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A Reversible O_2 Binding System: $Co(CN)_5^{3-}$ Inside Zeolite Y

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An anionic cobalt(II) cyanide complex which reversibly binds oxygen inside zeolite Y, $Na_{56}[(SiO_2)_{136}(AlO_2)_{56}]\cdot 250H_2O$, has been prepared by treating CoY with CsCl, followed by the addition of a methanolic solution of NaCN. EPR parameters of the complex inside cesium ion treated CoY are characteristic of a five-coordinate $Co(CN)_5^{3-}$ compound. Quantitative gas uptake and EPR measurements show that this complex is highly selective for oxygen binding. Our best sample has an equilibrium constant for oxygen binding of 18 ± 2 $Torr^{-1}$, with an oxygen binding cobalt species concentration of 43 ± 4 $\mu mol\ g^{-1}$ material.

Introduction

Our concern is with the synthesis of new absorbents for the purification and separation of oxygen from nitrogen by entrapping transition-metal complexes, of oxidation-resistant ligands, that *reversibly* bind oxygen at or above room temperature inside a zeolite. Zeolites are of interest[1,2] as a matrix for synthesizing coordinatively unsaturated complexes that are reactive intermediates in heterogeneous catalysis. The three-dimensional pore structure of zeolites provides the possibility of site isolation and of preparing complexes inside the zeolite that are unstable in solution. This trapping is described as making a "ship-in-a-bottle" complex.[3] Zeolites can simultaneously influence the stability of complexes with their unique solvating and ligating properties and cause the formation of unique complexes that cannot be prepared in solution. Acting as a ligand, zeolites can also stabilize complexes by anchoring them to the lattice by coordination to framework oxygens.[4]

Most of the "ship-in-a-bottle" transition-metal complexes that have been reported are cationic or neutral. We recently reported the formation of anionic cobalt cyanide complexes inside zeolite Y,[5] which represents the first case in which an anionic complex has been synthesized inside a zeolite cavity. The major species formed in the reaction of $Co^{II}Na$–Y with a methanolic solution of sodium cyanide is the $Co(CN)_6^{3-}$ ion, which was characterized by an infrared CN stretching frequency at 2129 cm^{-1}.[5b] At high cobalt loadings, a complex can be formed in every large cavity. Oxidation of the cobalt occurs even under conditions which exclude oxygen and minimize water.

The most interesting species formed in the reaction of CoNa–Y with NaCN is a low-spin cobalt(II) complex capable of reversibly binding oxygen. The EPR parameters and equilibrium constant for oxygen binding suggest that this active complex is a square-planar $Co(CN)_4^{2-}$ ion which may be five-coordinate via bonding to the lattice oxygen of the zeolite framework.[5] This complex is stable to repeated cycling in air and, even in low concentration, increases the amount of oxygen absorbed at 100 Torr by 100% over that of the pure zeolite. The concentration of active complex synthesized is limited.

The oxidation of cobalt(II) to $Co(CN)_6^{3-}$ in aqueous solution is driven by the presence of excess cyanide. The reaction with water involves formation of hydrido and hydroxo species that are converted[6] to $Co(CN)_6^{3-}$. A similar mechanism involving the reduction of water may be operative in the zeolite with cobalt complexes interacting through the connecting channels of the large cavities. The majority of the cobalt is readily oxidized under the synthesis conditions previously reported.

In view of the unique oxidation resistance of the entrapped cyanocobalt(II) complex to repeated recycling of oxygen binding, our goal is to increase the amount of $Co(CN)_4^{2-}$ formed in Co(CN)Na–Y. By exchanging Cs^+ into CoNa–Y prior to the addition of cyanide, less oxidation of the cobalt is observed in the synthesis and a new, cobalt complex that reversibly binds oxygen, $Co(CN)_5^{3-}$ is formed inside the zeolite at higher concentration than the previously reported $Co(CN)_4^{2-}$ complex. These two complexes constitute the most oxidation-resistant, reversible oxygen carriers known. The identification and characterization of this new complex is presented here.

Experimental Section

Solvents and Reagents. The methanol used was reagent grade and dried over activated 3A molecular sieves. Linde Na–Y was obtained from UOP (Lot No Y-52 13076-81). All chemicals were used as obtained without further purification. $CoCl_2\cdot 6H_2O$ was an analytical reagent from Mallinckrodt. NaCN was ACS certified from Fischer Scientific. Ethylenediaminetetraacetic acid, tetrasodium salt 98% (Na_4EDTA), and cesium chloride (99.9%) were obtained from Aldrich Chemical Co. Oxygen, argon, nitrogen, and helium were obtained from Liquid Air Corp. All water used was distilled.

Cobalt-Exchanged Zeolites. Na–Y was first stirred in 0.25 M NaCl at room temperature and then washed with water until no precipitation was observed when the filtrate was tested with a 0.1 M $AgNO_3$ solution. The Na–Y was then dried at 100 °C overnight in a vacuum oven. Co–Y was then prepared by exchange of Co^{2+} for Na^+ in an aqueous $CoCl_2$ solution at 70 °C for 24 h. Aqueous $CoCl_2$ solutions were always less than 0.03 M and usually less than 0.01 M. There was very little cobalt remaining in the solution after the reaction. The resulting pink solid was then collected by filtration, washed with water until no Cl^- was present in the filtrate, and dried at 150 °C in the vacuum oven overnight. The resulting solid was deep purple/blue.

Cesium Treatment. Cesium-exchanged Co–Y samples were prepared by stirring Co–Y in a 0.1 M CsCl or CsOH solution. These exchanges were done at room temperature and allowed to stir for a minimum of 16 h. Often the treatment was repeated to ensure maximum Cs^+ exchange.

General Reaction Conditions. Unless otherwise specified, all reactions were carried out in the presence of atmospheric oxygen and moisture. Flasks were stoppered during stirring, but no precautions were taken to exclude air. Reactions done under inert atmosphere were carried out using Schlenk techniques under purging argon. In experiments where water was rigorously excluded, the methanol was freshly distilled from BaO and the argon passed over activated sieves and NaOH. During reactions where oxygen or water were excluded, the Co–Y was evacuated at 100 °C and filled with nitrogen at least three times prior to use.

Sample Identification Nomenclature. The mode of preparation for each sample is identified by the name. The order in which the exchange is carried out is given in the formula by metal from right to left. The source of Cs^+ is given by the salt used. Therefore, CsClCoCN-Y is a sample prepared by exchanging Co^{2+} into Na–Y, then Cs^+ (via CsCl) into Co–Y, followed by reaction of NaCN with CsClCo–Y.

Cobalt Cyanide Containing Zeolites. Dry Co–Y and CsCo–Y samples were allowed to react in a methanolic NaCN solution (CN:Co 10:1 minimum) at room temperature for 2–4 days. The resulting gray-blue solids labeled A–F in Table II were washed with copious amounts of methanol and dried at 60 °C in a vacuum oven. The Ni(CN)–Y samples were prepared in the same way, resulting in a yellow solid after drying.

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Table I. EPR Parameters for $Co(^{13}CN)_5^{3-}$

			^{59}Co		^{13}C	
	$g_\parallel$	$g_\perp$	$10^{-4}A_\parallel$, cm^{-1}	$10^{-4}A_\perp$, cm^{-1}	$10^{-4}A_\parallel$, cm^{-1}	$10^{-4}A_\perp$, cm^{-1}
$Co(CN)_5^{3-}$ in Cs–Y[a]	2.01	2.19	79	24		
$Co(CN)_5^{3-}$ in CH_3CN[b]	2.00	2.18	87	29		
$Co(^{13}CN)_5^{3-}$ in Cs–Y	2.01	2.19	79	24	37	32
$K_3Co(CN)_5$, powder[c]	2.004	2.175	82	24		
$K_3Co(^{13}CN)_5$, single crystal[c]					38	31
$Co(^{13}CN)_5^{3-}$ in MeOH[d]					39	

[a] From simulation of experimental spectrum. [b] Reference 13. [c] Reference 12. [d] Reference 22.

Table II. Active Cobalt Concentrations and K_{O_2} values for $Co(CN)_5^{3-}$ Samples inside Zeolite Y

sample	ID	$[Co]_t$, $\mu mol\ g^{-1}$		$p_{1/2}$ Torr	K_{O_2} $Torr^{-1}$
CsClCo(CN)–Y	A	38.1[a]	41.2[b]	0.24	4.13
CsClCo(CN)–Y	B	28.3	29.4	0.32	3.10
CsClCo(CN)–Y	C	48.5	48.3	0.25	3.95
CsOHCo(CN)–Y	D	18.7		0.32	3.12
Co(CN)Cs(Cl)–Y	E	4.39		1.56	0.64
CsClCo(CN)–Y	F	21.3	23.0	0.15	6.76
CsClCo(CN)–Y	G	42.8	45.0	0.06	17.8

[a] From $[CoO_2]$ vs $[CoO_2]/p_{O_2}$ least-squares fit. [b] From $[CoO_2]$ vs p_{O_2} curve(s).

Table III. Thermodynamic Parameters for Sample C

T, K	$10^{-3}T^{-1}$, K^{-1}	K_{O_2}, atm^{-1}	ln K_{O_2}	ΔH, kcal mol^{-1}	ΔG, kcal mol^{-1}	ΔS, cal mol^{-1} K^{-1}
283.0	3.53	3960	8.28	−8.3	−4.7	−13.0
298.5	3.50	2360	7.77		−4.6	−12.5
314.5	3.18	942	6.85		−4.3	−12.9
326.0	3.07	594	6.39		−4.1	−12.9

Sample G was prepared by addition of CsClCo–Y to a methanolic solution of NaCN and CsCl (CN^-:Co^{2+} ratio 10:1; Cs^+Cl^-:Na^+CN^- ratio 1:1). Oxygen was bubbled into the reaction mixture during the synthesis. The solid was filtered, washed with methanol, and dried overnight at 60 °C to yield a tan-yellow solid.

Spectral Measurements. All IR spectra were recorded as Nujol mulls using a Nicolet DXB FTIR spectrophotometer. X-band EPR spectra of powder samples were recorded using a Bruker ER200D-SRC spectrometer equipped with a variable-temperature unit. For removal or exclusion of oxygen from the EPR samples, tubes were fitted with o-ring connectors and attached to stopcocks, thus allowing connection to a vacuum line. EPR spectral simulations were calculated using the "QPOW" EPR simulation program.[7] Elemental analysis of dissolved samples were conducted using a Perkin-Elmer Plasma II emission spectrometer.

Elemental Analysis. Cobalt concentrations were determined by ICP analysis of the dissolved zeolite. A typical sample was dissolved as follows: A 0.1-g sample of the zeolite was refluxed in 15 mL of 2 M HCl. Next 10 mL of 6 M NaOH and 15 mL of 0.1 M Na_4EDTA were added, and the mixture was refluxed again. This treatment completely dissolved the solid. Analysis for nitrogen content was carried out by the Microanalysis Laboratory at the University of Florida. To ensure a constant weight during analysis for Co and N, the samples were allowed to equilibrate over H_2O in a closed chamber for several days prior to analysis. Water contents were calculated from the hydrogen content of the sample and the reported weight percents are corrected back to dry samples. CsClCo(CN)–Y was 1.6 wt % Co and CsOHCo(CN)–Y was 2.2 wt % Co. Both had a N:Co ratio of 3.

Absorption Measurements. The absorption isotherms were determined using a volumetric technique. A sample (3–5 g) was placed in a container of known volume and deoxygenated at 60 °C for 24 h. It was then exposed to a known volume of gas at a known pressure and temperature. From this the amount of gas absorbed by the sample was determined by pressure differences. Pressure measurements were made using a MKS Baratron with a 390A sensor head and 270B signal conditioning unit. Two sensor heads were attached via a MKS Type 274 channel selector to give a readable range of 10^{-5} to 1000 Torr. The temperature was monitored during each experiment and did not vary more than ±1 °C. The raw absorption data are contained in the accompanying microfilm addition. Making use of a least-squares fit of the data to eq 3 (see text), we obtained the equilibrium constant K_{O_2} at various temperatures. The values of ΔH, ΔG, and ΔS were determined through a van't Hoff plot. (See Table III.)

Results and Discussion

Characterization of CsClCo(CN)–Y. The EPR spectrum of CsClCo(CN)–Y exhibits a large, broad signal at $g = 2.0$, typical of a cobalt–oxygen adduct.[7b] (See Figure 1a.) A smaller signal at $g = 2.2$ is also present and is attributed to a small amount of deoxygenated cobalt complex. The presence of this deoxygenated complex is surprising considering that the cyanide reaction is carried out in air and may suggest that the pores are crowded or blocked due to the presence of Cs^+ or the formation of cobalt oxide.

The Co–O_2 adduct can be deoxygenated under vacuum, resulting in a decrease in the signal at $g = 2.0$ and an increase in the signal at $g = 2.2$. Figure 1b shows the EPR spectrum resulting from evacuation of this material for 15 min at room temperature. This spectrum shows the presence of both $Co(CN)_5^{3-}$ and $Co(CN)_5(O_2)^{3-}$. Complete deoxygenation of this material results after evacuation for 10 min at 100 °C, yielding a spectrum typical of low-spin cobalt(II), which is very similar to that of $Co(CN)_5^{3-}$ in acetonitrile. (See Figure 2b.) Dramatic color changes accompany the oxygenation and deoxygenation of this material. The deoxygenated sample is light blue in color. Upon exposure to oxygen, the color quickly changes to yellow/green. These color changes are reversible.

Low-spin five-coordinate cobalt(II) complexes have a single unpaired electron mainly in the d_{z^2} orbital which is involved in σ-bonding to the axial ligand. The bonding leads to direct delocalization of the unpaired electron onto the axial ligand.[8] If the axial cyanide is labeled with ^{13}C, ligand nuclear hyperfine coupling[9] is expected. When the synthesis of CsClCo(CN)–Y is repeated with $Na^{13}CN$, an entrapped $Co(^{13}CN)_5^{3-}$ is prepared. The EPR spectrum for this complex, shown in Figure 3, shows that each EPR component is split into two lines by coupling with the axial $^{13}CN^-$. Of the five coordinated, labeled cyanides, only the axial splitting is resolved. The unresolved equatorial cyanide splitting increases the line width.[9]

The carbon-13 hyperfine coupling constants, listed in Table I, provide estimates of the hybridization employed by the carbon of the axial cyanide in binding to cobalt. The isotropic ^{13}C coupling constant corresponds to a 2s orbital contribution of 0.033 and the anisotropic coupling corresponds to a carbon 2p orbital contribution of 0.049. The percent s character in the axial carbon σ donor orbital is 40%, which corresponds to a little more p character than an sp hybrid.

Unlike solution behavior, where exposure to oxygen results in irreversible μ-peroxo dimer formation,[6] $Co(CN)_5^{3-}$ prepared inside the zeolite is a monomer that can be reversibly oxygenated and deoxygenated. This behavior is also in sharp contrast to solid $[NH_4]_3[Co(CN)_5(O_2)]$ where oxygen can only be liberated by pyrolysis, resulting in decomposition of the complex.[10] In comparison to the sodium form of the zeolite which produced Co-

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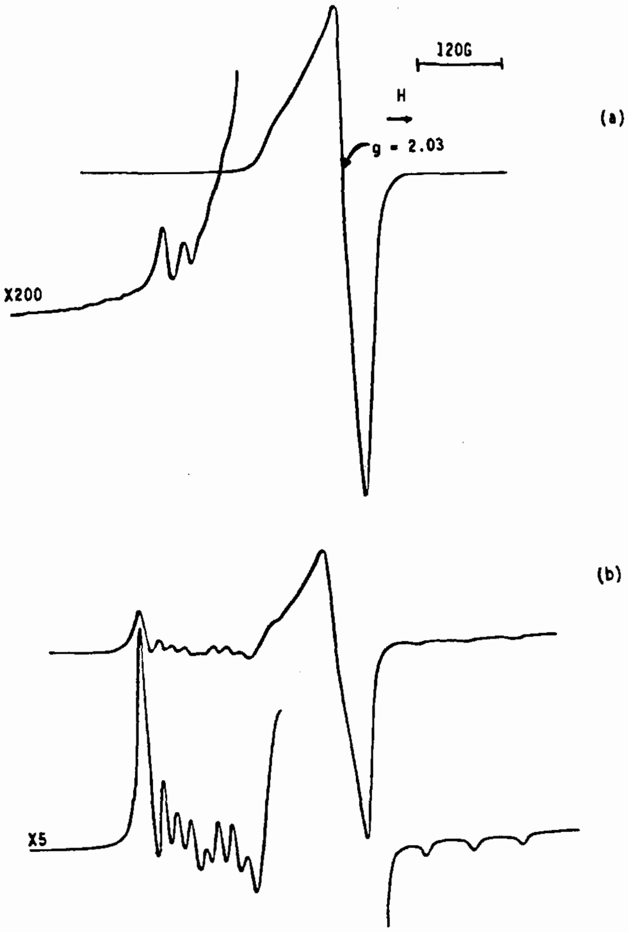

Figure 1. (a) Spectrum for $Co(CN)_5(O_2)^{3-}$ inside CsClCo(CN)-Y measured at 98 K. (b) EPR spectrum of CsClCo(CN)-Y measured at 98 K after evacuation for 15 min at 298 K.

$(CN)_4^{2-}$, the presence of cesium has led to the formation of $Co(CN)_5^{3-}$.

The C-N stretching region in the IR spectrum of the material prepared from CsClCo-Y shows a single, sharp band at 2120 cm^{-1} which shifts to 2127 cm^{-1} upon exposure to moisture. This band is unaffected by outgasing, and its intensity is not dependent on the concentration of active cobalt, suggesting that it is not due to the active complex. Wilmarth[11] reported the formation of $Ag_2[Co(CN)_5]$ and its ability to reversibly bind water, but its IR spectrum has not been reported.

Characterization of CsOHCo(CN)-Y. CsOHCo(CN)-Y is prepared by first extensively washing CoNaY with CsOH to form CsOHCo-Y. Elemental analysis shows that very little of the cobalt is removed during this CsOH exchange. After drying, CsOHCo-Y is reacted with a methanolic sodium cyanide solution to form the cobalt cyanide complexes. The EPR spectrum for CsOHCo(CN)-Y (sample D) is almost identical to that prepared from CsClCoY shown in Figure 1. The IR spectrum for the C-N stretching region of the resulting material is shown in Figure 4a. Assignment of these bands is complicated by the unknown influence of cesium and hydroxide on the ν_{CN} values and the possibility of hydroxide acting as a ligand. Outgasing of this material results in no change in the IR spectrum, suggesting that these bands are not due to the active complex but are rather from an oxidized species which is inactive. The presence of cesium has been shown[12] to shift the C-N stretching band of anionic complexes to higher energy leading to a ν_{CN} value for $Cs_2Li[Co(CN)_6]$ at 2142 cm^{-1}. Formation of a similar complex inside the zeolite

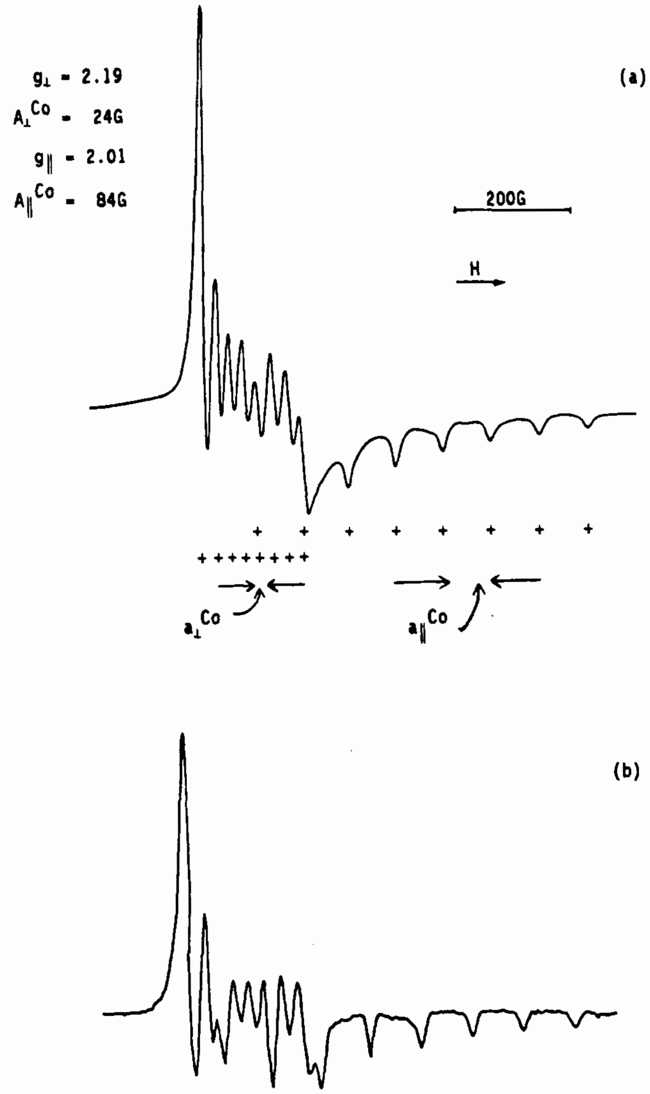

Figure 2. (a) EPR spectrum for $Co(CN)_5^{3-}$ inside CsClCo(CN)-Y measured at 98 K. (b) EPR spectrum for $Co(CN)_5^{3-}$ in a 5:1 CN/Co mixture in acetonitrile.[13]

may be the source of the band at 2138 cm^{-1}.

The elemental analysis of CsClCo(CN)-Y shows that 40-50% of the cobalt is removed during the CsCl exchange. Much less is removed with CsOH, suggesting that the formation of cobalt hydroxide keeps the cobalt from being washed out when CsOH is used. CsCo(CN)-Y samples prepared with CsCl and CsOH are both stable above 150 °C under vacuum; however, their O_2 affinity decreases when kept at elevated temperatures under oxygen. CsClCo(CN)-Y was shown to slowly react with O_2 irreversibility at 120 °C. After exposure to 1 atm of O_2 at 120 °C the samples oxygen affinity decreased to the point where it equaled the selectivity for Ar. This problem most likely arises from decomposition resulting from the increased mobility of the $Co(CN)_5^{3-}$ complexes at elevated temperatures.

Quantitative Gas Uptake Measurements. The presence of a trapped complex that reversibly binds oxygen in a zeolite has a significant influence on the gas uptake characteristics exhibiting a high selectivity for O_2 over N_2. The gas absorption properties of the CsClCo(CN)-Y materials were studied by volumetric gas uptake measurements.

Figure 5 shows the equilibrium absorption isotherms for N_2, O_2, and Ar obtained by Na-Y at 298 K. The enhanced affinity of Na-Y for N_2 over O_2 and Ar is due to the quadrupole interaction of the N_2 molecule with the ions present inside the framework.[13] Gases for which these interactions are minimal,

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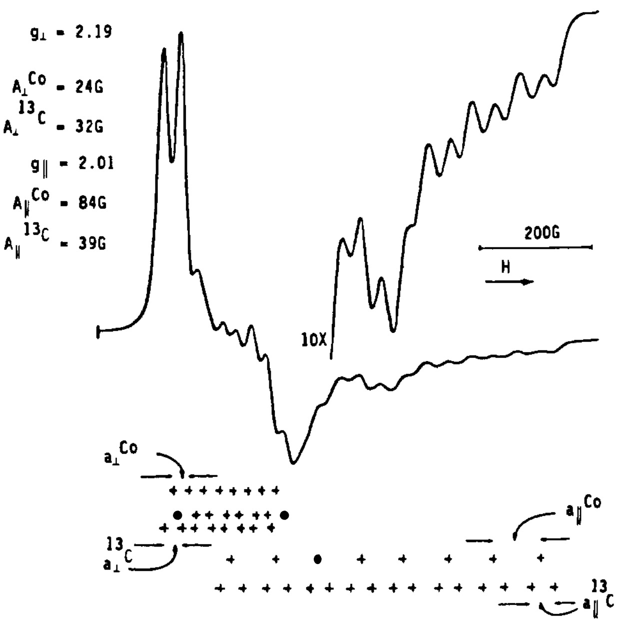

Figure 3. EPR spectrum for $Co(^{13}CN)_5^{3-}$ inside CsClCo(CN)–Y measured at 98 K.

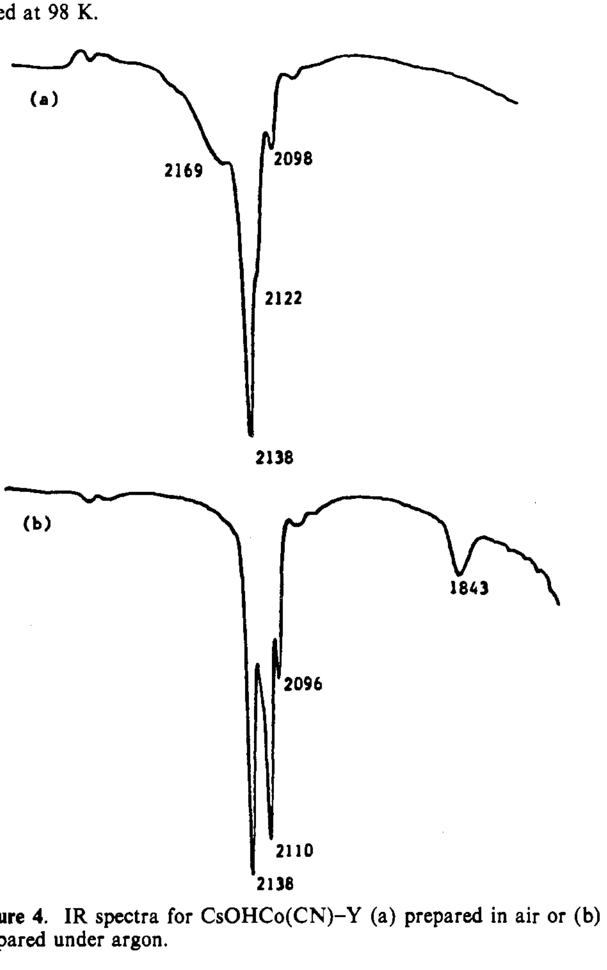

Figure 4. IR spectra for CsOHCo(CN)–Y (a) prepared in air or (b) prepared under argon.

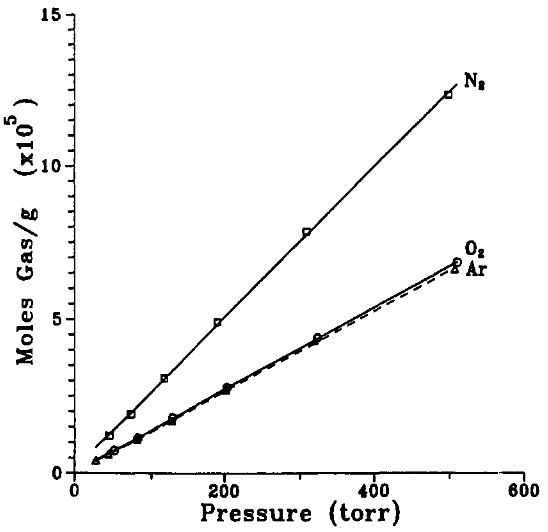

Figure 5. Gas absorption isotherms for Na–Y measured at 298 K.

such as O_2 and Ar, show very similar absorption isotherms. Consequently, Ar is used as the blank when trying to determine any increase in oxygen uptake resulting from the active, oxygen-binding complex.

Figure 6 shows the absorption isotherms for N_2, O_2, and Ar on CsClCo(CN)–Y, sample C. From these isotherms the concentration of active cobalt is calculated to be 48.4 μmol g^{-1}, which corresponds to 18% of the total cobalt present. This corresponds to a concentration of active complex that is significantly larger than that previously reported. The resulting material has a large affinity for oxygen and a high selectivity for O_2 over N_2 in a gas mixture. The separation factor, α_i, is a measure of this selectivity for gas i over gas j and is defined in eq 1. X_i and Y_i are the

$$\alpha_{i/j} = \frac{X_i/Y_i}{X_j/Y_j} \qquad (1)$$

equilibrium mole fraction of component i in the adsorbed and gas phases, respectively, and X_j and Y_j are corresponding quantities for j. As a first approximation, the pure-gas isotherms can be considered additive to yield the absorption isotherm for a mixture[14] allowing the separation factor to be calculated. If a mixture of O_2 and N_2, each at a partial pressure of 10 Torr, is exposed to 3.1 g of CsClCo(CN)–Y (sample C) in a 245-mL apparatus, the final partial pressures of O_2 and N_2 would be 0.57 and 9.7 Torr, respectively. This results in an α_{O_2/N_2} of 5022. However, as the partial pressure of oxygen increases, the separation factor decreases because the active complex is quickly saturated and oxygen absorption by the solid is no longer dominated by Co–O_2 adduct formation.

The observed equilibrium constant for the binding of O_2 to the active cobalt can be expressed as follows:

$$K_{O_2} = \frac{[CoO_2]}{[Co]p_{O_2}} \qquad (2)$$

Here $[CoO_2]$ is the concentration of complexed cobalt, [Co] is the concentration of active cobalt which remains uncomplexed at equilibrium, and p_{O_2} is the pressure of O_2 above the zeolite. Although the active cobalt complex is in the solid state, the [Co] and $[CoO_2]$ terms are still used in the equilibrium expression. These solid-state species in the zeolite are considered to be in a solid solution,[15a] with the zeolite functioning as the solvent in the formation of these transition-metal complexes. Since the total concentration of active cobalt, $[Co]_T$, is the sum of [Co] and $[CoO_2]$, we can write

$$K_{O_2} = \frac{[CoO_2]}{\{[Co]_T - [CoO_2]\}p_{O_2}} \qquad (3)$$

The difference between the oxygen and argon absorption isotherms at the same gas pressure above the zeolite, Figure 6, corresponds to the amount of CoO_2 formed at that pressure. Simultaneous equations corresponding to a series of measurements are solved for the two unknowns K_{O_2} and $[Co]_T$. The K_{O_2} determined is 4.0 ± 1.0 Torr^{-1}. As expected, this value is much larger

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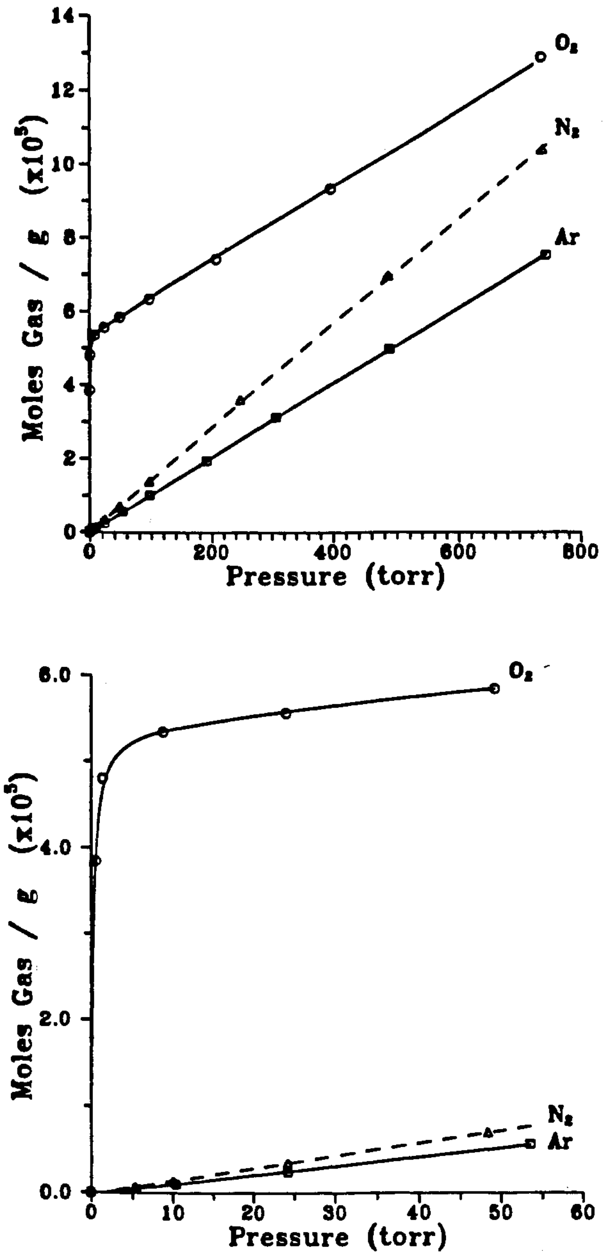

Figure 6. Gas absorption isotherms for CsClCo(CN)–Y measured at 298 K.

than that previously reported for NaCo(CN)–Y materials (0.12 ± 0.01 $Torr^{-1}$),[5b] where the active complex was shown to be a lattice-bound tetracyanocobalt complex. Gas uptake measurements on sample D show the concentration of $Co(CN)_5^{3-}$ to be 19 μmol g^{-1}. This corresponds to 4% of the total cobalt present and produces a K_{O_2} of 3.1 ± 0.8 $Torr^{-1}$. This equilibrium constant is within experimental error of the material prepared from CsClCo–Y (sample C). Equation 3 is plotted for CsClCo(CN)–Y in Figure 7.

Influence of Synthesis Variation on Uptake. The order of cesium addition is important in increasing the amount of the pentacyano complex formed in the zeolite. When Na–Y is exchanged first with CsCl and then $CoCl_2$, very little $Co(CN)_5^{3-}$ is formed. Gas uptake isotherms for O_2 and Ar on Co(CN)CsCl–Y (sample E) prepared in this way show that the concentration of active cobalt is only 4.4 μmol g^{-1}, much lower than when CsCl is added after the cobalt. The K_{O_2} value of 0.6 ± 0.1 is substantially lower than that of sample C. The EPR spectrum for this material shows the presence of both $Co(CN)_4^{2-}$ and $Co(CN)_5^{3-}$, with the pentacyano complex being present in the higher concentration.

The preparation of CsOHCo(CN)–Y from CsOHCo–Y was repeated under Ar in an attempt to increase the concentration of $Co(CN)_5^{3-}$. The IR spectrum of the resulting material is shown in Figure 4b. The C–N stretching bands seen in the previous sample are all present as well as new bands at 2110 and 1843 cm^{-1}. These new bands match those reported for $Cs_2Na[Co(CN)_5H]$[16] formed from the reaction of an aqueous solution of $Co(CN)_5^{3-}$ with hydrogen and CsCl. No other combination of cations (including Li^+, K^+, Rb^+, NH_4^+, NMe_4^+, NEt_4^+, NBu_4^+, NMe_3Cetyl^+, $MeNH_3^+$, $Me_2NH_2^+$, and NH_3OH^+) lead to the formation of this salt in water.[15b] The presence of $Co(CN)_5H^{3-}$ formed in the zeolite in the absence of hydrogen suggests that water plays a role in the oxidation of cobalt. The slow decomposition of $Co(CN)_5^{3-}$ in water has been shown[17] to occur as described in eq 4. The hydride has been detected by NMR in

$$2Co(CN)_5^{3-} + H\text{–}OH \rightarrow Co(CN)_5H^{3-} + Co(CN)_5OH^{3-} \quad (4)$$

an aqueous solution of cobalt cyanide.[18] This is the most likely source of $Cs_2Na[Co(CN)_5H]$ seen when the cyanide reaction is carried out under argon. In air the hydride species would not be expected because it quickly reacts with O_2 to form $Co(CN)_5OOH^{3-}$,[19] which decomposes to the hydroxide. In the presence of free cyanide, the next step in this reaction is the irreversible formation of the very stable hexacyano species,[17b] as shown in eq 5.

$$Co(CN)_5OH^{3-} + CN^- \rightarrow Co(CN)_6^{3-} + OH^- \quad (5)$$

The rates of these reactions in solution are accelerated as much as 60 times by the presence of alkali-metal cations, and cesium has been shown[20] to have the greatest effect. The cause of this increase is unknown, but its magnitude does not parallel the degree of hydration or the acidity of the metal ion.[18]

The oxidation of cobalt occurs through an intermolecular mechanism involving two cobalt centers.[11] In the zeolite this reaction is accelerated by the large concentration of cations present. Cesium must therefore act to shield the cobalt complexes from each other and slow the oxidation process. In doing so it leads to an increase in the amount of $Co(CN)_5^{3-}$ formed. Once the reaction is completed and the methanol solution is removed, the mobility of the complex is decreased, the excess CN^- is removed, and the complex is not oxidized.

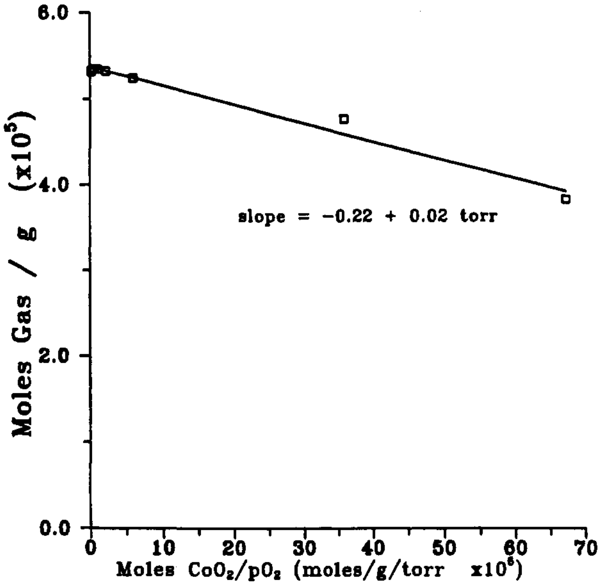

Figure 7. Plot of eq 3 for CsClCo(CN)–Y.

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The nature of the intermolecular interaction between cobalt centers is still in question. The formation of $(Co(CN)_5)_2^{6-}$ complexes in one large cavity seems unlikely since this would require a large molecule with a total charge of −6 to be accommodated. The presence of charge-balancing cations, beyond those needed to balance the framework charge, would also be needed and would further crowd the cavity. The size of the dimer molecules alone would push the limits of the zeolite cage, and this crowding would be worsened by the extra cations needed to balance the −6 charge. The absence of any experimental evidence for dimer formation in the presence or absence of O_2 also suggests that this does not occur. A more reasonable explanation is the interaction of two cobalt centers in separate large cavities through the interconnecting channels. This would allow the oxidation to readily occur in materials where the mobility of $Co(CN)_5^{3-}$ is unrestricted, as is the case in CoNa–Y. The presence of cesium sterically inhibits a portion of the cobalt centers from interacting and stabilizes $Co(CN)_5^{3-}$.

Preparation of CsClCo(CN)–Y (sample F) under Ar was also repeated. The IR spectrum for the resulting material was identical to that prepared in air. Gas uptake measurements, however, show that this material actually has more active cobalt when prepared in air. This suggests that oxygen does not hamper the formation of $Co(CN)_5^{3-}$ but may even aid in its formation. This most likely occurs because oxygen can occupy the sixth coordination site and prevent the reaction with water shown in eq 4. The K_{O_2} value for this material (sample F) is 6.8 ± 3.3 $Torr^{-1}$.

Sample G, prepared in the presence of O_2, further demonstrates that the formation of the cobalt–O_2 adduct increases the amount of the O_2-binding species in the synthesis. Pressure absorption data taken on this sample show the active cobalt concentration to be 43 ± 4 $\mu mol\ g^{-1}$, and a K_{O_2} of 18 ± 2 $Torr^{-1}$ is found.

Conclusions about CsCo(CN)–Y. The presence of cesium in Co–Y prior to the addition of cyanide stabilizes $Co(CN)_5^{3-}$ inside zeolite Y by inhibiting the oxidation of cobalt(II) to $Co(CN)_6^{3-}$. It was shown in the study of Co(CN)Na–Y that this oxidation is driven by a high CN:Co ratio and most likely occurs through an intermolecular reaction of two $Co(CN)_5^{3-}$ complexes with water. Due to its large size, cesium appears to shield $Co(CN)_5^{3-}$ complexes from each other and inhibits their oxidation. In our best synthesis, a K_{O_2} of 18 ± 2 $Torr^{-1}$ has been measured with an active cobalt concentration of 43 ± 4 $\mu mol\ g^{-1}$. The large affinity this complex has for O_2 results in a material which is highly selective for absorbing O_2. A separation factor above 5000 has been calculated for O_2 absorption from a mixture of O_2 and N_2.

Registry No. $CoCl_2$, 7646-79-9; CsCl, 7647-17-8; CsOH, 21351-79-1; NaCN, 143-33-9; O_2, 7782-44-7; $Co(CN)_5^{3-}$, 14971-18-7; $Co(CN)_5(O_2)^{3-}$, 45044-10-8.

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Two-Electron Reduction of Carbon Disulfide at a Triply Bonded Dirhenium(II) Center with Preservation of the Dimetal Unit

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The triply bonded dirhenium(II) complexes $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) and $Re_2Br_4(dpam)_2$ (dpam = $Ph_2AsCH_2AsPh_2$) react with CS_2 via a 2-electron redox process to afford the dirhenium(III) compounds $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$ (LL = dppm, dpam) which may be derivatized by reaction with $TlPF_6$ in the presence of various monodentate ligands L′ to give the salts $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-}LL)_2(L')]PF_6$, where L′ = CH_3CN, C_2H_5CN, 4-$CH_3C_6H_4CN$, *t*-BuNC, or xylylNC. A single-crystal X-ray structure analysis of $[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(\mu\text{-}dpam)_2(NCC_2H_5)]PF_6{\cdot}CH_2Cl_2$ (**1**) shows the Re-Re distance to be unexpectedly long (2.956 (2) Å), a value that is intermediate between those of the dirhenium(III) complexes $Re_2(\mu\text{-}Cl)_2Cl_4(dppe)_2$ (no Re–Re bond) and $Re_2(\mu\text{-}Cl)_2Cl_4(\mu\text{-}dppm)_2$ (Re–Re double bond). Crystal data for **1** at 20 °C: triclinic space group $P\bar{1}$, $a = 12.653$ (2) Å, $b = 16.901$ (7) Å, $c = 17.368$ (7) Å, $\alpha = 65.88$ (4)°, $\beta = 78.91$ (2)°, $\gamma = 72.12$ (3)°, $V = 3216$ (2) $Å^3$, and $Z = 2$. The structure was refined to $R = 0.062$ ($R_w = 0.073$) for 3786 data with $I > 3\sigma(I)$.

Introduction

One of the reaction pathways often encountered in the interaction of carbon disulfide with metal complexes[1] is its insertion into metal–hydride,[2] metal–halide,[3] metal–alkyl,[4] and metal–dialkylamido[5] ligand bonds. Redox reactions can also occur, and these include the reductive dimerization of CS_2 (in head-to-head or head-to-tail fashions)[6] as well as its reductive cleavage to give sulfido and carbon monosulfide fragments.[1,7–9] The latter reaction course proceeds via a CS_2 adduct and may or may not give a final product in which *both* S^{2-} and CS are incorporated into the *same* metal-containing species.[1,7–9] The latter features are quite well defined in mononuclear and polynuclear platinum chemistry. For example, one such reaction is the formation of $Pt_2Cl_2(\mu_2\text{-}\eta^2\text{-}CS_2)(\mu\text{-}dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) from $Pt_2Cl_2(\mu\text{-}dppm)_2$ and excess CS_2.[10] On the other hand, the reaction of the mononuclear complex $Pt(\eta^2\text{-}CS_2)(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ yields the diplatinum complex $(dppe)Pt(\mu\text{-}S)Pt(PPh_3)_2(CS)$ through the 2-electron reduction of CS_2.[11] The oxidative addition of CS_2 to trinuclear Pt clusters has also been reported,[9] although in some of these instances cluster degradation can occur.[12,13] We now report the first examples of the 2-electron reduction of CS_2 by a multiply bonded dimetal complex.[14] We find that the triply bonded dirhenium(II) complexes

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(14) The addition of CS_2 to the triply bonded dimolybdenum compounds $(\eta^5\text{-}C_5R_5)_2Mo_2(CO)_4$ (R = H, CH_3) has been reported to yield a η^2-CS_2 complex, but there is no evidence for an ensuing redox reaction; see: Brunner, H.; Meier, W.; Wachter, J. *J. Organomet. Chem.* **1981**, *210*, C23.

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