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Carbon Dioxide Activation by Cobalt Macrocycles: Evidence of Hydrogen Bonding between Bound CO_2 and the Macrocycle in Solution

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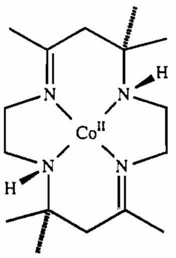
The equilibrium between five-coordinate $CoL(CO_2)^+$ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and six-coordinate $CoL(CO_2)(CD_3CN)^+$ (formed at the expense of the five-coordinate form as the temperature is lowered) was examined by both ^1H NMR and FT-IR. The equilibration is rapid on the NMR time scale, but the spectra of the limiting forms have been derived from the temperature dependence of the spectrum. The FT-IR spectra measured over the range 25 to –75 °C in CD_3CN and in a CD_3CN/THF mixture indicate the existence of four CO_2 adducts, two with intramolecular hydrogen bonds between the bound CO_2 and the amine hydrogens of the ligand: a five-coordinate, non-hydrogen-bonded form ($\nu_{C=O} = 1710\ cm^{-1}$, $\nu_{NH} = 3208\ cm^{-1}$), a five-coordinate intramolecularly 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 ($\nu_{C=O} = 1544\ cm^{-1}$, $\nu_{NH} = 3145\ cm^{-1}$). The binding of CO_2 *via* both its electrophilic center (carbon atom) and its nucleophilic center (oxygen atom) is thus implicated in the stabilization of the CO_2 complex at low temperature.

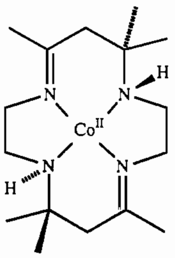
Introduction

Metal complexes with 14-membered tetraazamacrocyclic ligands have shown interesting properties, especially as catalysts for H_2O and CO_2 reduction. $[CoL(H_2O)](ClO_4)_2$ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)[1,2] and $Ni(cyclam)Cl_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane)[3] have been used as electrocatalysts for the reduction of CO_2 in H_2O or aqueous CH_3CN. The CO/H_2 production ratio is ~1 for $[CoL(H_2O)](ClO_4)_2$ and >100 for $Ni(cyclam)Cl_2$. Beley et al.[3] suggested that the large selectivity for the electroreduction of CO_2 over that for water is related to the size of the macrocyclic ligand and to the presence of N–H groups in $Ni(cyclam)Cl_2$. Although evidence of interactions between the bound CO_2 via both its electrophilic center (carbon atom) and nucleophilic center (oxygen atoms) has not been reported for solutions,[4,5] it has been found in the solid state. For example, in crystals of $Co^I(salen)Na(CO_2)$ (salen = *N,N'*-ethylenebis(salicylideneaminato) dianion)[6] the oxygen atoms of the C-bonded CO_2 interact with the alkali metal ions.

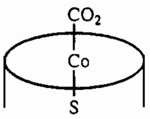
In earlier work, we and others characterized the interaction of low-spin d^8 Co^IL^+ with CO_2 in acetonitrile[7–9] and in water.[10] Schmidt et al. have characterized the binding thermodynamics as a function of organic solvent.[11] The chiral N–H centers of the macrocycle give rise to two diastereomers of CoL complexes (and in the case of the racemic complex to two isomers, depending on which face an axially coordinated fifth ligand such as CO_2 occupies). The equilibration between the *N-rac-* and *N-meso*-cobalt(II) isomers is slow in aqueous acid and in organic media,[12] but equilibration of the two cobalt(I) isomers is relatively rapid ($>2 \times 10^{-3}\ s^{-1}$) in acetonitrile.[8] For both oxidation states, the racemic isomer is the more stable in acetonitrile at room temperature.



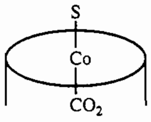
N-rac-$Co^{II}L^{2+}$



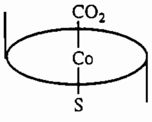
N-meso-$Co^{II}L^{2+}$



primary,*rac*



secondary, *rac*



meso

The *rac*-$Co^IL–CO_2$ complex studied here is a 1:1 complex in which the CO_2 is believed to be bound η^1-C (*i.e.*, Co–C(O)O) to an axial metal coordination site on the primary macrocycle face (that toward which the N–H, as opposed to the axial methyl groups, face).[7,8] The prim, *rac*-$Co^IL–CO_2$ isomer is assumed to be the dominant species in CH_3CN since the CO_2 binding constant is more than 300 times larger for *rac*-Co^IL^+ than for the *meso*-Co^IL^+ complex and the equilibration between the two isomers of Co^IL^+ is rapid.[7,8] Acetonitrile and aqueous solutions of *rac*-$Co^IL–CO_2^+$ are thermochromic, being purple at room temperature and yellow at low temperature.[8] We attributed this thermochromism to the addition of a solvent molecule to the five-coordinated $Co^IL–CO_2^+$ complex. In our earlier work[7,8] we also found that solids isolated from $Co^IL–CO_2^+$ solutions at different

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temperatures have different IR spectra, especially in the C═O stretching region. The spectrum of solid isolated at 5 °C from CH_3CN/THF shows "two" C═O stretching bands at 1702 and 1620 cm^{-1}, which differ significantly in frequency from that of Co(salen)Na(CO_2) (1680 cm^{-1}). Solid isolated at −70 °C has an unusually low C═O stretching frequency at 1558 cm^{-1}.

To further clarify the nature of the CO_2 binding mode and better characterize the origin of the thermochromism, we undertook NMR and IR studies in solution as a function of temperature. The results of these studies are reported here.

Experimental Section

Materials. The complexes *rac*-[CoL(H_2O)](ClO_4)$_2$ and *meso*-[CoL(H_2O)$_2$](ClO_4)$_2$ were prepared as previously described[12-14] and characterized by UV–vis, IR, and ^1H NMR spectroscopy. The anhydrous *rac*-$Co^{II}L$ complex was obtained by placing the compound under vacuum.[14] Cobalt and anion analyses were satisfactory.

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

Acetonitrile and THF were purified by published methods[15] and stored under vacuum over activated molecular sieves (3A) or CaH_2, and Na–K, respectively. Research grade CO_2 was used without further purification.

Spectroscopic Measurements. The Co^IL^+ complex was prepared by sodium amalgam (Na–Hg) reduction or bulk electrolysis of the anhydrous $Co^{II}L^{2+}$ complex in CD_3CN and the $Co^ILCO_2^+$ complex by the introduction of CO_2 (room temperature, atmospheric pressure) into solutions of the Co^IL^+ complexes. An excess of Na–Hg was generally used, it being established that the same results were obtained with stoichiometric and excess amounts of the reductant. Similarly $NaClO_4$ produced by the Na–Hg reduction does not interfere with the experiments, since the results obtained with Na–Hg reduction and with bulk electrolysis were identical within experimental error. A sealed cell equipped with a reagent reservoir was used for bulk electrolysis.[16] The "solvent", containing purified CD_3CN and electrolyte (0.1 M tetrapropylammonium perchlorate), was kept over activated alumina overnight in the reagent reservoir under argon and then filtered through a frit into the electrolysis chamber and mixed with the solid Co(II) complex. The bulk electrolyses were performed with a BAS100 electrochemical analyzer. The end point of the reduction was determined by monitoring the coulometry. Infrared samples of cobalt complexes (0.001–0.09 M Co) were prepared by syringe transfer of the solution to an Ar- or CO_2-flushed, vacuum-tight IR cell (0.1–1.0-mm path length, CaF_2 windows) yielding solutions with CO_2 concentrations 0.2–0.3 M,[7,11] depending on the solvent composition. Spectra were immediately determined on a Mattson Polaris FT-IR spectrometer equipped with a SPECAC Model 21000 variable-temperature cell with CaF_2 windows. The temperature at the sample cell was calibrated with use of a thermocouple and found to be about 30 °C lower than at the temperature-control unit. UV–vis spectra were measured in sealed cells under vacuum or a CO_2 atmosphere on a Cary 17 spectrophotometer equipped with a homemade quartz dewar.

NMR spectra were obtained on a Bruker AM-300 300-MHz spectrometer. NMR samples of Co^IL^+ solutions in purified CD_3CN were prepared from $Co^{II}L^{2+}$ by Na–Hg reduction in sealed glassware.

Spectral Analysis. The temperature-dependent spectral data were analyzed by use of singular value decomposition (SVD).[17-19] The original data consist of n spectra of m points each. (For the IR data, there were 11 spectra of 706 points each.) Each spectrum was taken at a different temperature. The data were combined into an $m \times n$ matrix **A** where each column of **A** is a complete spectrum. Through SVD the original data, **A**, were decomposed by $\mathbf{A} = \mathbf{USV}^T$ where **U** is an $m \times n$ matrix of n orthonormal basis spectra; **S** is a diagonal matrix of nonnegative elements (s_{jj}), the singular values of **A** which decrease as j increases; and $\mathbf{V}^T$ is the transpose of **V**, an $n \times n$ matrix in which each column is the temperature dependence of the corresponding basis spectrum. The singular values measure the contribution of the corresponding basis spectra to the original data. The first basis spectrum contributes the most to the observed data, and the last, the least. Ideally the first few basis spectra correspond to distinct physical species while the later basis spectra are the result of noise in the measurement. The singular values and the column vectors of **U** and **V** can be analyzed to suggest the number of physically significant independent species (i) observed in the experiment. Our analysis used the first i columns of **V**. These columns were fit using a thermodynamic model that assumes i species in equilibrium ($K = \exp(-\Delta G°/RT)$, $\Delta G° = \Delta H° - T\Delta S°$) each with a unique spectrum. The limiting spectra, $\Delta H°$, and $\Delta S°$ were assumed to be temperature independent, and no correction for the thermal expansion or contraction of the solvent was made. The derived parameters were used to calculate predicted spectra. In most cases the calculated spectra approximate the observed spectra to better than 0.002 absorbance units (AU).

Results

Cobalt(II) and Cobalt(I) Complexes. In addition to known differences in the critical 1200–1500-cm^{-1} region,[12,20] *rac*-[$Co^{II}L$(H_2O)](ClO_4)$_2$ has a single ν_{NH} band at 3215 cm^{-1}, while *meso*-[$Co^{II}L$(H_2O)$_2$](ClO_4)$_2$ has two bands at 3223 and 3185 cm^{-1} in CD_3CN. Deformation bands (δ_{NH}) for these complexes are quite weak compared to the $\nu_{C=N}$ bands and are not observed. When *rac*-[$Co^{II}L$(H_2O)](ClO_4)$_2$ was treated with D_2O, a weak band appeared at 2400 cm^{-1} which is attributed to ν_{ND} resulting from the H/D exchange of the amine protons. The *N-meso* complex isomerized in parallel with exchange, and so the spectrum of the pure material could not be determined.

Immediately after preparation (≤5 min) of a 0.07 *M* solution of Co^IL^+ from *rac*-[$Co^{II}L$(H_2O)](ClO_4)$_2$ in CD_3CN, the ν_{NH} band is at 3201 cm^{-1} and the $\nu_{C=N}$ band is at 1571 cm^{-1}. Over the next 1 h the ν_{NH} band decreases in intensity, the $\nu_{C=N}$ band shifts from 1571 cm^{-1} to 1556 cm^{-1}, and weak bands appear at 1650 cm^{-1} and ~2400 (ν_{ND}) cm^{-1}. When C_3H_7CN was used as solvent instead of CD_3CN, the intensities of both the 1570 and 3200 cm^{-1} bands remained intact over 3 h.[21]

$CoLCO_2^+$ Complexes. We have proposed that the thermochromism of $Co^IL{-}CO_2^+$ in acetonitrile is due to the addition of an acetonitrile molecule to the 5-coordinated $Co^IL{-}CO_2^+$ complex as shown in eq 1. By contrast, THF solutions of the $Co^IL{-}CO_2$ complex are not thermochromic but remain purple at all temperatures examined (40 to −150 °C). The steric bulk of THF might account for the lack of solvent coordination to the cobalt center. To substantiate eq 1, we studied the dependence of the electronic spectrum of 0.4–0.7 mM $Co^IL{-}CO_2^+$ on acetonitrile concentration in THF at 15 °C. The 530-nm molar absorptivity (M^{-1} cm^{-1}) is 1160 in pure THF, 1070 in 1.44 M CH_3CN, 1140 in 3.80 M CH_3CN, 1030 in 9.57 M CH_3CN, and 830 in pure CH_3CN. Due to the air-sensitive and moisture-sensitive nature of the Co(I) complex, there are significant errors in the data. With use of the limiting ϵ values observed in pure THF at 15 °C and in acetonitrile at low temperature for the five- and six-coordinate species, respectively, the ratio of six- to five-coordinate species was evaluated for the different solutions. The results are shown in Figure 1. The slope of the line, 0.02 ± 0.01 M^{-1}, is the equilibrium constant (eq 2) for eq 1.[22] This experiment confirms

$$\mathrm{Co^IL{-}CO_2^+ + CH_3CN \rightleftharpoons CH_3CN{-}Co^IL{-}CO_2^+} \qquad (1)$$

$$K_6 = [\mathrm{CH_3CN{-}Co^IL{-}CO_2^+}]/[\mathrm{Co^IL{-}CO_2^+}][\mathrm{CH_3CN}] \qquad (2)$$

that acetonitrile is serving as a ligand to the $Co^IL{-}CO_2^+$ complex.

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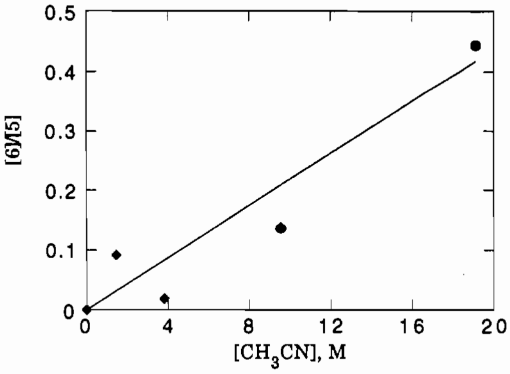

Figure 1. The ratio of concentrations of 6-coordinate ("6") to five-coordinate ("5") Co^{I}LCO$_2^+$ species as a function of acetonitrile concentration in tetrahydrofuran–acetonitrile mixtures at 15 °C. The concentration ratio was calculated from the 530-nm absorbance (ϵ_5 = 1160, ϵ_6 = 85 M^{-1} cm^{-1}). The slope of the line K_6 is 0.02 ± 0.01 M^{-1}.

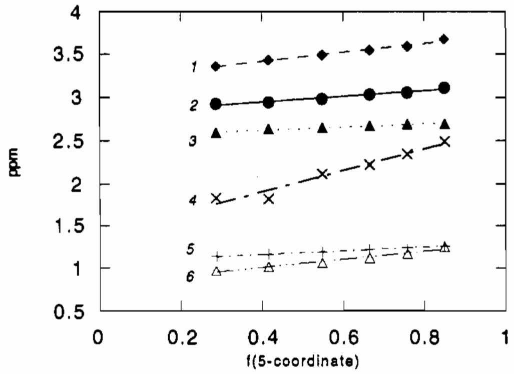

Figure 2. Positions of methylene (1–3) and methyl (4–6) resonances of Co^{I}LCO$_2^+$ solutions in CD$_3$CN at 24, 10, 0 –10, –20, and –30 °C. The × values are calculated from the temperature and the thermodynamic parameters for the five-/six-coordinate interconversion determined from UV–vis experiments in CH$_3$CN ($\Delta H°$ = –7.0 kcal mol^{-1} and $\Delta S°$ = –27 cal K^{-1} mol^{-1}).

The agreement with earlier data for pure acetonitrile solvent (K_6 = 0.013 ± 0.01 M^{-1} at 15 °C with 1 M acetonitrile as standard state[8]) is regarded as satisfactory given the differing solvent media.

The ^{1}H NMR spectra of Co^{I}L–CO$_2^+$ solutions in CD$_3$CN were determined as a function of temperature in an effort to determine the spectra of both five- and six-coordinated forms. At all temperatures examined, only three peaks assignable to the methyl groups were observed. However, their positions shifted with temperature. This behavior is consistent with eq 1 if interconversion of the two species is rapid on the NMR time scale.[23] In Figure 2, the peak positions are plotted as a function of the fraction of five-coordinate form, with the latter calculated from the thermodynamic parameters obtained from the UV–vis data (see below). The x = 0 and 1 intercepts give the spectra of the six- and five-coordinate forms, respectively.

We have not detected the ^{13}C resonance for the bound CO$_2$ in CD$_3$CN solutions of CoL^{13}CO$_2^+$. As with Co(en)$_2$CO$_2^+$,[24] the carbon is expected to have a long relaxation time and to be broadened by the quadrupolar cobalt nucleus. For the present system, our failure to observe the bound CO$_2$ in CoLCO$_2^+$ solutions is probably also due to rapid chemical exchange; since the free CO$_2$ concentration (ca. 0.3 M[7]) is at least 30 times greater than that of the complex (10 mM), the bulk CO$_2$ peak shifts little—outside the accuracy of our measurements.

The IR spectra of CoLCO$_2^+$ were measured as a function of temperature in a CD$_3$CN/THF mixture (v/v = 1/4). This solvent mixture was chosen to extend the liquid range of acetonitrile. The infrared spectra of the various CoL, CoL–CO$^+$, CoLCO$_2^+$, and CoL(C(O)OH)CoL^{3+} complexes are summarized in Table I, and the spectra are shown in Figures 3 and 4. (The free CO$_2$ in the solution absorbs significantly only at 2342 cm^{-1}, outside the range shown in the figures.) Near room temperature, the purple solution exhibits a band (A$_2$) at 1710 cm^{-1} and a shoulder (B$_2$) at 1626 cm^{-1}. As the temperature decreases, the 1710-cm^{-1} band decreases in intensity, the 1626 (B$_2$) cm^{-1} band shifts toward 1609 (C$_2$) cm^{-1}, and a new band at 1544 (D$_2$) cm^{-1} increases in intensity. No isosbestic point is observed in this region. The N–H stretching region also changes on cooling: the 3208 (A$_1$) cm^{-1} band decreases in intensity and two bands at 3224 (C$_1$) and 3145 (D$_1$) cm^{-1} increase in intensity. At –75 °C the solution is brownish red with absorptions at 1609 (C$_2$) and 1544 (D$_2$) cm^{-1} and a weak solvent band at 1700 cm^{-1}. The 1609 (C$_2$) cm^{-1} band decreases and the 1544 (D$_2$) cm^{-1} band increases on cooling below –75 °C, and the color of the solution changes to yellow. These changes indicate that the C$_2$ and D$_2$ bands are from different species. The original spectrum is recovered when the solution is warmed to 0 °C. The decomposition of the CoLCO$_2^+$ complex is extremely slow below 10 °C and can be neglected.

Similar spectral changes were observed on cooling both pure CD$_3$CN and C$_3$H$_7$CN solutions of the carbon dioxide complex. In CD$_3$CN, although the limiting spectrum was not observed at 28 °C and the solution froze around –50 °C, ν_1 CO modes could be observed for several species. On cooling, a band at 1285 cm^{-1} decreases in intensity, bands at 1320 and 1227 cm^{-1} shift toward 1327 and 1231 cm^{-1}, respectively, and a new band at 1347 cm^{-1} increases in intensity. Below 0 °C the band at 1551 cm^{-1} is associated with a shoulder at 1567 cm^{-1} in CD$_3$CN. In C$_3$H$_7$CN the solvent absorptions were so great that the quality of the data is poorer.

The SVD spectral analysis fitting of the variable-temperature IR data between 0 and –70 °C is consistent with the presence of two species. The fitting gives $\Delta H°$ = –6.94 kcal mol^{-1} and $\Delta S°$ = –27.5 cal K^{-1} mol^{-1} for the 1500–3300-cm^{-1} region. These values are similar to those obtained from the SVD fitting of the UV–vis data ($\Delta H°$ = –7.0 kcal mol^{-1} and $\Delta S°$ = –27 cal K^{-1} mol^{-1} over the range –40 °C to 26 °C in CH$_3$CN, in good agreement with the results reported earlier[8] from a simplified treatment). While the SVD fitting is consistent with the presence of only two species, the analyses of the 1500–1750-cm^{-1} region suggest that more than two species may be present. Furthermore, although we could not include the IR data below –70 °C for SVD fitting because of the baseline shift of the frozen solution, the IR data below –70 °C clearly indicate that the C$_2$ and D$_2$ bands belong to separate species. Thus we suggest the existence of four distinct CO$_2$ species. As discussed later, we propose that these are two five-coordinated isomers and two six-coordinated isomers. The isomers differ by internal hydrogen bonding between the coordinated CO$_2$ and the amine hydrogens.

Decomposition of Co^{I}LCO$_2^+$ in Acetonitrile. We previously monitored the decomposition of Co^{I}LCO$_2^+$ by UV–vis and GC and found Co^{II}L^{2+}, CO, H$_2$, and NaHCO$_3$,[7] with yields of 1.0, 0.3, 0.05, and 0.75, respectively, based on initial Co(II). Here FT-IR was used to monitor the species present during the decomposition of Co^{I}LCO$_2^+$ in CD$_3$CN at room temperature. The Co^{I}LCO$_2^+$ complex was prepared by the introduction of CO$_2$ (room temperature, atmospheric pressure) into solutions of the Co^{I}L$^+$ complex produced by Na–Hg reduction. Peaks at 1706, 1620, 1320, 1285, and 1227 cm^{-1} diminish and peaks at 1917 and 1662 cm^{-1} increase with time. The intensity of the CO

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(22) Note that this treatment assumes that K_6 is constant over the range varying from 100% THF to 100% CH$_3$CN. Given the solvent dependence of CO$_2$ binding equilibria,[11] it is possible that K for eq 2 is also solvent dependent, in which case, the dependence of eq 2 on CH$_3$CN should not be linear. The errors in our data are so great that we cannot resolve this issue here.

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Table I. Infrared Spectra of Cobalt Macrocycle Complexes at Room Temperature[a]

no.	complex	medium	ν_{NH} or ν_{ND} (ϵ), cm^{-1} (M^{-1} cm^{-1})	$\nu_{C=N}$ (ϵ), cm^{-1} (M^{-1} cm^{-1})	ν_{CO} (ϵ), cm^{-1} (M^{-1} cm^{-1})
1	*rac*-$Co^{II}L$	CD_3CN	3215 (296)	1661 (258)	
2	d-*rac*-$Co^{II}L$	CD_3CN	2400, 2376	1661	
3	*rac*-$Co^{II}L$	Nujol	3228	1661	
4	d-*rac*-$Co^{II}L$	Nujol	2400, 2381 (w)	1660	
5	*meso*-$Co^{II}L$	CD_3CN	3223 (208), 3185 (195)	1656 (264)	
6	*rac*-$Co^{I}L$[b]	CD_3CN	3201 (~200[c])	1571 (264)	
7	*rac*-$Co^{I}L$[b]	Nujol	3205	1591	
8	*meso*-$Co^{I}L$[b]	CD_3CN	3201 (>136)	1571 (308)	
9	$Co^{I}L-^{12}CO$	CD_3CN		1660 (316)	1917 (1590)
10	$Co^{I}L-^{13}CO$	CD_3CN		1660	1871
11	$Co^{I}L-^{12}CO$	Nujol	3253	1652	1912
12	$Co^{I}L-^{13}CO$	Nujol		1652	1871
13	$Co^{I}L-^{12}CO_2$	CD_3CN	3198 (>166)	1648 (291)	1706 (400[d]), 1620 (220), 1320 (w), 1285, 1227
14	$Co^{I}L-^{13}CO_2$	CD_3CN	3198 (>160)	1648[e]	1658,[d] 1576 (210), 1290 sh, 1249, 1209
15	$Co^{I}L-^{13}CO_2$	Nujol[f]	3215, 3205	1643	1702, 1620, 1290, 1217
16	$Co^{I}L-^{13}CO_2$	Nujol[f]	3200	1638	1658, 1570, 1260, 1192
17	$Co^{I}L-^{13}CO_2$	Nujol[g]	~3110	1654	1558, 1340, 1228
18	$Co^{I}L-^{12}COOH-Co^{I}L$	Nujol	3229, 3212, 3164	1643	1662, 1638, 1610, 1288, 1234, 1221

[a] Molar absorptivities of Co^I, Co^I-CO_2, and Co^I-CO complexes assume 100% conversion from the parent Co(II) complexes. "d" denotes samples in which macrocycle NH group have been exchanged to give ND. [b] The isomer notation only indicates which Co^{II} complex was used as starting material. [c] This value was estimated from the data in C_3H_7CN in which the absorbance ratio, $\epsilon_{3200}/\epsilon_{1570}$ = 0.76). [d] Due to the decomposition of the Co^I-CO_2 complex, the ϵ is a lower limit. [e] Since the peak overlaps with another peak, the ϵ was not measured. [f] Solid was isolated from CH_3CN/THF at 5 °C, measured at 25 °C. [g] Solid was isolated from CH_3CN/THF at –70 °C, measured at 25 °C.

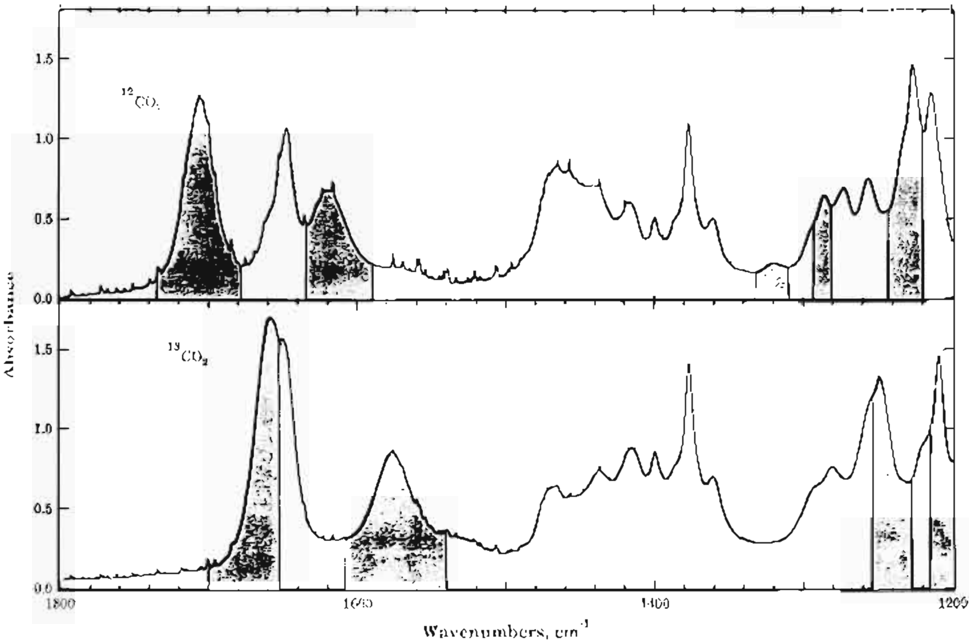

Figure 3. Infrared spectra of $^{12}CO_2$ (top) and $^{13}CO_2$ (bottom) adducts (0.06 and 0.09 M, respectively) in CD_3CN at room temperature (path length 0.5 mm). The spectra have been corrected for solvent absorption and offset for display purposes. Shaded areas indicate the CO stretching frequencies of the CO_2 adducts.

stretching band at 1917 cm^{-1} clearly indicates the production of one Co^ILCO^+ molecule per about 4 molecules of $CoLCO_2^+$ during the decomposition to $Co^{II}L^{2+}$. The production of $NaHCO_3$, which has a broad band at 1610 cm^{-1} (with $^{12}CO_2$) and at 1575 cm^{-1} (with $^{13}CO_2$), was also observed. Thus the infrared observations are in accord with the earlier product assignments.

Discussion

$CoLCO_2^+$ Complexes. At room temperature, the solubility of CO_2 in THF, 0.2 M at 1 atm,[11] is comparable to that in acetonitrile, 0.28 M at 1 atm,[7] and the affinity of CoL^+ for CO_2 in acetonitrile and THF is similar.[11] Thus the species observed in THF/CD_3CN (Figure 4) are believed to be 1:1 complexes, $CoLCO_2^+$. We propose that two five-coordinated isomers and two six-coordinated isomers are observed in the IR studies and that the isomers differ by internal hydrogen bonding between the coordinated CO_2 and the amine hydrogens.[25] The species proposed are (A) a five-coordinate, non-hydrogen-bonded form ($\nu_{C=O}$ = ~1710 (A_2) cm^{-1}, ν_{NH} = 3208 (A_1) cm^{-1}), (B) a five-coordinate intramolecularly hydrogen-bonded form ($\nu_{C=O}$ = 1626 (B_2) cm^{-1}), (C) a six-coordinate non-hydrogen-bonded form ($\nu_{C=O}$ = 1609 (C_2) cm^{-1}, ν_{NH} = 3224 (C_1) cm^{-1}), and (D) a six-coordinate intramolecularly hydrogen-bonded form ($\nu_{C=O}$ = 1544 (D_2) cm^{-1}, ν_{NH} = 3145 (D_1) cm^{-1}) (see Chart I). In pure CD_3CN at room temperature the band at 1620 (B_2) cm^{-1} is more pronounced in intensity due to the presence of species B. Although an asymmetrically hydrogen-bonded species (E) might also exist in solution, it would be very difficult to observe them in our present

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[25] In this discussion we have assumed that the isomers arise solely from η^1-CO_2 isomers bound to the primary face of the macrocycle. Since we have not studied the temperature dependence of the *rac/meso*-CoL^+ equilibrium, the possibility that meso isomers are observed cannot be completely ruled out. In addition, secondary CO_2 isomers could play a role, as could η^2 species. However, given our earlier results for both water and acetonitrile solutions, we feel the model presented in the text is the most reasonable.

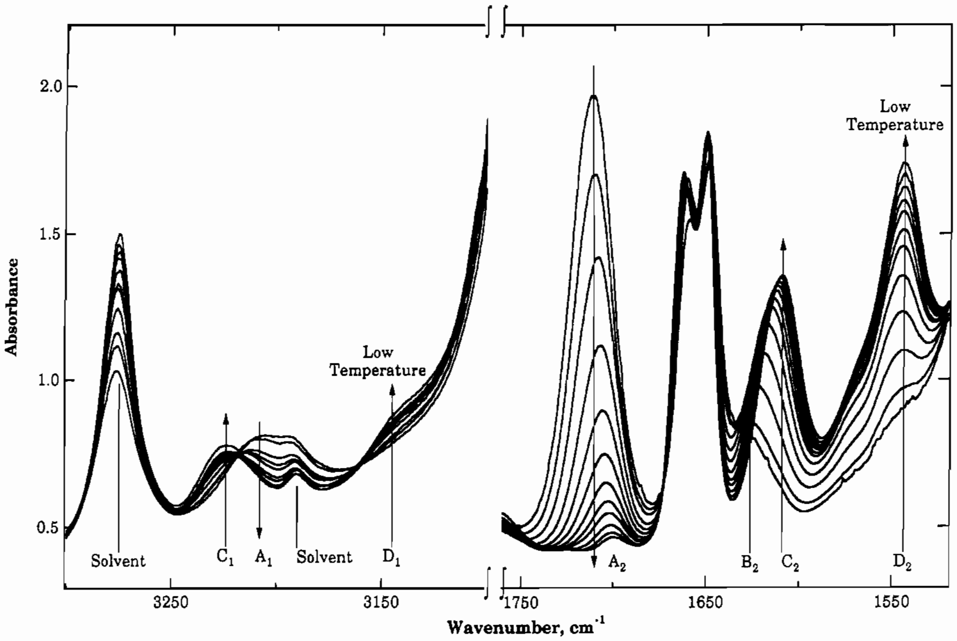
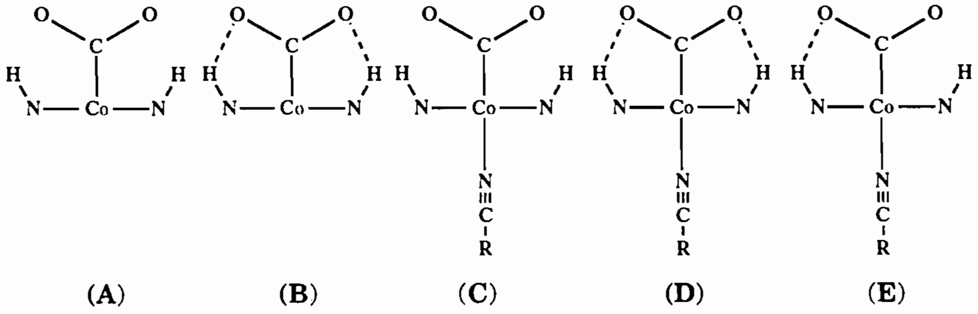


Figure 4. Infrared spectra of *N-rac*-$Co^ILCO_2^+$ in CD_3CN/THF (v/v = 1/4) as a function of temperature. (Initial [Co(I)] = 0.07 M, path length 1.0 mm.) The spectra were taken at 270, 263, 253, 243, 233, 228, 223, 218, 213, 208, 203, and 198 K. Peaks at 1648 and 1661 cm^{-1} are assigned to $\nu_{C=N}$ for $Co^ILCO_2^+$ and $Co^{II}L^{2+}$, respectively. A small amount of $Co^{II}L^{2+}$ was produced during the sample transfer at room temperature.

Chart I



experiments. The shoulder observed at 1567 cm^{-1} in CD_3CN may arise from such a species. Experiments using a complex without an inversion center (cobalt(I) 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene complex) were attempted to test the existence of unsymmetrically hydrogen-bonded species; however the CO_2 species could not be observed because of the low stability of the CO_2 complex. Since the SVD analyses suggests only two species corresponding to a five- and a six-coordinated species, the differences between the thermodynamic parameters for the hydrogen-bonded and non-hydrogen-bonded isomers must be small, making it difficult to distinguish between them except below -75 °C.

While the nitrile stretch region of the spectra could not be monitored in the experiments in Figure 4, evidence for the presence of bound nitrile (as in D) comes from the data shown in Figure 1 and from the spectrum of a solid isolated in earlier work (entry 17, Table I) from a mixture of CH_3CN and THF at -70 °C. The tan solid has strong and weak bands at 2337 and 2325 cm^{-1} arising from the coordinated CH_3CN, in addition to two bands at 2272 and 2255 cm^{-1} from free CH_3CN.[8] (These are assigned by analogy with results reported for $[Co^{III}L(CH_3CN)_2](ClO_4)_3$: sharp doublet or broad singlet in the 2290–2350-cm^{-1} region for coordinated CH_3CN.[26]) The tan solid has CO and NH stretching frequencies (ν_{CO} = 1558, 1340, 1228 cm^{-1}, ν_{NH} = ~3110 cm^{-1}) similar to those of six-coordinate intramolecular hydrogen-bonded form (D). Since no ν_{NH} is observed at 3200 cm^{-1}, both N–H groups must be involved in hydrogen bonding. The binding of CO_2 *via* both its electrophilic center (carbon atom) and its nucleophilic center (oxygen atom) is thus implicated in the stabilization of the CO_2 complex at low temperature.

Table II summarizes the spectral assignments for the four species.

Spectral Comparisons. The $\nu_{C=N}$ bands provide information about the oxidation state of the metal center. The electron-rich cobalt(I) center donates significant electron density to the imine moiety, causing the C=N stretching frequency (1571 cm^{-1}) to be much lower than for CoL^{2+} (~1660 cm^{-1}). Axial coordination of Co^IL^+ to CO_2 (~1650 cm^{-1}) or CO (~1660 cm^{-1}) reduces the degree of electron donation from the cobalt center to C=N, raising $\nu_{C=N}$ (Table I).

The assignment of binding modes for CO_2 complexes in solution and for those solids not characterized by diffraction methods is presently a difficult problem. As tools to the assignment of bonding mode from vibrational spectroscopy, both isotopic shifts (Δ_{C13}) and the difference ($\nu_3 - \nu_1$) between C=O and C–O stretching bands have been proposed:[27,28] For η^1-C coordination, $\nu_3 - \nu_1 \leq 400$ cm^{-1}, while, for η^2-C–O coordination, this splitting is > 500 cm^{-1}. In Table II, we summarize the values of these

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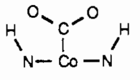
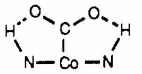
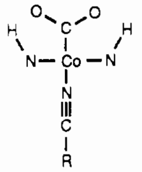
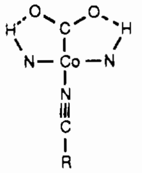
(26) Tait, A. M.; Lovecchio, F. V.; Busch, D. H. *Inorg. Chem.* **1977**, *16*, 2206.

(27) Jegat, C.; Fouassier, M.; Mascetti, J. *Inorg. Chem.* **1991**, *30*, 1521.

(28) Jegat, C.; Fouassier, M.; Tranquille, M.; Mascetti, J. *Inorg. Chem.* **1991**, *30*, 1529–1536.

Table II. Vibrational Assignments (cm^{-1}) for the Four $CoLCO_2^+$ Species

species	solvent	ν_{NH}	ν_3, CO_2	ν_1, CO_2	$\nu_3 - \nu_1$	$\Delta_{C13}(\nu_3)$	$\Delta_{C13}(\nu_1)$
	Nujol	3198	1702	1290	412	44	30
				1217	485		25
	THF/CD_3CN	3208	1710				
(A)	CD_3CN	3198	1706	1285	421	47	36
				1227	479		18
	C_3H_7CN	3208	1720				
	Nujol		1620			50	
	THF/CD_3CN		1626				
	CD_3CN		≥1621	1320	≥301	~44	
(B)	C_3H_7CN		1630				
	THF/CD_3CN	3224	1609				
	CD_3CN		1609	1327	282		~30
				1231[a]	378		
	C_3H_7CN		1610				
(C)							
	Nujol	3110	1558	1340,	218		
				1228	330		
	THF/CD_3CN	3145	1544				
	CD_3CN		1551	1347	204		
			1567[b] sh	1231[a]	320		
	C_3H_7CN		1560				
			1570[b] vw				
(D)							

[a] The bands due to C and D could not be resolved. [b] The weak absorption at ~1570 cm^{-1} could be due to a small amount of E.

shifts for the A–D species deduced above.[29] Both $\nu_3 - \nu_1$ and Δ_{C13} values for species A and B are consistent with η^1-CO_2 species. For the five-coordinated species $\nu_3 - \nu_1$ is a little greater than 400 cm^{-1}, while, for the six-coordinated species in Table II, the splittings are about 300 cm^{-1} or less, more similar to values recorded for purely organic carboxylates, for which the splittings are generally ≤ 200 cm^{-1}.[30] The $\nu_{C=O}$ value of species A is quite high, but shifts to lower frequency (~1610 cm^{-1}) with conversion to six-coordinate C and to even lower frequency (~1550 cm^{-1}) in the hydrogen-bonded species D. This progression suggests a lowering of the C–O bond order across the series. In fact the frequency reported for $Co^I(salen)Na(CO_2)$, 1680 cm^{-1}, is lower than that of A because of the interaction of the oxygens of the bound CO_2 with Na^+ as is revealed in its crystal structure. The frequency reported[31] for six-coordinate $Rh(diars)_2Cl(CO_2)$ (1620 cm^{-1}) is very similar to that found here for six-coordinate C.

The electron distributions of CO_2 complexes are of some interest. MO calculations for a model complex suggest that[32–34] extensive charge donation from Co(I) to CO_2 in $Co^ILCO_2^+$ results in an electronic distribution better described as $Co^{II}L(CO_2^-)^+$. However, there is no evidence that cobalt(II) (a d^7 metal center) is actually present. The ^1H NMR spectra of $CoL(CO_2)^+$ in CD_3CN at various temperatures indicate the existence of only diamagnetic CO_2 adducts. To our knowledge, low-spin, six-coordinate cobalt(I) has never been observed. Therefore the six-coordinate species $Co^IL(CO_2)(CH_3CN)^+$ is most reasonably formulated as a cobalt(III) complex $Co^{III}L(CO_2^{2-})(CH_3CN)^+$,[35] closely related to the yellow diamagnetic complexes $Co^{III}(en)_2(CO_2^{2-})(OH)$ in solution and polymeric $Co^{III}(en)_2(CO_2^{2-})^+$ in the solid.[24,36]

Concluding Remarks. In acetonitrile containing ca. 0.2 M CO_2, purple, prim, *rac*-$Co^ILCO_2^+$ (A, $\nu_{C=O}$ = 1710 cm^{-1}) is in rapid equilibrium with a yellow six-coordinate species (C) in which acetonitrile is bound trans to the CO_2 on the secondary face of the macrocycle. C forms at the expense of A as the solution is cooled, but in addition, a six-coordinate intramolecularly hydrogen-bonded form D ($\nu_{C=O}$ = 1544 cm^{-1}, ν_{NH} = 3145 cm^{-1}) also grows in at low temperature. With binding of the sixth ligand and the formation of hydrogen bonds from the N–H groups to the oxygens of the bound CO_2, increasing charge density is transferred from the metal to the bound CO_2 and C═O frequencies decrease and C═N frequencies increase as a consequence. The binding of CO_2 *via* both its electrophilic center (carbon atom) and its nucleophilic center (oxygen atom) is thus implicated in the stabilization of the CO_2 complex at low temperature.

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(29) For A and D, two bands (for A, 1285 and 1227 cm^{-1}; for D, 1347 and 1231 cm^{-1}) are observed in the region assignable to ν_1 (ν_{C-O}). On the basis of isotopic shifts, the higher frequency bands are assigned to ν_1. We cannot assign the lower frequency bands.

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(31) Herskovitz, T. *Inorg. Synth.* **1982**, *21*, 99.

(32) Sakaki, S.; Dedieu, A. *J. Organomet. Chem.* **1986**, *314*, C63.

(33) Sakaki, S.; Dedieu, A. *Inorg. Chem.* **1987**, *26*, 3278.

(34) Sakaki, S. *J. Am. Chem. Soc.* **1992**, *114*, 2055.

(35) Preliminary XANES (X-ray absorption near-edge structure) results for $[CoL(CO_2)(CH_3CN)]^+$ in CH_3CN at 150 K indicate that the oxidation state of the cobalt center can be interpreted as Co(III): E. Fujita, M. W. Renner, and L. R. Furenlid, work in progress.

(36) Katz, N. E.; Szalda, D. J.; Chou, M. H.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 6591.