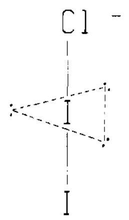
s^{-1}. Under our conditions this reaction would have a diffusion-controlled rate. Therefore, the rate of I_2 formation via eq 2 and 22 would depend only on the rate of hydrolysis of ICl ($=k_h$[ICl]). Accordingly, $k_I \approx k_hK_I/[Cl^-]$, but we did not observe a reciprocal $[Cl^-]$ dependence for k_I. If k_I were as large as 400 s^{-1}, then k_h could be between 7×10^3 s^{-1} for 0.1 M Cl^- and 7×10^4 s^{-1} for 1 M Cl^-. These values seem unreasonably large compared to hydrolysis rate constants of 28.6, 110, and 3.0 s^{-1} for Cl_2, Br_2, and I_2, respectively.[1] Thus, at present the rate of hydrolysis of ICl is not known.

Another possible path for the formation of I_2 in the absence of added I^- is the disproportionation of ICl. However, this rate depends on $[ICl]^2$ and is much too slow[24] to account for the k_I term.

A path for the direct attack of I^- on ICl_2^- to give I_2Cl^- and Cl^- is omitted from the mechanism because of the large uncertainty of the value, $(1 \pm 3) \times 10^6$ M^{-1} s^{-1}, for this second-order rate constant. A $I_2Cl_2^{2-}$ transition state would require a central iodine atom with six electron pairs (three nonbonding pairs around I^+ and three bonding electron pairs from one I^- and two Cl^- ions). This would be expected to be very unfavorable in contrast to the five electron pairs around the central iodine in I_2Cl^-, where structure I corresponds to the geometry expected from valence shell electron pair repulsion theory.[25]



I

Conclusion

The PAF method is used to study the kinetics of irreversible atom-transfer reactions that are too fast to study by stopped-flow methods. Reaction rate constants from 3800 to 70 000 s^{-1} have been measured for the reaction of ICl_2^- solutions with I^-. In this study, it has been shown that the reaction of I^- with ICl has a second-order rate constant of 1.1×10^9 M^{-1} s^{-1}, whereas the rate constant for the reaction of I^- with ICl_2^- is at least 1000 times smaller.

Acknowledgment. This investigation was supported by National Science Foundation Grant No. CHE-8319935.

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Notes

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Kinetic Study of the Conversion of *cis*-Diaqua(1,4,7,10-tetraazacyclotridecane)nickel(II) to the Planar Complex[1]

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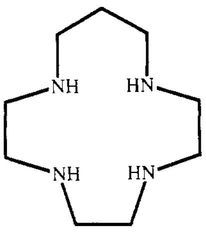
The recent publication by Hay and Akbar Ali[2] of some rates of cis-to-planar interconversion of the Ni(II) complex of the macrocyclic ligand 1,4,7,10-tetraazacyclotridecane ($13aneN_4$, structure I) prompts us to report our extensive investigation of the same system. We find that, during the conversion of *cis*-$Ni(13aneN_4)(H_2O)_2^{2+}$ to the planar complex $Ni(13aneN_4)^{2+}$, a transient species, identified as a configurational isomer of planar $Ni(13aneN_4)^{2+}$, is observed. Similar configurational isomers have been postulated in the similar reaction of the corresponding *cis*-$Ni(14aneN_4)(H_2O)^{2+}$ complex,[3] but the Ni(II)–$13aneN_4$ system is the first in which such isomers have been observed as intermediates during the course of the reaction. We therefore report our preliminary findings despite the fact that some aspects of the mechanism remain to be elucidated.



I

Experimental Section

The ligand $13aneN_4$ was synthesized by following the method of Fabbrizzi[4] and isolated as the tetrahydrochloride salt. The ligand was converted to the nickel complex; well-formed yellow crystals of $Ni(13aneN_4)(ClO_4)_2$ were obtained and were recrystallized from hot water. Aqueous solutions of the complex exhibited the reported λ_{max} at 425 nm,[4] characteristic of square-planar nickel(II).

The cis complex, *cis*-$Ni(13aneN_4)(H_2O)_2^{2+}$, was generated in solution according to our earlier procedure[5] by adding a slight excess of ethylenediamine to form the mixed-ligand complex $Ni(13aneN_4)(en)^{2+}$, followed by acidification to yield the folded complex *cis*-$Ni(13aneN_4)(H_2O)_2^{2+}$. A few rates were measured by using *cis*-$Ni(13aneN_4)Cl_2$, prepared by our earlier procedure.[5]

Rates of interconversion of *cis*-$Ni(13aneN_4)(H_2O)_2^{2+}$ were measured by following the increase in absorbance at 425 or 430 nm. Rates were measured at 25 °C and, with the exception of a few rates at pH values below 1, at $I = 0.10$ ($NaClO_4$). Hydrogen ion and hydroxide ion concentrations were obtained from measured pH by using the following relationships: $-\log [H^+] = pH - 0.10$ and $K_w = 13.78$ (25 °C, 0.10 M $NaClO_4$).

Results and Discussion

The d–d spectrum of *cis*-$Ni(13aneN_4)(H_2O)_2^{2+}$ is similar to that of other *cis*-$Ni^{II}N_4O_2$ chromophores,[6] with bands at the following wavelengths (ϵ, M^{-1} cm^{-1}, in parentheses): 340 nm (15), 535 nm (9), 900 nm (18). *cis*-$Ni(13aneN_4)(H_2O)_2^{2+}$ spontaneously isomerizes to the stable planar complex $Ni(13aneN_4)^{2+}$.

At pH values below approximately 6 the interconversion reaction exhibits biphasic first-order kinetics (see Figure 1). Rate constants for the two reactions were obtained by standard methods.[7] From pH 1 to 4 the second reaction is some 50 times slower than the first, which enabled us to record the spectrum of the solution during the fast reaction with essentially no in-

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[1] Presented in part at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983.

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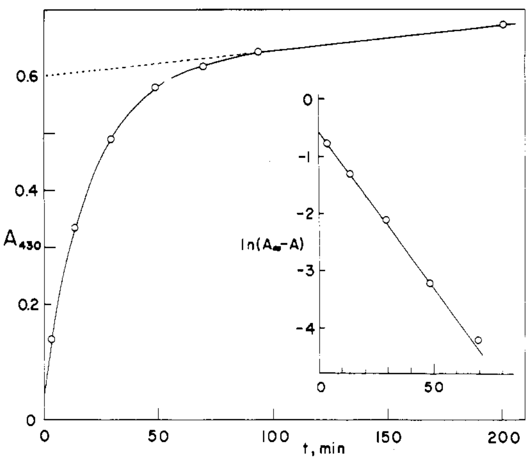

Figure 1. Typical biphasic rate data for the interconversion of *cis*-Ni(13aneN$_4$)(H$_2$O)$_2$$^{2+}$ to β-Ni(13aneN$_4$)$^{2+}$ (initial concentration 1.05 × 10^{-3} M, cell path 10 cm, pH 2.10). The final absorbance reading was 0.925. The inset illustrates the first-order nature of the fast reaction.

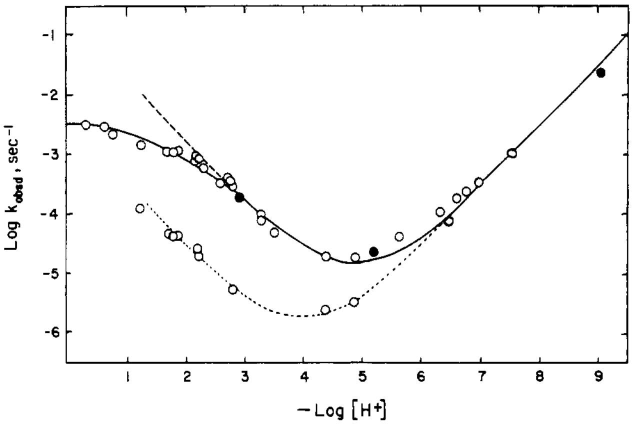

Figure 2. Rate-pH profile of the fast (solid line) and slow (dashed line) reactions: open circles, reactions using Ni(13aneN$_4$)(en)$^{2+}$; solid circles, reactions using Ni(13aneN$_4$)Cl$_2$. The upper broken line represents a slope of -1, corresponding to first-order hydrogen ion catalysis.

terference from the product of the slow reaction. During the course of the fast reaction the octahedral peaks decrease and a new peak appears with λ_{max} of 435 nm, consistent with the formation of an intermediate planar species α-Ni(13aneN$_4$)$^{2+}$ (eq 1).

$$cis\text{-Ni(13aneN}_4\text{)(H}_2\text{O)}_2{}^{2+} \rightarrow \alpha\text{-Ni(13aneN}_4\text{)}^{2+} \rightarrow \beta\text{-Ni(13aneN}_4\text{)}^{2+} \quad (1)$$

Good isosbestic points were observed, indicating the presence of only the cis octahedral species and the planar intermediate α-Ni(13aneN$_4$)$^{2+}$ during the fast reaction. During the second reaction λ_{max} shifts to 425 nm and new isosbestic points are observed, indicating the conversion of the intermediate α-Ni(13aneN$_4$)$^{2+}$ to the stable planar isomer β-Ni(13aneN$_4$)$^{2+}$.

The observed rate constants are shown in Figure 2. The pH profile exhibits a number of features:

(i) Above pH 7 the reaction (eq 2) is base-catalyzed and monophasic. Our results for this pH region agree with those of

$$cis\text{-Ni(13aneN}_4\text{)(H}_2\text{O)}_2{}^{2+} \rightarrow \beta\text{-Ni(13aneN}_4\text{)}^{2+} + 2\text{H}_2\text{O} \quad (2)$$

Hay and Akbar Ali,[2] who published rate data for the pH range 7.6–8.9 only. They report base catalysis with a second-order rate constant of 2.4 × 10^3 M^{-1} s^{-1}; we find a second-order rate constant of 1.9 × 10^3 M^{-1} s^{-1} under the same experimental conditions.

(ii) From pH 1 to 6 the reaction is biphasic and both reactions are acid-catalyzed. When the fast reaction is essentially complete, the absorbance at 425 nm has reached 60% of the expected A_∞. From the absorbance of the 535-nm octahedral band remaining at the end of the fast reaction, we estimate that 50% of the folded complex has isomerized to the α-Ni(13aneN$_4$)$^{2+}$ form.

Table I. Base Catalysis Rate Constants for Ni(II) Complexes of Tetraaza Ligands[a]

complex	isomerizn reacn	k_{OH}, M^{-1} s^{-1}
Ni(2,3,2-tet)(H$_2$O)$_2$$^{2+}$	cis–planar	450[b]
Ni(14aneN$_4$)(H$_2$O)$_2$$^{2+}$	cis–planar	560[c]
Ni(13aneN$_4$)(H$_2$O)$_2$$^{2+}$	cis–planar	1900[d] 2400[e]
Ni(tetb)$^{2+}$[f]	planar–planar	800[g]

[a] 25 °C, I = 0.1. [b] Reference 5. [c] Reference 3. [d] This work. [e] Reference 2. [f] tetb = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. [g] Robinson, D. S.; Billo, E. J., unpublished work.

Fabbrizzi[4] estimated the equilibrium constant for high-spin–low-spin conversion (eq 1) of Ni(13aneN$_4$)$^{2+}$ at 25 °C and 0.1 M NaClO$_4$ to be 7 (13% high spin, 87% low spin). At completion of the fast reaction, the Ni(13aneN$_4$)(H$_2$O)$_2$$^{2+}$ to α-Ni(13aneN$_4$)$^{2+}$ interconversion effectively reaches equilibrium, and K for this reaction is approximately 1. The above observations are consistent with the kinetic scheme shown in eq 3, where in the pH range

$$cis\text{-Ni(13aneN}_4\text{)(H}_2\text{O)}_2{}^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \alpha\text{-Ni(13aneN}_4\text{)}^{2+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \beta\text{-Ni(13aneN}_4\text{)}^{2+} \quad (3)$$

1–4 the relative values of the rate constants k_1, k_2, k_3, and k_4 are 10:10:1:0.1. These four rate constants can be estimated from the two experimental rate constants k_{1obsd} and k_{2obsd} and the two equilibrium constants K_{12} (eq 3) and K for the octahedral-to-planar conversion (eq 2), which is equal to $K_{12}K_{34}$. The fast reaction can be treated as an approach to equilibrium, and thus $k_{1obsd} = k_1 + k_2$. Since $K_{12} = k_1/k_2$, $k_1 = k_{1obsd}K_{12}/(1 + K_{12})$ and $k_2 = k_{1obsd}/(1 + K_{12})$. The slow reaction can be treated as a reaction with prequilibrium, for which $k_{2obsd} = K_{12}k_3/(1 + K_{12})$. Thus $k_3 = k_{2obsd}(1 + K_{12})/K_{12}$ and $k_4 = 0.1k_3$.

(iii) In the pH range 1–2 the first-order acid catalysis of the fast reaction can be seen to be tending toward zero order in hydrogen ion. This suggests one of two possibilities: either the macrocyclic complex is extensively protonated in this pH region, or the rate-determining step has become Ni(II)–N bond breaking, followed by rapid proton-assisted isomerization. We discard the first possibility, since the ligand would necessarily be tridentate and there should be a detectable shift of the spectrum of the cis complex (typical Ni^{II}N$_4$O$_2$ complexes have λ_{max} of 350–360 and 550–560 nm while Ni^{II}N$_3$O$_3$ chromophores have λ_{max} values of 360–370 and 580–600 nm[8]). We have been able to detect no difference in the spectrum of the cis complex in 0.1 M acid (recorded immediately after mixing) compared to the spectrum in solutions of near-neutral pH.

In the base-catalyzed region, the reaction is monophasic. Interestingly, the base-catalysis rate constant for the isomerization of several linear and macrocyclic tetraaza ligands are very similar (Table I), suggesting the possibility of similar pathways despite the difference in geometrical change.

Although the structure of neither the folded reactant nor the planar product has been determined, it is likely that *cis*-Ni(13aneN$_4$)(H$_2$O)$_2$$^{2+}$ has the *cis*-IV or (+−+−)[9] structure, since this is the structure in which all four chelate rings have their minimum-energy conformation.[10] However, unlike the case for the Ni(14aneN$_4$)$^{2+}$ complex, there are three *trans*-Ni(13aneN$_4$)$^{2+}$ complexes of apparently similar stability, each having three of the four chelate rings in favorable conformation. In the absence of X-ray data we assume for the β isomer the trans-II or (+−−+) structure, which has been shown to be the structure adopted by the planar Ni(II) complex of 3,3-Me$_2$-13aneN$_4$.[11] If this is indeed the case, then the 13aneN$_4$ complex, like the 14aneN$_4$ complex,

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(9) A plus or minus sign indicates the orientation of the amino hydrogens above or below the plane, respectively, of the macrocycle. Nitrogen configurations are designated according to their number in the compound 1,4,7,10-tetraazacyclotridecane.

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must undergo two nitrogen inversions during isomerization. However, unlike the 14aneN$_4$ complex, the 13aneN$_4$ complex provides the first example of a configurational isomer intermediate that is observable during the course of the isomerization reaction. The slightly lower energy of λ_{max} for the intermediate α complex (435 nm), compared to that of the stable β isomer, is consistent with a somewhat poorer match between metal ion and macrocycle cavity size.

The trans-V or (+ − + +) isomer, which differs from the cis complex by inversion of a single nitrogen and which in turn yields the trans-II β isomer by subsequent inversion of a second nitrogen, appears to be a likely structure for the α isomer.

One final point must be mentioned. Although the kinetic scheme shown in eq 1 is consistent with the observed biphasic kinetics, another kinetic scheme (eq 4) is also possible. Here the

$$\alpha\text{-Ni(13aneN}_4)^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} cis\text{-Ni(13aneN}_4)(\text{H}_2\text{O})_2^{2+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \beta\text{-Ni(13aneN}_4)^{2+} \quad (4)$$

species α-Ni(13aneN$_4$)$^{2+}$ is not an intermediate, but a dead-end species formed in a relatively rapid equilibrium and then disappearing as the more stable product β-Ni(13aneN$_4$)$^{2+}$ is formed. Computer simulation of absorbance–time data sets similar to that in Figure 1 showed that, with only minor adjustment of the rate constants k_1, k_2, k_3, and k_4, either kinetic scheme was able to reproduce the data equally well. At the present time no way of resolving this case of kinetic indistinguishability seems apparent.

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Binuclear Platinum(II) Photochemistry. Nucleophile-Induced Reduction of Electron Acceptors by Electronically Excited $Pt_2(P_2O_5H_2)_4^{4-}$

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The electronic excited states of a number of inorganic complexes have been used as reagents to induce electron-transfer reactions.[2,3] In such reactions, a powerful oxidant (reductant) is generated by oxidative (reductive) quenching of the excited state of the metal complex with a one-electron acceptor A (donor D), and this species generally back-reacts rapidly with photogenerated A$^-$ (D$^+$). Here we describe several oxidative quenching reactions of a strongly emissive complex, Pt$_2$(pop)$_4$$^{4-}$ (pop = P$_2$O$_5$H$_2$);[3-9] the most important result is that the back-reaction between photogenerated Pt$_2$(pop)$_4$$^{3-}$ and A$^-$ can be inhibited by axial–ligand binding.

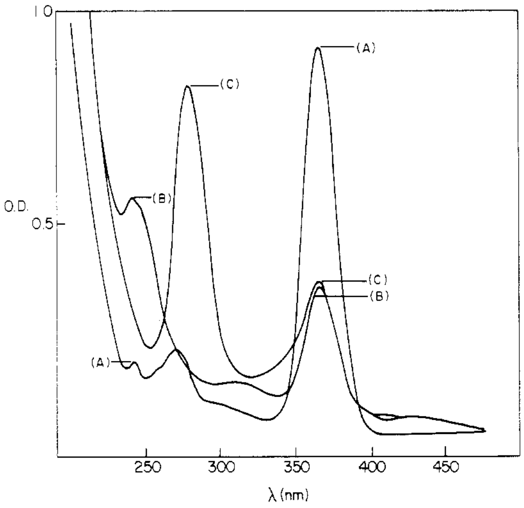

Figure 1. UV–vis spectral changes for the photolysis of Pt$_2$(pop)$_4$$^{4-}$ in an air-saturated 0.1 M HClO$_4$ aqueous solution: (a) before photolysis; (b) after photolysis for ~0.5 h; (c) after photolysis for the product with added KCl.

Experimental Section

Materials. K$_4$[Pt$_2$(pop)$_4$]·3H$_2$O and K$_4$[Pt$_2$(pop)$_4$X$_2$]·2H$_2$O (X = Cl,Br,SCN) were prepared and purified by standard procedures.[10-12] The structures of all four compounds have been determined by X-ray crystallographic methods.[4,11-15] The complexes *trans*-[Ru(en)$_2$Cl$_2$]ClO$_4$[16a] (en = 1,2-diaminoethane), [Ru(NH$_3$)$_5$His]Cl$_3$[16b] (His = histidine), and *trans*-[Os(NH$_3$)$_4$Cl$_2$]ClO$_4$[16c] were synthesized by published procedures. Horse heart cytochrome *c* (type VI) was purchased from Sigma and used without further purification. The protein as received contained (11.0 ± 0.5)% ferrocytochrome *c* (Cyto-C^{2+}) as determined by the addition of a slight excess of K$_3$Fe(CN)$_6$ to several concentrations of protein while optical changes were monitored at 550 nm. Other reagents were of analytical grade and doubly deionized water was used throughout the experiments.

Photochemistry. Photolyses were performed with a 350-W high-pressure mercury short-arc lamp (Illumination Industries, Inc.) coupled with a high-intensity monochromator (Bausch and Lomb). Incident light intensities were taken from average values measured just before and after each photolysis experiment by using ferrioxalate actinometry.[17] Electronic absorption spectra were measured with a Beckman Acta CIII spectrophotometer. To minimize any effects arising from secondary photolysis, quantum yields (excitation at 367 nm) were determined within

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