

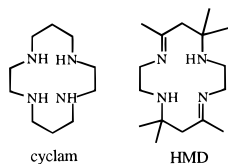
Direct XANES Evidence for Charge Transfer in Co–CO₂ Complexes

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Metallocoxyalates (and metallocoxylic acids) with 14-membered tetraazamacrocyclic ligands such as [Ni^{III}cyclam(CO₂²⁻)]⁺ (cyclam = 1,4,8,11-tetraazacyclotetradecane)¹ and [Co^{III}HMD(CO₂²⁻)]⁺ (HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)² are postulated intermediates in the electro- and photochemical CO₂ reduction and the water gas shift reaction (WGS). Metallocoxyalates are typically prepared by (1) insertion of CO into the M–OH bond; (2) reaction of OH[–] with M–CO; or (3) direct carboxylation of anionic metal complexes.^{3–12} However, it has been shown that CO₂ adducts and metallocoxyalates can be prepared by reaction of CO₂ with cationic low spin Co(I) (d⁸) complexes, such as Co^IHMD⁺.^{13–15}



Temperature-dependent UV–vis and IR spectra of the diamagnetic CO₂ adducts of Co^IHMD⁺ indicate a thermochromic equilibrium between a five- and six-coordinate complex in acetonitrile or butyronitrile as shown in eqs 1 and 2.^{14,15}



From flash photolysis studies we were able to detect the existence of both five- and six-coordinate CO₂ adducts as intermediates in the photocatalytic system containing *p*-terphenyl as a sensitizer, CoHMD²⁺ as a catalyst, and triethylamine as an electron donor.² We report here an X-ray absorption near-edge spectroscopy (XANES) study of the CO₂ adducts which

clearly indicates significant charge-transfer from the Co(I) to the bound CO₂ in both five- and six-coordinate species. The six-coordinate species can be interpreted as a Co(III) carboxylate, [Co^{III}HMD(CO₂²⁻)(CH₃CN)]⁺. This is the first unambiguous evidence that active metal catalysts, such as [Co^IHMD]⁺, can promote two-electron transfer to the bound CO₂ and thereby facilitate reduction of CO₂.

X-ray absorption spectroscopy is an attractive tool for the characterization of metal complexes in solution. The metal coordination number, geometry, and electronic properties can be studied using XANES, and the metal–ligand bond distances are obtained through analysis of the extended X-ray absorption fine structure (EXAFS). Previous work has also shown that the edge energy correlates with the oxidation state of the metal.^{16–18} EXAFS and XANES results^{19,20} for a series of the CoHMD complexes are summarized in Table 1 together with their IR data. XANES spectra for a series of the CoHMD complexes are shown in Figure 1.

The edge positions (*E*₀) of the CoHMD complexes studied here 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 as can be seen in Figure 1a. The 1s–4p_z pre-edge peak, located ~6 eV below the main edge, in the XANES spectra for [Co^IHMD]⁺ and [Co^{II}HMD]²⁺ is characteristic of a four-coordinate square-planar geometry,¹⁸ see Figure 1b. The edge for [Co^IHMD]⁺ is broadened, indicating a possible mixture of Co(II) and Co(I) or possible oxidative addition of CH₃CN;²¹ however, the XANES for [Co^IHMD]⁺ shows no change with time or temperature, and repeated experiments gave similar results. Interestingly, the IR spectrum of [Co^IHMD]⁺ indicates that the electron-rich Co(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 [CoHMD]²⁺ (1661 cm^{–1}).¹⁵ This is consistent with the small *E*₀ change upon one-electron reduction in the [Co^IHMD]⁺ complex.²²

Axial coordination of [Co^IHMD]⁺ by CO₂ (1648 cm^{–1}) or CO (1660 cm^{–1}) reduces the degree of electron donation from the cobalt center to C=N, raising ν_{C=N}. In the XANES, addition of an axial ligand along the *z*-axis decreases the intensity of the 1s–4p_z type transition and increases the weak quadrupolar

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(19) The samples were prepared as previously described using vacuum techniques in EXAFS cells of published design.^{27,28} Sample purity was confirmed before and after X-ray experiments by optical absorption spectroscopy. The [CoHMD(CO₂)]⁺ data at room temperature may be contaminated by ~10% [S-CoHMD(CO₂)]⁺ and up to 10% [CoHMD]²⁺. Higher temperatures reduce the amount of [S-CoHMD(CO₂)]⁺ but increase the [CoHMD]²⁺ through the decomposition.

(20) X-ray absorption experiments were performed on beamline X-9A, X-10C, and X-19A at the National Synchrotron Light Source using Si 111 (X-9A) and Si 220 (X-10C and X-19A) monochromator crystals. The slits were adjusted to give ~1 eV resolution. The beam was adjusted to 1 × 0.3 cm² before the sample; the average beam current throughout the experiments was ~150 mA. The samples were 3–4 mM in the complex and were measured in fluorescence mode using either a Canberra 13-element solid-state detector or a Lytle detector. Sufficient 20-min scans were collected (6–15 scans) to yield a minimum of 10⁶ effective counts of signal. Data analysis was performed using previously published procedures.²⁷

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(22) Comparison of the XANES and IR data for the Co and Ni macrocycles is interesting. XANES and IR spectra of [Ni^{II}HMD]²⁺ and [Ni^IHMD]⁺ are published.^{27,28} The main edge and the C=N stretching frequency shift –3.0 eV and –15 cm^{–1} upon the reduction, respectively. This indicates that Ni(I) center does not donate significant electron density to the imine moiety. Previous study has also shown that the main edge for [Ni^IHMD(CO)]⁺ is –1.5 eV relative to [Ni^{II}HMD]²⁺. XANES and ν_{CO} IR data ([Ni^IHMD(CO)]⁺: 1962 cm^{–1}, [Co^IHMD(CO)]⁺: 1917 cm^{–1}) are consistent with stronger backbonding interaction in the Co complex than in the Ni complex.

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Table 1. EXAFS and XANES Results^a and IR data^b for Various Cobalt HMD Complexes

compound	<i>N</i>	<i>r</i> (Å)	$\Delta\sigma^2$	χ^2_{gof}	<i>E</i> ₀ (eV)	$\nu_{\text{C=O}}$ (cm ⁻¹)	ν_{CN} (cm ⁻¹)
[Co ^{II} HMD](ClO ₄) ₂ ^c	4	1.94	0.010	0.044	7718.1		1661
[Co ^{II} HMD](ClO ₄) ^c	3.4	1.92	-0.001	0.021	7717.3		1571
[Co ^I HMD(CO)](ClO ₄) ^c	4	2.08	0.003	0.034	7717.5		1660
	1	1.74	0.001				
[CoHMD(CO ₂)](ClO ₄) ^d	4	1.93	-0.003	0.029	7718.3	1706	1648
	1	2.09	-0.006				
[CoHMD(CO ₂)(CH ₃ CN)]-(ClO ₄) ^d	4	1.92	-0.001	0.041	7719.3	1544	1648
	2	2.01	0.009				
[Co ^{III} HMD(CO ₃ ²⁻)]-(ClO ₄) ^e	6	1.94	0.001	0.041	7720.2	1669	1662
						1634	

^a Standards: Co^{II}OEP, solid Co^{II}HMD(ClO₄)₂, and FEFF 3.0. *E*₀ values were determined from the absorption edge step midpoint. A linear pre-edge background and a least squares cubic spline EXAFS background were extrapolated to normalize the XANES absorption intensities. XANES spectra are all calibrated relative to a cobalt foil (7709 eV) as usual, and *E*₀ values are reproducible to within ~0.2 eV between scans. When *E*₀ values are obtained using the peak of the first derivative, the *E*₀ values are typically 1.5–2 eV higher than our values obtained by the absorption edge step midpoint. However the shift (ΔE_0) from [Co^{II}HMD](ClO₄)₂ is the same for both methods within experimental error. Errors in *r* values are ± 0.02 Å. ^b See ref 15. ^c Acetonitrile, room temperature. ^d Acetonitrile, 150 K. ^e Water, room temperature.

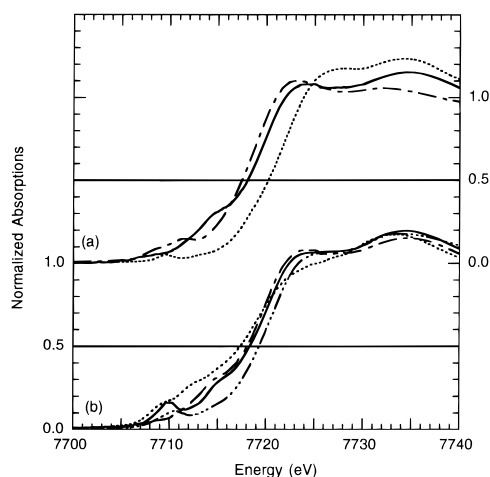


Figure 1. XANES spectra for a series of CoHMD complexes in various oxidation and ligation states. (a) [Co^{II}HMD](ClO₄)₂ in acetonitrile at 150 K (—), [Co^{III}HMD(CO₃²⁻)]ClO₄ in H₂O at room temperature (···), and [Co^IHMD(CO)]ClO₄ in acetonitrile at room temperature (---). (b) [Co^{II}HMD](ClO₄)₂ in acetonitrile at 150 K (- · - ·), [Co^IHMD]ClO₄ in acetonitrile at room temperature (···), five-coordinate [CoHMD(CO₂)]ClO₄ in acetonitrile at room temperature (—), six-coordinate [S-CoHMD(CO₂)]ClO₄ in acetonitrile at 150 K (- · · - ·).

1s-3d transition (~11 eV below the edge) indicating a square pyramidal geometry around the cobalt, as found previously.¹⁸

The thermochromic behavior of the CO₂ adducts was studied via XANES. The XANES spectra of an acetonitrile solution of the CO₂ adducts at room temperature and 150 K are shown in Figure 1b. At room temperature the Co–CO₂ adduct is 90% five-coordinate [CoHMD(CO₂)]⁺ and 10% six-coordinate [S-CoHMD(CO₂)]⁺, whereas cooling the solution to 150 K results in 100% conversion to the six-coordinate species.¹⁵ Prolonged XANES measurements of [CoHMD(CO₂)]⁺ at room temperature showed a gradual decrease in the 1s-3d peak due to decomposition to [Co^{II}HMD]²⁺. The XANES spectrum for [S-CoHMD(CO₂)]⁺ at 150 K shows a small decrease of the 1s-3d peak and almost complete loss of the 1s-4p_z transitions, indicative of a six-coordinate distorted octahedral geometry. The *E*₀ for [CoHMD(CO₂)]⁺ at room temperature is similar to that of [Co^IHMD]²⁺ ($\Delta E_0 = + 0.2$ eV, which is within the reproducibility of the measurements), consistent with theoretical

predictions²³ that the bound CO₂ receives 0.71 electrons mainly from the Co d_{z²} orbital. The six-coordinate [S-CoHMD(CO₂)]⁺ species shows a 1.2 eV shift toward Co(III) and is interpreted as a Co(III)–CO₂²⁻ carboxylate complex. This assignment is consistent with the change of asymmetric ν_{CO} from 1706 cm⁻¹ for [CoHMD(CO₂)]⁺ to 1544 cm⁻¹ for [S-Co^{III}HMD(CO₂²⁻)]⁺.¹⁵

Results from analysis of the EXAFS data are tabulated in Table 1. The *k*³ weighted EXAFS, Fourier transform *k*³ weighted EXAFS, isolated first shell EXAFS oscillations, and the corresponding least squares fits are deposited as Supporting Information, Figures S1–S3. Comparison of the EXAFS and single crystal X-ray diffraction results for the Co(I), Co(II), and Co(III) complexes shows good agreement of the average Co–N distances. The average Co–N distances from x-ray diffraction are as follows: [Co^IOMD]⁺ (OMD = 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), 1.946 Å;¹⁴ [Co^{II}HMD(OCIO₃)]⁺, 1.943 and 1.924 Å (two independent molecules in the unit cell);^{24,25} and [Co^{III}HMD(CO₃)]⁺, 1.938 Å.²⁶ EXAFS fitting results for the [Co^IHMD(CO)]⁺ complex reveals a short Co–C distance of 1.74 Å and longer Co–N distances of 2.08 Å, similar to the crystallographic results (Co–C = 1.797 Å and Co–N = 2.116 Å; the Co is 0.57 Å above the plane of the four N atoms.) reported earlier.²⁶

The five- and six-coordinate Co–CO₂ complexes have similar Co–N distances of 1.93 and 1.92 Å, respectively, however the axial Co–CO₂ distance is 0.08 Å shorter for the six-coordinate species. In contrast to [CoHMD(CO)]⁺, the Co atom in the five-coordinate Co–CO₂ complex seems to be practically in the plane of four N atoms. Binding of CO₂ to the cobalt through the electrophilic carbon, with the oxygens bending back in a η^1 -CO₂ configuration is the best model to account for the observed charge transfer. The solvent coordination to [CoHMD(CO₂)]⁺ allows stronger Co d_{z²} to CO₂ charge transfer resulting in a shorter Co–C distance and thus stabilizes the Co(III) carboxylate.

Our XANES data for a series of CoHMD complexes clearly shows the expected shifts in the edge energy with changes in the oxidation state of the metal. Temperature dependent XANES data for [CoHMD(CO₂)]⁺ further confirms solvent molecule binding at low temperatures. More importantly, the edge energy for the complex, which is between Co(II) and Co(III), is the first direct observation of Co → CO₂ charge transfer. The effective electronic structure for the [S-CoHMD(CO₂)]⁺ species is best described as a (d⁶) Co(III) carboxylate (CO₂²⁻) complex.

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Supporting Information Available: Figures of the *k*³ weighted EXAFS spectra, Fourier transform *k*³ weighted EXAFS spectra, and the isolated first shell EXAFS oscillations and the corresponding least squares fits for the series of CoHMD complexes (3 pages). See any current masthead page for ordering and Internet access instructions.

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