Table I. Experimental Conditions and k_{obsd} Values[a]

ester	solvent	$[H_2O]$/M	temp/°C	k_{obsd}/s^{-1}
methyl	MeOH	0.092	20.3	0.57
			29.2	0.89
			39.3	1.35
			48.0	2.06
methyl	CH_3CN	17.3	25.0	76
ethyl	CH_3CN	13.0	15.3	2.58
			25.0	3.22
			35.0	6.75
			46.5	10.9
isopropyl	CH_3CN	13.0	9.8	0.053
			15.0	0.069
			26.0	0.123
			37.0	0.208
			44.0	0.284
cage	CH_3CN	13.0	15.0	49
			25.0	54
			36.0	69
			45.0	86

[a] The average standard deviation on k_{obsd} values was 7%.

Table II. Rate Constants and Activation Parameters

ester	$k_{25}/M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
methyl[a]	8.3	33 ± 1	−116 ± 5
methyl[b]	4.4		
ethyl[b]	0.29	35 ± 5	−138 ± 17
isopropyl[b]	0.0086	34 ± 3	−170 ± 2
cage[b]	4.7	12 ± 2	−190 ± 7

[a] CH_3OH as solvent. [b] CH_3CN/30% H_2O as solvent.

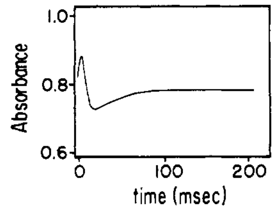

Figure 4. Stopped-flow oscilloscope trace of triethyl arsenite hydrolysis monitored with phenol red indicator at 598 nm. $[As(OEt)_3] = 2.62 \times 10^{-3}$ M; [phenol red] $= 2.5 \times 10^{-4}$ M.

formed. This is what was observed in the oscilloscope trace reproduced in Figure 4.

Experiments determining k_{obsd} at concentrations of water from 13 to 20 M were performed. In general, plots of k_{obsd} vs. $[H_2O]$ were linear in this range, although scatter was present. An initial rate study was done with triethyl arsenite to further clarify the order with respect to water. Methanol was employed as solvent to allow low water concentrations to be used, and a plot of $\Delta A/\Delta t$ vs. $[H_2O]$, Figure 3, was linear. We conclude, therefore, that the general rate law for the compounds studied has the following form at low water concentrations:

$$-d[As(OR)_3]/dt = k_1[As(OR)_3][H_2O] \qquad (5)$$

We approximate k_1 values where low water concentrations were not possible as $k_1 = k_{obsd}/[H_2O]$ and use the values so derived in the determination of activation parameters. Of course, no such approximation was necessary in the case of the trimethyl arsenite hydrolysis in methanol. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained and values of k_1 at 25 °C are reported in Table II. It should be noted that the values of $\Delta S^{\ddagger}$ are subject to systematic error of up to 20%; however, this error is not sufficient to alter the interpretation.

For the trialkyl arsenites the rate decreases by roughly an order of magnitude with each substitution of a carbon atom in the alkyl group, triisopropyl arsenite hydrolyzing some 300 times more slowly than trimethyl arsenite. The activation enthalpies are small for the trialkyl arsenites, and the activation entropies are large and negative. These results are in accord with previous work involving oxygen exchange between arsenite monoanion and water[9]: $k_{25} = 167\ s^{-1}$, $\Delta H^{\ddagger} = 25$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -120$ J K^{-1} mol^{-1}. They are also remarkably similar to results on the rates of hydrolysis of arsenate triesters[6] and pyroarsenate ion[7] and the rates of alcohol exchange with arsenate triesters[5] where activation enthalpies ranged from 0 to 50 kJ mol^{-1} and activation entropies from −100 to −200 J K^{-1} mol^{-1}. As in these other cases, a highly associative mechanism is indicated with the probable formation, in this case, of a four-coordinate intermediate.

The results obtained with the cage arsenite, on the asumption that the basic features of the mechanism are the same, would suggest that attack of the incoming nucleophile, H_2O, occurs on a face of the arsenite defined by two oxygen atoms and the lone pair of electrons. If attack were to take place on the unique face, defined by the three oxygen atoms, the formation of four-coordinate arsenic would be expected to be more energetically unfavorable than for the trialkyl arsenites. Approach to the arsenic atom from this direction would be sterically hindered by the cage structure, and coordination of the incoming nucleophile, H_2O would require considerable bond breaking in at least one of the rings of the cage. The observed rate constant, $k_1 = 4.7\ M^{-1}\ s^{-1}$, and activation parameters, $\Delta H^{\ddagger} = 12$ kJ mol^{-1} and $\Delta S^{\ddagger} = -190$ J K^{-1} mol^{-1}, certainly do not support such a mechanism. We conclude, therefore, that nucleophilic attack occurs "back side" to the leaving alkoxy group. The considerably lower value of $\Delta H^{\ddagger}$, compared with those of the trialkyl arsenites, is interesting. Possible explanations are (1) the incoming nucleophile is less hindered sterically, allowing for a closer approach to the arsenic in the transition state compared to the case of the trialkyl esters, and thus more bond formation, (2) there is some alleviation of ring strain in the cage upon formation of the proposed four-coordinate intermediate, and (3) some combination of (1) and (2) occurs.

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Registry No. $As(OMe)_3$, 6596-95-8; $As(OEt)_3$, 3141-12-6; $As(OPr\text{-}i)_3$, 39936-83-9; 4-methyl-2,6,7-trioxa-1-arsabicyclo[2.2.2]octane, 22223-55-8.

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Comparative Studies of the Kinetics of Macrocycle Dissociation from Nickel(II) in the Presence of Excess Copper Ion and 1,10-Phenanthroline

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Previously, the thermodynamics of complexation and the kinetics of formation[2] and dissociation (in the presence of

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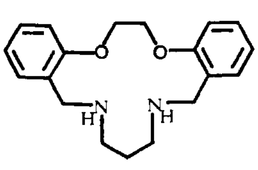
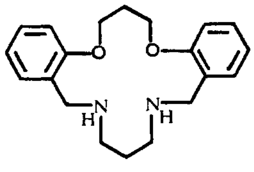
acid)[3,4] of nickel(II) complexes of a series of O_2N_2-donor macrocycles such as **1** and **2** have been studied as part of an



1 OenNtnH$_4$



2 OtnNtnH$_4$

overall investigation of the use of such ligands for metal ion recognition studies.[5] X-ray diffraction structures of the nickel chloride complex of **1**[6] and the nickel bromide complex of **2**[7] indicated that both have similar trans-halo, pseudooctahedral geometries.

A study of the kinetics of dissociation (in both aqueous hydrochloric acid and hydrochloric acid in 95% methanol) of the nickel complexes of the 14- to 17-membered macrocycles of the present type indicated that macrocyclic structure strongly influences the observed dissociation rates.[3,4] The kinetic labilities were found to follow the ring size sequence 14 > 15 > 16 < 17. In contrast to other studies involving all nitrogen-donor macrocycles,[3,8,9] the dissociation rates were found to be independent of acid concentration.

The present paper reports the results of an investigation of the dissociation of the nickel chloride complexes of **1** and **2** in the presence of excess copper(II) chloride or excess 1,10-phenanthroline. The effect of bidentate ligands on macrocycle dissociation has been little studied previously since bidentate ligands do not usually bind sufficiently strongly to displace most macrocycles from their central metal ion. It is the use of O_2N_2-donor macrocycles with their moderate affinity for nickel(II) which has made such studies possible in the investigation now reported.

Experimental Section

Stock solutions of recrystallized Ni(OenNtnH$_4$)Cl$_2$ and Ni(OtnNtnH$_4$)Cl$_2$ were prepared and analyzed as described previously.[4] All the studies were performed with 95% methanol (prepared from distilled AR methanol), and where necessary, the ionic strengths of all solutions were maintained at 0.1 M with Fluka tetramethylammonium chloride, which had been recrystallized from a methanol/acetone mixture. The bidentate amines (from BDH) were recrystallized from 20% methanol before use. All other reagents were of analytical grade.

The copper-exchange reactions were followed spectrophotometrically at 805 nm for Ni(OenNtnH$_4$)Cl$_2$ and at 770 nm for Ni(OtnNtnH$_4$)Cl$_2$ by using a Beckman Acta IV spectrophotometer fitted with a quartz two-compartment cell. Equal volumes of complex and copper chloride solutions were loaded into the cell compartments and rapidly mixed after temperature equilibration had occurred. Plots of ln $(A_t - A_\infty)$ vs. time, which were linear for at least 3 half-lives, were used to obtain values of the first-order rate constants. Alternatively, the constants were obtained by analysis of the data with the locally written computer program KINFIT 1, which gives a weighted linear least-squares fit to the first-order rate equation. For the ligand-exchange reactions, the kinetics were followed with use of the stopped-flow apparatus described previously[10] or, for a number of runs involving Ni(OenNtnH$_4$)Cl$_2$, the split-cell technique was employed. Both procedures gave values which were identical within experimental error. The respective pseudo-first-order constants (k_{obsd}) were calculated by using the procedures described above. All measured constants are the mean of at least three separate (and up to twelve) determinations; errors are standard deviations from the mean. The rapid-scan, stopped-flow runs were performed on a custom-built apparatus to be described elsewhere.[11]

Table I. First-Order Dissociation Rates in the Presence of Hydrochloric Acid[a] and Copper Chloride [in 95% Methanol; $I = 0.1$ ((CH$_3$)$_4$Cl)]:[b] $Ni(mac)^{2+} \rightarrow Ni^{2+} + mac$ (Rate Determining)

	scavenger	$[H^+]/[Cu^{2+}]$	k, s^{-1}
Ni(OenNtnH$_4$)Cl$_2$	H$^+$	0.1	$(1.1 \pm 0.1) \times 10^{-2}$
Ni(OenNtnH$_4$)Cl$_2$	H$^+$	0.05	$(1.2 \pm 0.1) \times 10^{-2}$
Ni(OenNtnH$_4$)Cl$_2$	Cu^{2+}	1.4×10^{-2}	$(1.6 \pm 0.1) \times 10^{-2}$
Ni(OenNtnH$_4$)Cl$_2$	Cu^{2+}	1.6×10^{-2}	$(1.6 \pm 0.1) \times 10^{-2}$
Ni(OenNtnH$_4$)Cl$_2$	Cu^{2+}	2.9×10^{-2}	$(1.5 \pm 0.1) \times 10^{-2}$
Ni(OenNtnH$_4$)Cl$_2$	Cu^{2+}	3.3×10^{-2}	$(1.5 \pm 0.1) \times 10^{-2}$
Ni(OtnNtnH$_4$)Cl$_2$	H$^+$	0.1	$(5.4 \pm 0.3) \times 10^{-3}$
Ni(OtnNtnH$_4$)Cl$_2$	Cu^{2+}	3.3×10^{-2}	$(6.7 \pm 0.2) \times 10^{-3}$

[a] From ref 7. [b] Complex concentrations were between 2×10^{-3} and 4×10^{-3} M in each case.

Results and Discussion

Dissociation in the Presence of Copper Ion. The rates of dissociation of the nickel chloride complexes of **1** and **2** in 95% methanol ($I = 0.1$) were measured in the presence of excess copper(II) chloride. The conditions used for the experiments were similar to those employed previously for dissociation studies in the presence of acid. The results from previous potentiometric stability studies indicate that the stability constants of the 1:1 complexes of copper are ~10^2 times greater than for nickel.[12,13] Consequently, under the conditions of excess copper used for the measurements, metal exchange will proceed to completion. The first-order dissociation rate constants are independent of copper ion concentration (Table I) and are very similar to the values obtained when acid was used as the ligand scavenger. The relatively small differences in the rates between corresponding reactions may be attributed, at least in part, to medium effects arising from the use of hydrochloric acid in one case and copper chloride in the other to maintain ionic strength. The overall reaction can therefore be considered to involve the slow dissociation of the macrocycle from the nickel complex followed by fast scavenging of the free macrocycle by acid in one case and by copper ion in the other.

For open-chain polydentate-ligand complexes, metal exchange is usually dependent on the concentration of the exchanging metal ion.[14,15] It has been postulated that a binuclear complex is formed as an intermediate in such cases. However, with cyclic ligands of the type used in the present study, bridge formation will be more difficult, and the spontaneous dissociation of the complex is found to dominate the kinetic behavior.[16]

In related studies, Kaden and Kallianou[17] observed no copper ion dependence when this ion was used for an inves-

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Table II. Rate Data (k_{obsd} Values) for the Dissociation Reactions Involving 1,10-Phenanthroline and 2,2′-Bipyridine[a]

$10^2[L]_0$, M	$10^3[Ni]$, M	$10^2 k_{obsd}$, s^{-1}	$10^2[L]_0$, M	$10^3[Ni]$, M	$10^2 k_{obsd}$, s^{-1}
		phen-Ni(OenNtnH$_4$)Cl$_2$ System			
2.90	2.4	3.2 ± 0.2	12.14	3.0	7.1 ± 0.2
3.84	2.4	3.7 ± 0.1	12.14	3.7	6.8 ± 0.3
3.84	3.7	3.7 ± 0.1	12.14	4.0	6.8 ± 0.2
4.50	3.7	4.1 ± 0.1	12.14	4.9	7.0 ± 0.2
5.28	2.4	4.7 ± 0.2	12.14	6.1	6.8 ± 0.2
6.07	2.4	4.8 ± 0.2	12.14	7.0	7.2 ± 0.2
7.23	3.7	5.2 ± 0.3	12.14	8.9	7.2 ± 0.2
7.23	6.1	5.4 ± 0.2	12.14	10.6	7.0 ± 0.2
12.14	2.4	7.1 ± 0.2	12.14	10.6	7.1 ± 0.2[b]
		bpy-Ni(OenNtnH$_4$)Cl$_2$ System			
4.04	3.8	2.0 ± 0.2	12.14	3.8	4.0 ± 0.2
6.07	3.8	2.6 ± 0.2	12.14	7.6	3.9 ± 0.2
8.09	7.6	3.3 ± 0.2			
		phen-Ni(OtnNtnH$_4$)Cl$_2$ System			
3.60	2.5	35 ± 2	6.60	6.3	43 ± 2[b]
3.88	2.5	37 ± 1	6.60	7.5	47 ± 2[b]
5.49	2.5	43 ± 1	13.20	2.5	56 ± 2
5.50	3.8	42 ± 1	13.20	3.8	57 ± 1
6.45	3.8	44 ± 1	13.20	6.3	55 ± 3[b]
6.60	3.8	44 ± 1	13.20	7.5	57 ± 1[b]
6.60	6.3	44 ± 1	13.20	12.6	56 ± 2[b]

[a] At 25 °C; $I = 0.1$ [(CH$_3$)$_4$Cl] in 95% methanol. All rates were measured spectrophotometrically at 365 nm unless otherwise designated. [b] Measured at 400 nm.

tigation involving exchange of nickel from a S$_2$N$_2$-donor macrocycle. For the nickel complex, the rate of dissociation of the macrocycle in the presence of acid was also found to be very similar to that obtained in the copper-exchange experiment. The present results are thus in accord with this previous study.

Dissociation in the Presence of 1,10-Phenanthroline. The interaction of excess 1,10-phenanthroline (phen) with Ni(OenNtnH$_4$)Cl$_2$ and Ni(OtnNtnH$_4$)Cl$_2$ in 95% methanol [I = 0.1, (CH$_3$)$_4$NCl] has been investigated. Spectrophotometric studies indicated that the following overall reaction occurs:

$$\mathrm{Ni(mac)Cl_2 + excess\ phen \rightarrow Ni(phen)_3^{2+} + mac + 2Cl^-}$$

The final spectrum in the visible region is that of [Ni(phen)$_3$]$^{2+}$ for each system. Further, spectrophotometric titration of Ni(OenNtnH$_4$)Cl$_2$ in 95% methanol with 1,10-phenanthroline clearly indicated a 1:3 end point, there being no further absorption change in the visible region shortly after the 1:3 ratio was reached.

Stopped-flow, rapid-scan spectral runs for the OenNtnH$_4$ system over the wavelength range 450–700 nm were consistent with the presence of a single dissociation process, with the spectra showing an isosbestic point near 570 nm. However, because of small absorbance changes in the visible range, it was found more appropriate to perform the majority of the kinetic runs at 365 nm, where larger absorbance changes occur for the ligand replacement reaction. In contrast to the visible region, rapid scans at this lower wavelength indicated the presence of a second, faster process, which appears to be complete within ~2 s after the initiation of the reaction. The fast reaction rate coupled with the moderate observed absorbance changes made the study of this reaction difficult, and no kinetic analysis was attempted. Similarly, at 365 nm, a faster reaction was also evident for the Ni(OtnNtnH$_4$)Cl$_2$ system but was not studied further; for both systems the nature of this fast process remains unresolved.

Table III. Values of K (M^{-1}) and k_1 (s^{-1}) for the Slower Dissociation Process[a]

complex	ligand	K	$10k_1$
Ni(OenNtnH$_4$)Cl$_2$	phen	11.6 ± 1.1	1.19 ± 0.05
	bpy	8.7 ± 2.8	0.77 ± 0.14
Ni(OtnNtnH$_4$)Cl$_2$	phen	26.8 ± 5.1	7.15 ± 0.51

[a] Obtained by means of a weighted nonlinear least-squares fit of the rate equation.

The kinetics of the slower reaction for each of the above complexes in the presence of large excesses of 1,10-phenanthroline indicated that this reaction is first order in nickel complex as shown by the linearity over several half-lives of plots of ln ($A_t - A_\infty$) vs. t (using data taken after completion of the fast reaction) and the independence of the rate constants on the initial complex concentration. Qualitatively similar behavior was observed for both macrocyclic systems although the observed rate constants (k_{obsd}) for the 16-membered ring system are approximately 1 order of magnitude greater than those for the 15-membered ring system under similar conditions (Table II). For each system, the presence of phenanthroline enhances the rate of removal of the macrocycle over that observed when either acid or copper ion is used to scavenge the free macrocycle once it has dissociated from the nickel ion.

Plots of [phen] vs. k_{obsd} for the slower reaction are curved in each case. Although other possibilities also exist, the rate data were found to be in accordance with the scheme[18]

$$\mathrm{A + B \overset{K}{\rightleftharpoons} AB \xrightarrow{k_1} C}$$

If B is in large excess, then it can be shown that

$$k_{obsd} = \frac{k_1 K[\mathrm{B}]_0}{1 + K[\mathrm{B}]_0} \qquad (1)$$

where $[\mathrm{B}]_0$ = initial concentration of B. Inverting (1) yields

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{1}{k_1 K[\mathrm{B}]_0} \qquad (2)$$

and hence a plot of $1/k_{obsd}$ vs. $1/[\mathrm{B}]_0$ will be linear with slope $1/k_1K$ and intercept $1/k_1$. Such plots for reactions involving both the 15-membered and 16-membered macrocyclic systems were linear and were used to obtain initial estimates of the respective preequilibrium binding constants (K) and the first-order dissociation rate constants (k_1). Using these estimates, a nonlinear least-squares fit of the experimental data given in Table II to eq 1 yielded the final values for K and k_1 listed in Table III. As required by (1), it was found that the computed curve passes through the origin for this system and each of the other two systems studied. It it noted that the values for the preequilibrium constants for the phen systems (Table III) do not differ greatly whereas the subsequent first-order dissociations are markedly dependent on ring size. Choice of a mechanism is not straightforward since there are a number of possibilities that satisfy the rate equation.

A tentative mechanism involves a preequilibrium (equilibrium constant K) between free and coordinated 1,10-phenanthroline, in which this ligand coordinates to an axial

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(16) Nevertheless, metal-exchange reactions involving porphyrin macrocycles in some instances have been demonstrated to show a dependence on both the macrocyclic complex and the exchanging metal ion (see ref 22). In these cases the exchange is slow and is assumed to proceed via a dimetallic activated complex. However, the macrocycles discussed in the text are all more flexible than the porphyrins and, for these, a dissociation pathway involving macrocycle folding appears to dominate the respective dissociation kinetics. In contrast, the rigidity of the porphine moiety will result in this pathway being nonaccessible for porphyrin complexes and, as a consequence, a further dissociation mechanism presumably involving a dinuclear species becomes significant.

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site of the nickel complex in a monodentate fashion. This initial adduct formation is followed by a slow ring-closing step (first-order rate constant k_1), during which the macrocycle simultaneously changes its coordination from (planar) trans to (folded) cis. Finally, the rapid replacement in the coordination sphere of the folded macrocycle by two 1,10-phenanthroline ligands occurs to yield $[Ni(phen)_3]^{2+}$.[19]

A parallel study involving reaction of excess 2,2′-bipyridyl with $Ni(OenNtnH_4)Cl_2$ has been performed. In this case the K and k_1 values (Table III) were both slightly reduced relative to those obtained with the more rigid ligand, 1,10-phenanthroline.[20]

Previously, ligand folding has been implicated in the dissociation of flexible macrocycles from complexes containing the macrocycle coordinated in a planar form.[17,21-23] The observation of enhanced dissociation in the presence of bidentate ligands (which, on coordination, will promote folding of the macrocycle) thus provides additional indirect support for this postulate.

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Registry No. $Ni(OenNtnH_4)Cl_2$, 66810-83-1; $Ni(OtnNtnH_4)Cl_2$, 66793-45-1; Cu, 7440-50-8; phen, 66-71-7; bpy, 366-18-7.

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(19) The following are in accord with the proposed mechanism: (i) the adduct of 1,10-phenanthroline with a square-planar macrocyclic nickel complex has been demonstrated by X-ray diffraction to have a cis distorted-octahedral structure of the general type postulated to occur during the dissociation reaction (see: Stephens, F. S.; Vagg, R. S. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3165), (ii) the formation of an intermediate involving singly N-bonded 1,10-phenanthroline to nickel has been postulated previously (see: Steinhaus, R. K.; Lee, B. I. *Inorg. Chem.* **1982**, *21*, 1829 and references therein), (iii) the ring-closing reaction involving coordination of the second nitrogen might be expected to be slow since it would be controlled by the rate with which the macrocycle changes from a planar to a folded form in the coordination sphere, and (iv) the k_1 values would be expected to be markedly dependent on macrocycle ring size (as observed), the larger value for k_1 obtained for the $OtnNtnH_4$ system being perhaps a reflection of the greater flexibility of this larger ring system aiding the folding of the macrocycle.

(20) Further kinetic runs involving $Ni(OenNtnH_4)Cl_2$ and 3,4,7,8-tetramethylphenanthroline (Me_4phen) at two concentrations (the restricted solubility of this ligand prevented a more detailed study) gave k_{obsd} values that are identical within the experimental error ($[Me_4phen] = 0.030$ M, $k_{obsd} = 0.033\ s^{-1}$; $[Me_4phen] = 0.059$ M, $k_{obsd} = 0.0480\ s^{-1}$) with those found for the corresponding 1,10-phenanthroline system. The similarity of these values suggests that "self-stacking" interactions of the type found for 1,10-phenanthroline or 2,2′-bipyridyl in aqueous solution (see: Mitchell, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1079) or "outer-sphere stacking" interactions (see: Cayley, G. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, 1002) of the type postulated to occur between free aromatic ligands and a range of nickel complexes of coordinated aromatic ligands are not significant in the present systems. The presence of substituents on the phenanthroline moiety would be expected to affect the nature of any such "stacking" whereas the normal coordination behavior might be little affected since the methyl substituents are remote from the coordination sites. Thus, if stacking of either of the above types occurred, it seems unlikely that the k_{obsd} values would remain similar as observed. Further, ^1H NMR experiments confirm that ligand self-association is insignificant under conditions that approximate those used in the present work: Mitchell, P. R., Institute of Inorganic Chemistry, University of Basel, personal communication.

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Communications

Multiple Oxidation States of Ruthenium and Osmium Based on Dioxo/Diaquo Couples

Sir:

Recently it was shown that ruthenium(IV)–oxo complexes containing polypyridine ligands are accessible by sequential oxidation of the corresponding ruthenium(II)–aquo complexes (eq 1; py = pyridine, bpy = 2,2′-bipyridine, pH = 7).[1,2] The

$$(bpy)_2(py)Ru^{IV}{=}O^{2+} \underset{\substack{-e^-,-H^+\\(E\ =\ +0.53\ V)}}{\overset{+e^-,+H^+}{\rightleftharpoons}} (bpy)_2(py)Ru^{III}{-}OH^{2+} \underset{\substack{-e^-,-H^+\\(E\ =\ +0.42\ V)}}{\overset{+e^-,+H^+}{\rightleftharpoons}} (bpy)_2(py)Ru^{II}{-}OH_2^{\,2+}$$

oxidations involve the net loss of both protons and electrons in aqueous solution over a wide pH range. The importance of the oxo/aquo redox chemistry is shown by (1) the catalytic oxidation of alcohols, aldehydes, and C—H bonds adjacent to unsaturated hydrocarbons by $(trpy)(bpy)Ru{=}O^{2+}$ (trpy is 2,2′,2″-terpyridine),[3] (2) the reversible reduction of nitrate to nitrite by $(bpy)_2(py)Ru(OH_2)^{2+}$,[4] and (3) the catalytic oxidation of water by an oxidized form of the oxo-bridged dimer of ruthenium(III) $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$.[5] In contrast to the two-electron chemistry of the monomeric aquo complexes, there is a potential four-electron chemistry associated with the diaquo systems *cis*-$(bpy)_2M(OH_2)_2^{\,2+}$ (M = Ru, Os). We report here that oxidation states II, III, IV, V, and VI are all accessible to the metal in the diaquo systems through a series of concomitant electron–aquo–proton losses and that the higher oxidation states appear over a remarkably narrow potential range.

Figure 1a depicts a cyclic voltammogram and Figure 1b depicts a differential pulse polarogram for *cis*-$(bpy)_2Ru(OH_2)_2^{\,2+}$ at pH 1.4. When combined with the results of coulometric experiments, both experiments provide evidence for a series of four sequential one-electron oxidation steps. The reversible one-electron oxidation of Ru(II) to Ru(III) has been reported.[6] It is followed by three additional one-electron oxidation steps. The Ru(III)/Ru(IV) couple, as shown by both

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(1) All potentials are listed vs. the saturated sodium chloride calomel electrode (SSCE), in aqueous media at 25 °C. The working electrodes are glassy carbon or carbon paste.

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