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Notes

Effect of Pressure on the Reversible Binding of Acetonitrile to the “Co(I)−CO_2” Adduct To Form Cobalt(III) Carboxylate

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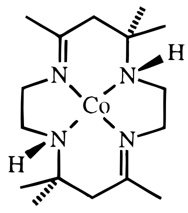
Introduction

In recent years cobalt complexes with 14-membered tetraazamacrocyclic ligands have been successfully used as catalysts for electrochemical and photochemical reduction of CO_2 and H_2O.[1−8] We and others have characterized the interaction of low-spin $[Co^{I}HMD]^+$ with CO_2 in CH_3CN[9−13] and H_2O[14,15] at various temperatures.



***rac* HMD**

The *N-rac*-$[CoHMD(CO_2)]^+$ adduct is stable enough to handle in extremely dry CH_3CN under a CO_2 atmosphere. It is thermochromic, being purple at room temperature and yellow at low temperature. The equilibrium between the five-coordinate $[CoHMD(CO_2)]^+$ (purple) and six-coordinate $[CoHMD(CO_2)(CH_3CN)]^+$ (yellow) was studied previously by UV−vis, ^1H NMR, FT-IR, XANES, and EXAFS spectroscopy in CH_3CN.[10,11,13]

$$[CoHMD]^+ + CO_2 \rightleftharpoons [CoHMD(CO_2)]^+ \tag{1}$$

$$[CoHMD(CO_2)]^+ + CH_3CN \rightleftharpoons [CoHMD(CO_2)(CH_3CN)]^+ \tag{2}$$

$$K = [CoHMD(CO_2)(CH_3CN)^+]/[CoHMD(CO_2)^+] \tag{3}$$

The singular value decomposition (SVD)[16−18] spectral analysis of the temperature-dependent UV−vis data between 26 and −40 °C is consistent with the presence of two species (i.e., the five- and six-coordinate complexes) in CH_3CN. The fit gives $\Delta H° = -7.0$ kcal mol^{-1} and $\Delta S° = -27$ cal K^{-1} mol^{-1} for eq 2.[11] The equilibration is rapid on the NMR time scale. The FT-IR spectra measured over the range of 25 to −75 °C in CD_3CN and in a CD_3CN/THF mixture indicates the existence of four CO_2 adducts: a five-coordinate, non-hydrogen-bonded form ($\nu_{C=O} = 1710$ cm^{-1}, $\nu_{NH} = 3208$ cm^{-1}), a five-coordinate intramolecular hydrogen-bonded form ($\nu_{C=O} = 1626$ cm^{-1}), a six-coordinate non-hydrogen-bonded form ($\nu_{C=O} = 1609$ cm^{-1}, $\nu_{NH} = 3224$ cm^{-1}), and a six-coordinate intramolecular hydrogen-bonded form ($\nu_{C=O} = 1544$ cm^{-1}, $\nu_{NH} = 3145$ cm^{-1}). Intramolecular hydrogen bonds are formed between the bound CO_2 and the amine hydrogens of the ligand. An X-ray absorption near-edge spectroscopy (XANES) study[13] of the CoHMD complexes indicates that the edge positions (E_0) are extremely sensitive to the oxidation state of the metal. The edge energy, relative to $[Co^{II}HMD]^{2+}$, decreases (1 eV) upon reduction and increases (2 eV) upon oxidation. The E_0 for the five-coordinate $[CoHMD(CO_2)]^+$ at room temperature is similar to that of $[Co^{II}HMD]^{2+}$, consistent with theoretical predictions[19,20] that the bound CO_2 receives 0.71 electrons mainly from the Co d_{z^2} orbital. The six-coordinate $[CoHMD(CO_2)(CH_3$-

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CN)]$^+$ species shows a 1.2 eV shift toward Co(III) and is interpreted as a Co(III)$-CO_2^{2-}$ carboxylate complex. Although the Co(III) carboxylates have been postulated as intermediates in CO_2 reduction and water−gas shift reactions, the XANES results provide the first unambiguous evidence that active metal catalysts, such as [Co^{I}HMD]$^+$, can promote two-electron transfer to the bound CO_2 and thereby facilitate reduction of CO_2.

To obtain further information on the equilibrium between the five- and six-coordinate [CoHMD(CO_2)]$^+$ species, we have investigated its pressure dependence. The results are reported here.

Experimental

Materials. *N-rac*-[CoHMD(H_2O)](ClO_4)$_2$ was prepared as previously described[21,22] and characterized by UV−vis and IR spectroscopies. Analyses for cobalt and anions of these complexes were satisfactory.

Warning: The perchlorate salts used in this study may be explosive and are potentially hazardous.

Acetonitrile was purified in the published manner[23] and was stored under vacuum over activated molecular sieves (3 Å). Research grade CO_2 (CO_2 > 99.998%) was used without further purification.

Spectroscopic Measurements. [CoHMD(CO_2)]$^+$ solutions (0.6−1.1 mM) were prepared under vacuum by sodium amalgam (Na−Hg, 0.5% Na in Hg) reduction in sealed glassware equipped with an optical cell, followed by the introduction of ~1.2 atm of CO_2 into the Co(I) complexes.[10] For high-pressure work, the solution was transferred by syringe to a vacuum-tight pillbox optical cell[24] that had been flushed with CO_2. To prevent leaks in the cell, a small amount of Apiezon grease was used on the surface between the two cylindrical sections of the pillbox cell. After excess CO_2 was removed, the pillbox was immediately placed in the high-pressure cell[24] mounted in a Cary 210 spectrophotometer. Although the solution is quite stable under high pressure (>20 atm) at 15 °C, typically 10−15% of [CoHMD(CO_2)]$^+$ decomposed to [CoHMD]$^{2+}$ during the first stage of the manipulation (especially on filling the pillbox), as estimated from the expected optical densities for the known concentrations of [CoHMD(CO_2)]$^+$. The corrected concentration of total [CoHMD(CO_2)]$^+$ was used for the determination of the standard reaction volume. The [CoHMD]$^{2+}$ formed by the decomposition of [CoHMD(CO_2)]$^+$ should not affect our analysis since it does not have any significant absorption at 530 nm.

Results

The spectral changes of [CoHMD(CO_2)]$^+$ in CH_3CN at 15 °C under various pressures are shown in Figure 1. When the pressure is increased, the intensity of the peak at 530 nm diminishes and that of the shoulder at 430 nm increases with a clean isosbestic point at 460 nm, indicating the formation of six-coordinate [CoHMD(CO_2)(CH_3CN)]$^+$. The spectral changes were highly reversible. It has previously been shown[10,11] that the equilibrium, eq 2, lies toward the left at atmospheric pressure and room temperature. Using the values ($\Delta H° = -7.0$ kcal mol^{-1} and $\Delta S° = -27$ cal K^{-1} mol^{-1}) obtained from the SVD fit of the UV−vis data over the range of −40 to 26 °C in CH_3CN,[11] K is 0.258 at 15 °C. The solution contains ~80% five-coordinate [CoHMD(CO_2)]$^+$ species (purple) and ~20% six-coordinate [CoHMD(CO_2)(CH_3CN)]$^+$ species (yellow) under atmospheric pressure. The ratio of concentrations of six-coordinate to five-coordinate [CoHMD(CO_2)]$^+$ under various pressures was calculated from the 530−nm absorption ($\epsilon_5 = 1160$ M^{-1} cm^{-1}, $\epsilon_6 = 85$ M^{-1} cm^{-1}).[11] In these calculations no correction to the absorbance for the compressibility of the solvent was made since this is almost compensated for by the shortening of the optical path length of the pillbox cell during compression.[25] The equilibrium constant increases with pressure, which is consistent with the observed spectral change. The solution contains ~50% five-coordinate [CoHMD(CO_2)]$^+$ species and ~50% six-coordinate [CoHMD(CO_2)(CH_3CN)]$^+$ species at 2000 atm pressure.

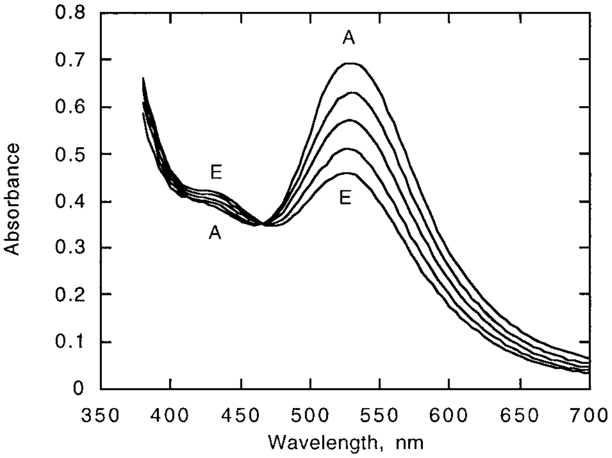

Figure 1. UV−vis spectra of [CoHMD(CO_2)]$^+$ in CH_3CN at pressures of 50, 500, 1000, 1500, and 2000 atm at 15 °C for A to E, respectively.

$$\ln K = \ln K° - (\Delta V° p/RT) \qquad (4)$$

The plot of ln K versus pressure using data from two fillings of the cell with different solutions is shown in Figure S1 (Supporting Information). The relation is linear, and the least-squares fit gives a slope of 7.47×10^{-4} atm^{-1} and an intercept of −1.34. Therefore the overall reaction volume of equilibrium (eq 2) is $\Delta V° = -17.7 \pm 1.0$ mL mol^{-1}.

Discussion

The five-coordinate [CoHMD(CO_2)]$^+$ adduct we studied here is the N-racemic form in which CO_2 binds to the open face.[10] (The open face is the face toward which hydrogen atoms of the amine nitrogen point, not the face toward which the axial methyl groups point.) At low temperature the acetonitrile is bound trans to the CO_2, that is, on the face congested with two axial methyl groups of the ligand. As shown in Figure 1, increasing pressure shifts the equilibrium to the six-coordinate [CoHMD(CO_2)(CH_3CN)]$^+$. A similar shift occurs on lowering temperature. A comparison of the temperature and pressure dependence of the equilibrium indicates that an increase in pressure of 2000 atm causes the same shift in equilibrium as a decrease in temperature of ca. 40 °C. The significantly negative reaction volume, $\Delta V° = -17.7 \pm 1.0$ mL mol^{-1} at 15 °C in CH_3CN, is consistent with the strongly negative reaction entropy, which demonstrates that the six-coordinate complex is highly ordered and very compact.

Although the reaction volumes of various equilibrium reactions involving ligand substitution, isomerization, elimination, and electron transfer reactions have been measured, only a very small amount of data is available for simple addition reac-

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tions.[26,27] In general, the coordination of a solvent molecule is expected to be associated with a volume decrease. The magnitude of this effect depends on a number of factors. Swaddle[28] estimated that in the case of a divalent or trivalent octahedral complex the dissociation of a water molecule can result in a maximum volume increase of 13 mL mol^{-1} compared to its molar volume of 18 mL mol^{-1}. Conversely a maximum volume decrease of 13 mL mol^{-1} is estimated for the association of a water molecule. If there is significant rearrangement in the six-coordinate species, such as an increase in the metal−ligand bond length on binding the solvent molecule, then this can partially cancel the volume collapse expected for the binding step. For example, consider the equilibrium between the low-spin planar $[\mathrm{NiL}]^{2+}$ complex and the high-spin octahedral $[\mathrm{NiL(H_2O)_2}]^{2+}$ complex in eq 5, where L = 1,4,8,11-tetramethyl-

$$[\mathrm{NiL}]^{2+} + 2\mathrm{H_2O} \rightleftharpoons [\mathrm{NiL(H_2O)_2}]^{2+} \qquad (5)$$

1,4,8,11-tetraazacyclotetradecane. The ΔV° was found[29] to be -8.6 ± 0.3 (from the pressure dependence of the UV−vis spectrum) or -10.1 ± 0.2 mL mol^{-1} (from the relaxation amplitude). The volume change is quite small, probably due to the lengthening of the Ni−N bonds (∼0.12 Å) associated with the spin change, which will balance the volume collapse resulting from the binding of the water molecules. Coordination of $\mathrm{CH_3CN}$ to the five-coordinate $[\mathrm{CoHMD(CO_2)}]^{+}$ species is not expected to be accompanied by a significant volume collapse, since it is reasonable to expect that the vacant coordination site in the five-coordinate species is highly solvated and occupied by weakly bound solvent molecules. The rotation of this species sweeps out a volume very similar to that of the six-coordinate species in which bonding to a specific solvent molecule is present.

A more important contribution can arise from the intramolecular electron-transfer process and associated change in oxidation state of the metal center. For instance, during the binding of $\mathrm{O_2}$ to $[\mathrm{Co^{II}(Me_6cyclam)(H_2O)_2}]^{2+}$ ($\mathrm{Me_6cyclam}$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), only a few milliliters are associated with the substitution of $\mathrm{H_2O}$ by $\mathrm{O_2}$, whereas the major volume collapse (in total −22 mL mol^{-1}) is associated with the oxidation of Co(II) to Co(III) and the reduction of $\mathrm{O_2}$ to $\mathrm{O_2}^{-}$.[30] Similar effects are observed for the binding of radicals $^{\bullet}\mathrm{R}$ to Co(II), Ni(II), and Cr(II) complexes, during which $\mathrm{M^{III}}-(\mathrm{R}^{-})$ species are formed.[31−33] In fact, the overall volume changes are very similar to the volume of activation reported for some oxidative addition reactions,[34] which are also accompanied by volume decreases resulting from ligand binding and subsequent electron-transfer processes.

Structural changes of cobalt macrocyclic complexes associated with redox reactions are summarized in Table S1 (Supporting Information). Although low-spin Ni macrocyclic complexes indicate that the Ni−N (macrocyclic N) distances typically become 0.05 and 0.12 Å longer upon oxidation and reduction, respectively,[35,36] the intrinsic volume change associated with oxidation and reduction of the Co(II) center is almost negligible in the square-planar portions of Co macrocycles. The five- and six-coordinate $\mathrm{Co-CO_2}$ complexes have similar Co−N distances of 1.93 and 1.92 Å, respectively; however, the axial $\mathrm{Co-CO_2}$ distance is 0.08 Å shorter for the six-coordinate species.[13] The axial bond length change and, especially, electrostriction effects associated with the formal $\mathrm{Co(I)-CO_2}$ to $\mathrm{Co(III)-CO_2}^{2-}$ conversion have major consequences. Interaction of the polar solvent with the negatively charged carboxylate group will cause a considerable volume collapse. In fact, Tregloan et al.[37] demonstrated that the electrostriction effect follows the square of the charge and can account for the observed reaction volume in cases where no intrinsic volume effects contribute. The reaction volume of −17.7 mL mol^{-1} found for reaction 2 is therefore most probably due to a small volume collapse of a few milliliters associated with the binding of the additional solvent molecule and a major volume collapse due to the intramolecular electron-transfer process accompanied by a shortening of the $\mathrm{Co-CO_2}$ bond length, as found in our previous XANES and EXAFS studies,[13] and a significant increase in electrostriction.

The reversible intramolecular two-electron-transfer process during which $[\mathrm{Co^{I}HMD}]^{+}$ is converted by the addition of $\mathrm{CO_2}$ to $[\mathrm{Co^{III}HMD(CO_2{}^{2-})}]^{+}$ is unique. The equilibrium between the five-coordinate $[\mathrm{CoHMD(CO_2)}]^{+}$ and the six-coordinate $[\mathrm{CoHMD(CO_2{}^{2-})(CH_3CN)}]^{+}$ exhibits a characteristic temperature and pressure dependence, which could be of fundamental importance to processes dealing with the reduction of $\mathrm{CO_2}$. A systematic variation of temperature and pressure can lead to a precise tuning of the electron density on the Co and $\mathrm{CO_2}$ centers.

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Supporting Information Available: Table S1 and Figure S1 (2 pages). Ordering information is given on any current masthead page.

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