Articles

Kinetics of CO Addition to Ni(cyclam)$^+$ in Aqueous Solution

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The addition of CO to Ni(cyclam)$^+$ in homogeneous aqueous solution has been studied by pulse radiolysis and laser flash photolysis. The reaction was found to proceed by a sequential, two-step mechanism. The CO addition rate constant was found to be $(2.0 \pm 0.2) \times 10^9$ M^{-1} s^{-1} at ambient temperature. Addition is followed by a slower, first-order reaction with a rate constant of 1.8 ± 0.2 s^{-1} at ambient temperature. A variable temperature study of the latter reaction yielded $\Delta H^\ddagger = 12.7 \pm 0.1$ kcal mol^{-1} and $\Delta S^\ddagger = -14.4 \pm 0.1$ cal K^{-1} mol^{-1}. The mechanism of the reaction sequence and the possibility that the slow, first-order process represents an isomerization of the macrocyclic ligand are discussed.

Introduction

The addition of CO to the one-electron reduction product of an extended series of nickel(II) tetraazamacrocyclic complexes was first reported 15 years ago.[2] The CO binding constants were quite large, typically 10^4−10^5 M^{-1}, but varied from ≤ 10 M^{-1} to $>10^5$ M^{-1}.[2] EPR spectra at 100 K in propylene carbonate provided convincing evidence for axial binding of CO to nickel(I) to form the "19-electron" adduct.[2] IR data in pyridine solution showed a weakening of the CO bond as the Ni(I) complex became more strongly reducing.[2] Structural details of several nickel(I) tetraazamacrocyclic CO adducts in acetonitrile at 300 K were elucidated using EXAFS that show the Ni(I) to be five-coordinate with a short, 1.78−1.82 Å, Ni−CO bond.[3]

Continuous electrolysis of Ni(cyclam)$^{2+}$, in aqueous or DMF solutions under CO or CO_2 atmospheres, has been shown to result in the formation of a species attributed to Ni(cyclam)(CO)$^+$, based on EPR, IR, and UV−vis spectral data.[4] The UV−vis spectrum showed a strong transition centered around 350 nm[4] that is distinct from either the spectrum of Ni(cyclam)$^+$ or representative Ni(cyclam)$^{3+}$ spectra.[5] Fujihira and coworkers studied the electrochemistry of Ni(cyclam)$^{2+}$ under CO by cyclic voltammetry on glassy carbon and Hg−Au electrodes in 0.1 M $NaClO_4$ aqueous solution and observed a reversible reduction at a potential 170 mV more positive than the Ni(cyclam)$^{2+/+}$ couple.[6] The positive shift was attributed to the formation of the CO adduct, eq 1.[6] Although the CO binding constant, eq 2, was not reported, a value of 7.5×10^5 M^{-1} can be inferred from their data.[6] This value is somewhat greater than that observed in acetonitrile, $K_2(CH_3CN) = (2.8 \pm 0.6) \times 10^5$ M^{-1}.[3] Reduction of Ni(cyclam)$^{2+}$ in water under CO was further studied by Balazs and Anson using a mercury electrode.[7] By extending the cathodic sweep range beyond that of Fujihira et al.,[6] these authors observed a second, irreversible reduction coincident with the formation of a precipitate on the electrode surface attributed to eq 3.[7] Interestingly, Balazs and Anson did not observe reversible electrochemistry for eq 1 but did observe a reversible reaction analogous to eq 1 using the complex 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, Ni(TMC)$^{2+}$ (see Chart 1 for ligand structures).[7] The reversibility of the Ni(TMC)$^{2+}$ system allowed the determination of the CO binding constant, eq 4, for which they reported a value of 1.1×10^6 M^{-1}.[7] As previously noted, the solvent effect is quite pronounced in this case, the binding constant being an order of magnitude greater than that observed in acetonitrile, $K_4(CH_3CN) = (1.2 \pm 0.4) \times 10^5$.[8]

$$\mathrm{Ni(cyclam)^{2+} + e^- + CO \rightleftharpoons Ni(cyclam)(CO)^+} \qquad (1)$$

$$\mathrm{Ni(cyclam)^{+} + CO \rightleftharpoons Ni(cyclam)(CO)^+} \qquad (2)$$

$$\mathrm{Ni(cyclam)(CO)^{+} + e^- \rightarrow Ni(cyclam)(CO)^0} \qquad (3)$$

$$\mathrm{Ni(TMC)^{+} + CO \rightleftharpoons Ni(TMC)(CO)^+} \qquad (4)$$

Our interest in the addition of CO to Ni(cyclam)$^+$ arises from the observation that the same, ca. 350 nm absorbing, product is obtained under conditions where Ni(cyclam)$^{2+}$ is reduced to Ni(cyclam)$^+$ in heterogeneous electrochemical[4,9] or homogeneous γ-radiolysis[10] conditions in the presence of either CO or

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CO_2. As a result of our interest in the reduction of CO_2 to CO by Ni(cyclam)$^+$,[10,11] and because of the formation of the CO adduct during CO_2 reduction,[4,9,10] we wished to characterize the kinetic details of CO binding. While we expected to find a simple addition, we in fact observed a two step, sequential reaction. Recently, unusual time dependent behavior has been reported for the reaction of Ni(cyclam)$^+$ (and a C-methylated derivative) with CO in acetonitrile.[8] In the current work we report the kinetics of the CO addition to Ni(cyclam)$^+$ in water and discuss the possible nature of the reaction.

Experimental Section

Experimental details are as described previously[11] with the exception of the long time scale (i.e., greater than about 1 ms) measurements. Under these conditions, for both the pulse radiolysis and laser flash photolysis experiments, 50 W tungsten–halogen lamps were used as the monitoring light source. The laser flash photolysis setup was further modified by employing a Schottky barrier silicon photodiode (UDT PIN-8LC) as the detector and amplifying the diode output with a current amplifier (Stanford Research SR570). The pulse radiolysis detection scheme was not modified. The solubility of CO as a function of temperature was taken to be that in pure water, with a value at 22 ± 2 °C of 1.0×10^{-3} M atm^{-1}.[12]

Results

Pulse radiolysis of aqueous solutions containing 1.0 mM Ni(cyclam)$^{2+}$ and 0.5 M *tert*-butanol under a CO atmosphere, pH ~7, at ambient temperature resulted in the formation of Ni(cyclam)$^+$ according to eq 5, with a rate constant $k_5 = 4.1 \times 10^{10}$ M^{-1} s^{-1}.[11]

$$\mathrm{Ni(cyclam)}^{2+} + e_{aq}^{-} \rightarrow \mathrm{Ni(cyclam)}^{+} \qquad (5)$$

The decay of Ni(cyclam)$^+$ (monitored at 380 nm) was accelerated in the presence of CO, with a first-order rate constant that is proportional to the concentration of dissolved CO, Figure 1, inset. The decay is attributed to the CO addition reaction, eq 2, for which we obtain a bimolecular rate constant, $k_2 = (2.0 \pm 0.2) \times 10^9$ M^{-1} s^{-1} ([CO] = 0.1 to 1.0 mM). The decay at 380 nm is accompanied by the concomitant growth of a species that possesses an absorbance maximum at 470 nm ($\epsilon_{470} = 750 \pm 70$ M^{-1} cm^{-1}), Figure 1.

The use of $CO_2^{\bullet -}$ as a reducing agent for Ni(cyclam)$^{2+}$, generated either by pulse radiolysis or flash photolysis, results in the same 470 nm absorbing product as that observed using e_{aq}^{-}. However, extraction of the rate constant for CO addition is made difficult by the relatively slow rate of Ni(cyclam)$^+$ formation under these conditions.[11] The two step mechanism has previously been described, eqs 6 and 7, with rate constants,

$$\mathrm{Ni(cyclam)}^{2+} + CO_2^{\bullet -} \rightarrow [\mathrm{Ni(cyclam)(CO_2)}]^{+} \qquad (6)$$

$$[\mathrm{Ni(cyclam)(CO_2)}]^{+} \rightleftharpoons \mathrm{Ni(cyclam)}^{+} + CO_2 \qquad (7)$$

$k_6 = 6.7 \times 10^9$ M^{-1} s^{-1}, $k_{7f} = 2.0 \times 10^6$ s^{-1}, and $k_{7r} = 3.2 \times 10^7$ M^{-1} s^{-1}.[11] Under these conditions, the rate constant for the addition of CO to Ni(cyclam)$^+$ becomes limited by the rate of Ni(cyclam)$^+$ production, eq 7. Consequently, the decay of Ni(cyclam)$^+$ monitored at 380 nm and the growth of the 470 nm product were not linearly dependent on the concentration of CO. The limiting rate constant for CO addition, obtained at low concentrations of CO, is consistent with the value ($k_2 = 2 \times 10^9$ M^{-1} s^{-1}) reported above.

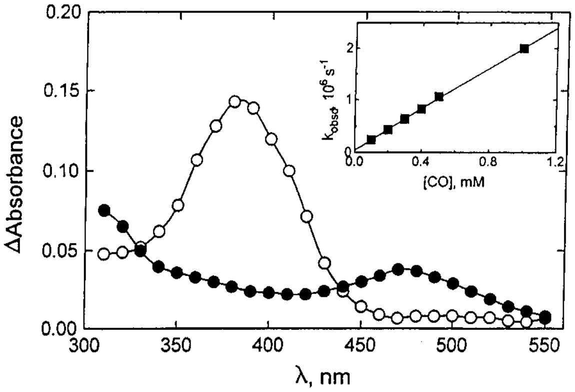

Figure 1. Spectral changes obtained from the pulse irradiation of an aqueous solution containing 0.5 mM Ni(cyclam)$^{2+}$, 0.1 M HCO_2^- and 0.1 mM CO at natural pH. Optical path = 2.0 cm; dose per pulse = 44.4 Gy. The spectra were taken 2 μs (○) and 37 μs (●) after the pulse, respectively. Inset: effect of [CO] on the decay kinetics at 380 nm from the pulse irradiation (dose = 42.5 Gy) of aqueous solutions containing 1.0 mM Ni(cyclam)$^{2+}$ and 0.5 M *tert*-butanol at natural pH.

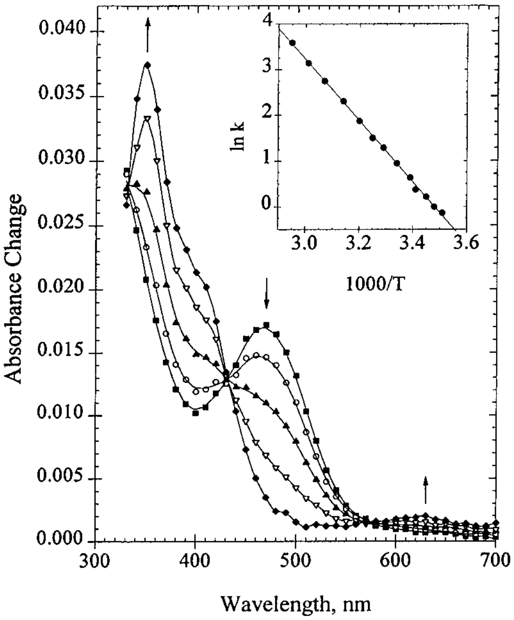

Figure 2. Spectral changes observed following flash photolysis of aqueous 0.5 mM Ni(cyclam)$^{2+}$, 10 mM oxalate and 1.0 mM CO. Spectra were observed at (■) 0.030, (○) 0.132, (▲) 0.334, (▽) 0.736 and (◆) 1.690 s after excitation at ambient temperature. Inset: Arrhenius plot of the decay monitored at 470 nm. Conditions were the same as above.

The initially observed product, hereafter P_{470}, was found to be unstable, decaying at 470 nm by a first-order process. Concomitant with the decay at 470 nm was a strong growth centered at 350 nm ($\epsilon_{350} = 1300 \pm 100$ M^{-1} cm^{-1}) and a weak growth centered around 630 nm ($\epsilon_{630} < 100$ M^{-1} cm^{-1}), Figure 2. Isosbestic points were observed at approximately 332, 432, and 575 nm. The 350 nm absorbing species, hereafter P_{350}, appeared to be quite stable in the absence of oxygen and a proton source. The decay at 470 nm and the growth at 350 nm, eq 8,

$$P_{470} \rightarrow P_{350} \qquad (8)$$

both followed first-order kinetics, independent of CO concentration, [CO] = 0.1–1.0 mM, and exhibited the same rate constants, $k_8 = 1.8 \pm 0.2$ s^{-1}. Identical results for k_8, within experimental error, were obtained using laser flash photolysis (pH 4.3) and pulse radiolysis (pH 7). The temperature dependence of the reaction was evaluated using laser flash

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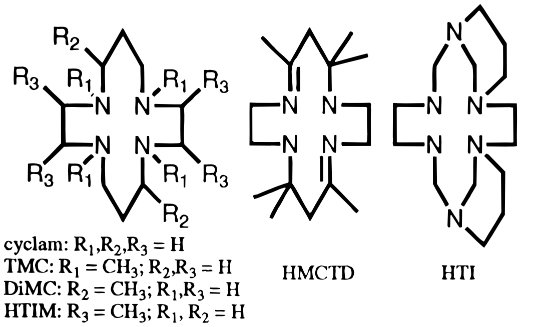
Chart 1. Macrocyclic Ligands Referred to in the Text



photolysis of aqueous solutions containing $Ni(cyclam)^{2+}$ and oxalate at pH 4.3 under a CO atmosphere over the temperature range 2−66 °C. An Arrhenius plot, Figure 2 inset, yielded $\Delta H^{\ddagger} = 12.7 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14.4 \pm 0.1$ cal K^{-1} mol^{-1}.

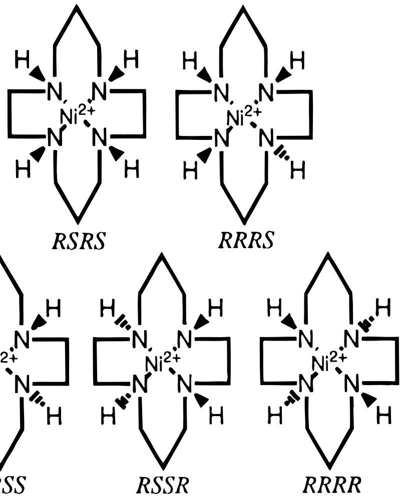
Discussion

The addition of CO to, presumably, an axial coordination site of $Ni(cyclam)^{+}$ proceeds near the diffusion limit with a bimolecular rate constant of 2.0×10^9 M^{-1} s^{-1}. The absorption spectrum of the product (P_{470}, $\lambda_{max} = 470$ nm, $\epsilon_{470} = 750$ M^{-1} cm^{-1}) is very similar to that observed by Szalda et al. for the reaction of CO with (2*R*,3*R*,9*S*,10*S*-tetramethyl-1*R*,4*R*,8*S*,11*S*-tetraazacyclotetradecane) nickel(I), *RRSS*-$Ni(HTIM)^{+}$ ($\lambda_{max} = 470$ nm, $\epsilon_{470} = 790$ M^{-1} cm^{-1}) produced by sodium amalgam reduction of the parent Ni^{2+} complex in acetonitrile (see Chart 1 for ligand structures).[8] The spectrum differs markedly from that observed for the reaction of CO with $Ni(cyclam)^{+}$ in water,[4] DMF,[4] or acetonitrile (in acetonitrile: $\lambda_{max} = 348$ nm, $\epsilon_{348} = 1540$ M^{-1} cm^{-1}).[8] However, the initial CO addition product of $Ni(cyclam)^{+}$ (i.e., P_{470}) is unstable, decaying slowly (1.8 s^{-1}) to the previously observed[4,8] product, P_{350}.

While the detailed mechanism of the P_{470} to P_{350} reaction remains unclear due to a lack of structural information on these species, sufficient data exist to allow insight into the reaction. A number of conceivable reactions may be ruled out based on the observed kinetics. First, the addition of a second CO cannot be rate limiting as noted by the lack of a CO concentration dependence on the reaction rate. The addition of a water as a sixth ligand is considered unlikely since the high water concentration would be expected to lead to a more facile reaction than that observed. Carbonyl isomerization is also considered unlikely since, due to the small size of CO, it is assumed that any rearrangement would proceed with a larger rate constant than that observed. There is also no indication that $Ni(cyclam)^{+}$ is capable of carrying out chemistry, either reduction or hydrolysis, on CO.[4,13] However, the rather negative activation entropy and sizable activation enthalpy suggests significant solvation and structural reorganization within the transition state. We believe a reasonable explanation for eq 8 involves isomerization of the macrocycle as the rate limiting step.

The Structure of $Ni(cyclam)^{+}$. The 14-membered tetraazamacrocycles under discussion here all possess four asymmetric amine donors. This results in five potential isomeric forms for the macrocycle, as depicted in Chart 2.[14] Although the structure of $Ni(cyclam)^{+}$ is not known, there have recently been several X-ray crystallographic studies carried out on related, four coordinate, Ni(I) complexes.[3,8,15,16] These structures all revealed essentially square planar Ni(I) geometries with average Ni−N bond lengths of 2.00 ± 0.09 Å.[3,8,15,16] The X-ray structure of the closely related $Ni(HTIM)^{+}$ has been shown to possess an *RRSS* nitrogen configuration with Ni^{+}−N bond distances of 2.068 ± 0.015 Å.[8] The structure of *RRSS*-$Ni(TMC)^{+}$ revealed an average Ni^{+}−N bond length of 2.107 ± 0.012 Å,[16] somewhat shorter than that observed for the high-spin *RRSS*-$Ni(TMC)(OH_2)_2{}^{2+}$ for which the average Ni^{2+}−N bond length was 2.142 ± 0.012 Å.[17] The high-spin *RRSS*-$Ni(cyclam)(OH_2)_2{}^{2+}$ structure was found to possess an average Ni^{2+}−N bond length of 2.068 ± 0.003 Å.[18] The ideal metal−nitrogen bond length for cyclam in the *RRSS* form has been estimated to be 2.07 Å for a metal in the plane of the four amine donors.[19] Since the starting material, $Ni(cyclam)^{2+}$, is predominantly *RRSS*[20] and since the *RRSS* nitrogen configuration appears to be preferred based on Ni−N bond lengths, there does not seem to be a driving force for isomerization to any other nitrogen configuration upon reduction. Consistent with this expectation, the d−d transition energies of $Ni(cyclam)^{+}$, $\lambda_{max} = 560$ nm, and $Ni(HTIM)^{+}$ (which presumably possesses an *RRSS* nitrogen configuration in solution as it does in the crystal structure), $\lambda_{max} = 564$ nm in acetonitrile,[8] are similar, suggesting similar coordination environments.

Chart 2. Isomers of 14-Membered Tetraazamacrocyclic Complexes



While we are assuming that the structure of $Ni(cyclam)^{+}$ exists predominantly in the *RRSS* nitrogen configuration, we can not rule out the possibility of a mixture of isomers. In fact, isomerization of the related complexes, *RRSS*- and *RSRS*-$Ni(TMC)^{+}$, to a ca. 3:1 ratio, respectively, has been reported to occur in aqueous solution over a several hour time period.[21] While the isomerization of *RRSS*-$Ni(TMC)^{2+}$ to the *RSRS*

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(14) Possible nitrogen configurations for metal complexes of 1,4,8,11-tetraazacyclotetradecane, and its methylated derivatives, are *RSRS* (+ + + +, trans-I), *RSRR* (+ − − −, trans-II), *RRSS* (+ − − +, trans-III), *RSSR* (+ + − −, trans-IV) and *RRRR* (+ − + −, trans-V), where + or − indicates the orientation of the amine hydrogen as above or below the plane of the planar macrocycle, in the order 1, 4, 8, 11.

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configuration is extremely slow in water, it has been shown that the rate of this isomerization can be increased in the presence of strongly coordinating solvents.[22]

In aqueous solution, 15% of the *RRSS*-Ni(cyclam)$^{2+}$ complex isomerizes to *RSRS* form over a period of 1−2 h at neutral pH.[20] On the basis of analogy with Ni(TMC)$^{n+}$ isomerization, isomerization of Ni(cyclam)$^+$ might be expected to occur with a larger rate constant than the parent Ni(cyclam)$^{2+}$. The isomerization of Ni(cyclam)$^+$ at a mercury electrode has been described.[23] However, adsorption of the nickel complex to the electrode surface appears to be important for the isomerization in that case.[23] Recently, the pulse radiolytic reduction of a series of tetradentate, hexaazamacrocyclic complexes related to cyclam has been reported.[24] Those authors have reported that following reduction, the absorbance of the Ni$^+$ complexes undergo an initial decay process with rate constants of $(0.1-2.6) \times 10^4$ s^{-1}, which they attribute to isomerization.[24] A similar kinetic process has not been reported for Ni(cyclam)$^+$.[24] Our studies of the decay mechanism of Ni(cyclam)$^+$ have not led to the observation of any process ascribable to isomerization in the absence of CO.[10] Consequently, we have no spectral evidence for isomerization of the Ni(cyclam)$^+$ complex over a time period of several seconds, in the absence of CO.

The Structure of P_{350}. The final product of CO addition to Ni(cyclam)$^+$, P_{350}, has been characterized in water (UV−vis and EPR),[4] DMF (UV−vis, EPR, and IR),[4] and acetonitrile (UV−vis and IR).[8] No carbonyl adducts of Ni(I) complexes related to Ni(cyclam)$^+$ have yet been characterized by X-ray diffraction. The UV−vis data suggest that a product closely resembling P_{350} is formed in each solvent. The EPR spectrum in frozen (77 K) DMF ($g_1 = 2.196$, $g_2 = 2.137$, and $g_3 = 2.017$)[4] is consistent with square pyramidal Ni(I) and is similar to that observed for *RSRS*-[Ni(HTI)(NHC(OH)CH$_3$]ClO$_4$ in frozen (77 K) acetonitrile ($g_1 = 2.264$, $g_2 = 2.169$ and $g_3 = 2.027$).[25] The IR spectra in DMF ($\nu_{CO} = 1945$ cm^{-1})[4] and CH$_3$CN ($\nu_{CO} = 1955$ cm^{-1})[8] are consistent with a single bound CO. An EXAFS investigation of the CO adduct of (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(I), Ni(HMCTD)(CO)$^+$, which possess two imine and two amine donors, was found to possess two Ni−N bonds of 2.02 Å, two Ni−N bonds of 2.19 Å and a single bond of 1.80 Å attributed to the Ni−CO bond.[3] Consequently, it is assumed that P_{350} is five-coordinate with an axial bound CO.

The Structure of P_{470} and the Nature of the Isomerization. The nearly diffusion-controlled addition of CO to Ni(cyclam)$^+$ limits the likelihood of macrocycle isomerization during the addition reaction. The kinetics are well behaved up to the highest concentration of CO used, implying that isomerization is not rate limiting under these conditions and must proceed, if at all, with a rate constant exceeding 2×10^6 s^{-1}. We consider such a rapid isomerization unlikely in the present case. The nitrogen configuration of P_{470} is therefore assumed to be the same as that for Ni(cyclam)$^+$, i.e., a presumed predominance of the *RRSS* configuration.

The P_{470} to P_{350} reaction may be accounted for by an isomerization of the cyclam ligand driven by coordination to CO. Such a reaction channel is apparently inaccessible to Ni(HTIM)(CO)$^+$ perhaps due to steric constraints imposed by the peripheral methyl groups of the ligand. Consequently, Ni(HTIM)(CO)$^+$ is "locked" in the kinetic product structure while the more flexible Ni(cyclam)(CO)$^+$ is free to isomerize to the more stable P_{350} form. Qualitative observations suggest that the C-methylated complex 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecanenickel(I), Ni(DiMC)$^+$, undergoes an isomerization similar to that observed for Ni(cyclam)$^+$ upon CO addition.[8] The methyl groups of this complex are unlikely to impose the steric constraints found for the HTIM complex. It is interesting that the 470 nm absorbing Ni(HTIM)(CO)$^+$ possesses a lower CO stretching frequency, $\nu_{CO} = 1939$ cm^{-1}, than the 350 nm absorbing Ni(cyclam)(CO)$^+$ and Ni(DiMC)(CO)$^+$, 1955 cm^{-1} and 1956 cm^{-1}, respectively, in acetonitrile.[8] It should be noted that this example of stronger donation to CO observed for Ni(HTIM)(CO)$^+$ occurs despite the fact that the parent Ni(HTIM)$^+$ is a weaker reducing agent than Ni(cyclam)$^+$ and Ni(DiMC)$^+$.[8]

It has been suggested that the five-coordinate Ni(I) ion may favor an out-of-plane coordination mode with the N$_4$ plane of the macrocycle,[3] similar to that observed for the Co(HMCTD)(CO)$^+$ complex.[26] It has been argued, based on molecular mechanics calculations, that the *RRSS* configuration is poorly suited for out-of-plane distortions and that the *RSRS* structure is preferred for such a geometry.[27]

The isomerization of macrocyclic ligands bound to nickel ions, both in the +1 and +2 formal oxidation states, initiated by binding of a donor molecule is not uncommon. As stated above, the isomerization of *RRSS*-Ni(TMC)$^{2+}$ to the *RSRS* isomer has been found to proceed in the presence of strongly donating solvents.[22] Complex formation reactions of Ni(II) and Cu(II), with cyclam and derivatives possessing varying degrees of N-methylation in DMF, have been shown to proceed by a two-step mechanism.[28] The mechanism is believed to proceed by near diffusion controlled complex formation followed by a slower macrocycle isomerization.[28] The latter reaction has been found to involve solvent coordination and, for the case of Ni(TMC)$^{2+}$, proceeds with activation parameters similar to those observed for the P_{470} to P_{350} isomerization.[28] A recent report of the isomerization of *RSRS*-Ni(HTI)$^{2+}$ to *RRSS*-Ni(HTI)$^{2+}$ was found to involve coordination of solvent water molecules to the metal center in acetonitrile/water.[25] These same authors have found that the isomerization of *RRSS*-Ni(HTI)$^+$, following the rapid addition of CH$_3$CONH$_2$, to *RSRS*-[Ni(HTI)(NHC(OH)CH$_3$)]$^+$ in acetonitrile is driven by coordination of the axial acetamide.[25] Lastly, the base promoted isomerization of *cis-RRRR*-[Ni(cyclam)(OH$_2$)$_2$]$^{2+}$ involves coordination of OH$^-$ to the central Ni(II) ion.[29]

Conclusions

The addition of CO to Ni(cyclam)$^+$ in homogeneous aqueous solution proceeds by a sequential mechanism which involves at least two steps. The formation, in a near diffusion controlled bimolecular reaction, of the addition product, P_{470}, is followed by a strongly activated, unimolecular rearrangement to yield a more stable product, P_{350}.

Unfortunately, in the absence of more detailed structural information, it does not appear to be productive at this time to

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speculate too much on the structures of Ni(cyclam)$^+$ or its CO addition kinetic, P_{470}, and thermodynamic, P_{350}, products. The P_{470} to P_{350} reaction is best described as a macrocycle isomerization that is achievable only in the absence of sterically constraining substituents on the macrocyclic ring. We have speculated that the P_{470} to P_{350} isomerization is of the type given by eq 9, which involves the inversion of two coordinated amines.

$$\textit{RRSS}\text{-Ni(cyclam)(CO)}^+ \rightarrow \textit{RSRS}\text{-Ni(cyclam)(CO)}^+ \qquad (9)$$

Further insight into the rearrangement would be greatly assisted by more detailed structural investigations of Ni(cyclam)$^+$, P_{350} or additional kinetic and structural work on closely related analogs.

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