × 10^{-4}–3.1 × 10^{-5} M), yielded successively smaller values for the apparent second-order rate constant, k_2' (=k_1/[Ru(II)]), suggesting incomplete conversion of Cu(II) to the kinetically active bis complex under those conditions. A least-squares plot of $1/k_2'$ vs $1/$[tmbp]^2 gave values of 1.6 × 10^9 M^{-2} for the formation constant, K_{II} (=[Cu(tmbp)$_2^{2+}$]/[Cu(II)][tmbp]^2), and 2.6 × 10^5 M^{-1} s^{-1} for k_2. A value of 3.0 × 10^7 M for K_{II} has been reported for the corresponding 6,6'-dimethyl-2,2'-bipyridine complex in 50% dioxane/50% water.[16]

The mean second-order rate constants for reduction of Cu-(tmbp)$_2^{2+}$ and Cu(dmbp)$_2^{2+}$ by the Ru(II) complexes, in reactions varying by 0.22 V in potential (Table I), show only a 3-fold increase in rate, compared to the 70-fold change predicted by the Marcus theory ($\Delta \log k_2/\Delta E° = 8.4$). Such behavior mirrors closely that found previously for reactions of the bis(2,9-dimthyl-1,10-phenanthroline)copper(II) complex[5] and appears to be a characteristic of sterically constrained bis(diimine) complexes of copper(II) in outer-sphere reactions with Ru(II) ammine reductants. Values of the self-exchange electron-transfer rate

Table I. Rate Constants[a] for Reduction of Methyl-Substituted Bis(diimine) Copper(II) Complexes by Ruthenium(II) Ammine Complexes

Ru(II) compd	$E°_{Ru(II)/Ru(III)}$, mV[d] vs. NHE	$10^{-5}k_2$, M^{-1} s^{-1}		
		L = tmbp[b]	L = dmbp[b]	L = dmp[c]
Ru(NH$_3$)$_5$py^{2+}	315	4.7	4.2	5.5
Ru(NH$_3$)$_5$isn^{2+}	294	2.5	3.4	4.6
Ru(NH$_3$)$_4$bpy^{2+}	533	1.5	1.2	3.9

[a] All data at 25.0 °C, pH 6.1, and 0.10 M ionic strength (LiCF$_3$C-O$_2$). [b] In 20% methanol/80% water. [c] In H$_2$O.[5] [d] In 20% methanol/80% water.

constants, k_{22}, calculated for the Cu(tmbp)$_2^{+/2+}$ (73, 3.1 × 10^2, and 2.3 × 10^3 M^{-1} s^{-1}) and Cu(dmbp)$_2^{+/2+}$ (77, 5.8 × 10^2, and 2.7 × 10^3 M^{-1} s^{-1}) couples by using the Marcus relations[17,18] are found to increase with decreasing driving force. This is not an uncommon finding in the application of the Marcus theory,[19,20] which works best when $K \simeq 1$, and agreement between theory and experiment, in systems with known exchange rates, is frequently poorer for the more exothermic reactions.[21]

Extrapolation of log k_{22} vs $\Delta E°$ to $\Delta E° = 0$ has therefore been used as a means of estimating the true rate constant.[19] Values of 1.0 × 10^4 and 6.8 × 10^3 M^{-1} s^{-1}, obtained for the Cu(tmbp)$_2^{2+/+}$ and Cu(dmbp)$_2^{2+/+}$ self-exchange rate constants, respectively, in 0.10 M LiCF$_3$CO$_2$ and 20% methanol/80% water by this procedure, are similar to the values 2 × 10^4–1 × 10^5 M^{-1} s^{-1} estimated for Cu(dmp)$_2^{+/2+}$ self-exchange from data involving Ru(II) ammine and other reductants.[3,9]

The variation in the calculated self-exchange values could be due to an assumption inherent in the Marcus theory that the reorganization energy for the Cu(I) oxidation or Cu(II) reduction process is half that for Cu(I)–Cu(II) self-exchange and is independent of the cross reaction involved. For Cu(I)/Cu(II) systems, where considerable structural differences often exist between the two oxidation states, this is less likely to be so.[23] The weak driving-force dependence could also be tied to rate control by a nonredox process, such as loss of coordinated water from the Cu(II) center.

Although crystal structures reported for the Cu(II) and Cu(I) complexes Cu(tmbp)$_2$(ClO$_4$)$_2$·2H$_2$O and Cu(tmbp)$_2$ClO$_4$ show a discrete five-coordinate Cu(II) cation, [Cu(tmbp)$_2$H$_2$O]$^{2+}$, with a bound water molecule and a four-coordinate Cu(I) cation, Cu(tmbp)$_2^+$, no evidence was found for the saturation kinetics at high excess Ru(II) concentration, which would be expected with the formation of an intermediate four-coordinate Cu(II) species prior to its reduction by Ru(II), at least not over the Ru(II) concentration ranges employed. The slight deviation from linearity found at the highest Ru(NH$_3$)$_5$py^{2+} concentrations is attributed to experimental uncertainty in the data.

The rapid self-exchange rates estimated for bis(diimine) Cu(II) complexes suggest a relatively small internal reorganization barrier to electron transfer in these sterically constrained systems. Much lower self-exchange rate constants estimated for other copper complexes having tetradentate tripodal N$_2$S$_2$ donor ligands[6] (k_{22} = 0.5–50 M^{-1} s^{-1}) and cyclic and open-chain tetrathiaether ligands[2b] (k_{22} = 73–470 M^{-1} s^{-1}) and for the aquo ions[5] Cu$^+$-(aq)/Cu^{2+}(aq) (k_{22} = 2 × 10^{-4} M^{-1} s^{-1}) have been attributed to the considerable structural changes accompanying reduction of

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(17) $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$ and log $f_{12} = (\log K_{12})^2/\log (k_{11}k_{22}/Z^2)$, where k_{12} is the cross-reaction rate constant, k_{11} and k_{22} are the self-exchange rate constants of the Ru(II)/Ru(III) and Cu(I)/Cu(II) couples, K_{12} is the equilibrium constant, and Z is a collision number (taken to be 10^{11} M^{-1} s^{-1}).

(18) With use of $E°$ = 0.315, 0.394, and 0.533 V, for Ru(NH$_3$)$_5$py$^{2+/3+}$, Ru(NH$_3$)$_5$isn$^{2+/3+}$, and Ru(NH$_3$)$_4$bpy$^{2+/3+}$, k_{11} = 1.1 × 10^5 and 7.7 × 10^5 M^{-1} s^{-1}.

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the Cu(II) center, particularly changes in coordination number accompanying loss of ligated water. The bis(diimine) values are closer to the highest apparent self-exchange rate constant (k_{22} = 1.3×10^5 M^{-1} s^{-1}) estimated[22] for the blue copper protein plastocyanin, in which a coordination number change is precluded by the rigid Cu center, held inaccessible to solvent by the enveloping protein. Cu(II)–H$_2$O bond breaking does not appear to make a significant contribution to the activation process of the Cu(tmbp)$_2^{2+}$ and Cu(dmbp)$_2^{2+}$ reactions. The similarity in the k_{22} values estimated from Cu(tmbp)$_2^+$–Ru(III) and Cu-(tmbp)$_2^{2+}$–Ru(II) cross-reaction data also accords with this. The second-order rate constant (k_2 = 4×10^5 M^{-1} s^{-1}) measured for the oxidation of Cu(tmbp)$_2^+$ by *cis*-[Ru(NH$_3$)$_4$(isn)$_2$]$^{3+}$ yields a value of 1×10^4 M^{-1} s^{-1} for Cu(tmbp)$_2^{+/2+}$ self-exchange. For the corresponding bipyridyl and phenanthroline couples Cu-(bpy)$_2^{+/2+}$ and Cu(phen)$_2^{+/2+}$, where considerable differences exist in the degree of solvation of the Cu(II) and Cu(I) states, Cu(II)–Cu(I) self-exchange rate constants estimated from Cu(I) oxidation reactions[8] differ considerably from the values obtained from corresponding Cu(II) reductions.[3] A more recent estimate of the Cu(phen)$_2^{+/2+}$ and Cu(bpy)$_2^{+/2+}$ self-exchange rate constants by Anson and Lee,[23] without the simplifying assumption that the Cu(I) oxidant and the Cu(II) reductant make the same contribution to the reorganization energy of the exchange process, has produced k_{22} = 1.55×10^4 and 4.41×10^3 M^{-1} s^{-1} for the Cu(phen)$_2^{+/2+}$ and Cu(bpy)$_2^{+/2+}$ couples, the latter value being in good agreement with an alternative value they have obtained electrochemically. Somewhat surprising is the similarity between these values and the rate constants estimated for self-exchange in the methyl-substituted counterparts Cu(dmp)$_2^{+/2+}$ and Cu-(tmbp)$_2^{+/2+}$, which show a less than 3-fold rate advantage. It is of interest that the considerable thermodynamic destabilization of the Cu(II) state in sterically constrained methyl-substituted bis(diimine) complexes ($E°$ = 0.603 and 0.600 V for Cu(dmp)$_2^{2+/+}$ and Cu(tmbp)$_2^{2+/+}$; $E°$ = 0.174 and 0.120 V for Cu(phen)$_2^{2+/+}$ and Cu(bpy)$_2^{2+/+}$) is not reflected to a greater degree in the kinetic reorganization barrier to electron transfer between the Cu(I) and Cu(II) states.

Registry No. Cu(tmbp)$_2^{2+}$, 47718-61-6; Cu(dmbp)$_2^{2+}$, 90316-91-9; [Ru(NH$_3$)$_5$py](ClO$_4$)$_2$, 19482-31-6; [Ru(NH$_3$)$_5$isn](ClO$_4$)$_2$, 31279-70-6; [Ru(NH$_3$)$_4$bpy](ClO$_4$)$_2$, 69793-91-5; *cis*-[Ru(NH$_3$)$_4$(isn)$_2$](ClO$_4$)$_3$, 31279-74-0.

Supplementary Material Available: Tables II–IV, listing kinetic data (3 pages). Ordering information is given on any current masthead page.

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A New Method for Depositing Platinum Exclusively on the Internal Surface of Zeolite L

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Received November 19, 1986

Natural and synthetic aluminosilicates are of practical importance as molecular sieves and catalysts. Synthetic zeolites modified with nonframework metals are among those materials that have been intensively studied with regard to cation-exchange properties, metal ion localization, and catalysis.[1-3] Transition metal ion exchanged zeolites have been found to be particularly

efficient for various catalytic reactions. For example, oxidation of propylene by cupric ion exchanged zeolite Y,[4] cyclodimerization of butadiene,[5] and the catalytic oxidation of ethylene by Pd^{2+}/Cu^{2+} metal ions on zeolite Y[6] have been described. Platinized zeolite L has been used in nonacidic catalytic re-forming and dehydrocyclization reactions.[7] Much of this chemistry has focused on creating encapsulated transition-metal catalysts. The principal role of the zeolite framework is to provide a compartmentalized environment, the metal being immobilized within the microporous structure. Molecules that poison the catalyst, if they are sufficiently large, may be size-excluded from the zeolite pore structure.[8] With smaller pore zeolites such as ZSM-5 and ZSM-11, reactant or product selectivity in a metal-catalyzed reaction is achieved by forcing the reactant molecule to pass though the intracrystalline volume in order to contact the metal. Good selectivity is usually obtained by poisoning the metal sites on the external surface with bulky ligands that are too large to access the internal metal sites.[9-11] Intrazeolite reactions are of course highly desirable in shape-selective catalysis since such selectivity may exceed that possible with liquid-phase catalysts.[12]

Some of the charge-balancing counterions of the anionic zeolite framework are readily exchangeable, and the usual route is to introduce metals by equilibration of cationic metal complexes or metal ions with a suspension of the zeolite. Thus Pt and Pd are easily loaded into the large-pore zeolites Y and L by exchanging Na$^+$ or NH$_4^+$ ions with Pt(NH$_3$)$_4^{2+}$ or Pd(NH$_3$)$_4^{2+}$.[8,13] Different loadings of noble metal are readily obtained by this ion-exchange method. Transmission electron microscopy and gas adsorption measurements have shown[8,13] that the bulk of the metal deposited is highly dispersed and lies within the zeolite pore structure. We have now prepared, using a neutral platinum complex, zeolite L powders that contain platinum metal exclusively on their inner surfaces. We describe two sensitive chemical tests that can differentiate between zeolites platinized both inside and outside and those platinized only on the inside. To our knowledge, this is the first time that chemical tests have established the absence of metal clusters or particles on the outer surfaces of a metalated zeolite. These platinized zeolite L powders are part of an integrated system for light-driven vectorial electron transport and hydrogen evolution that is described elsewhere.[14]

Experimental Section

Materials. Zeolite L (ideal formula K$_6$Na$_3$Al$_9$Si$_{27}$O$_{72}$·21H$_2$O) and zeolite Y (Na$_{56}$Al$_{56}$Si$_{136}$O$_{384}$·250H$_2$O) powders were obtained from Union Carbide, Linde Division. Scanning electron microscopy showed that the average particle size was in both cases about 1 μm. Tetraammine-platinum(II) chloride and platinum acetylacetonate (Pt(acac)$_2$) were obtained from Strem Chemicals. Methylviologen iodide was prepared

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