states. Indeed, the possible role of these excited states in reaction chemistry, such as excited state electron transfer and intermolecular C–H bond activation mechanisms, remains to be fully explored.

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Characterization of a Cobalt(II) Cyanide Complex inside Zeolite Y That Reversibly Binds Oxygen

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Abstract: We recently communicated the preparation of an anionic cobalt(II) cyanide complex inside zeolite Y that reversibly binds oxygen.[1] More complete characterization of this material is reported herein. Quantitative gas uptake measurements have shown this material to exhibit an enhanced adsorption of oxygen relative to its adsorption of argon. Enhanced oxygen adsorption was further demonstrated by comparison of zeolite Y containing an inert nickel cyanide complex to our active cobalt cyanide complex. This increase in oxygen uptake is due to the presence of an active cobalt complex. An equilibrium constant for the binding of oxygen to the active species was obtained from the oxygen and argon uptake isotherms. A similar result was obtained by measuring the intensity of the EPR signal for the Co–O$_2$ complex versus the oxygen pressure. The effect of the distribution coefficient for gas inside and outside the zeolite on the observed equilibrium constant is discussed. From the magnitude of the increased oxygen uptake, it is concluded that the active species is present in low concentration. This was confirmed by quantitative measurement of the EPR signal intensity for the oxygen adduct.

Cobalt complexes that reversibly bind dioxygen are available in a large variety of ligand systems.[2] The main drawback to the utilization of these materials in catalysis or oxygen enrichment from air arises from the fact that very few complexes bind oxygen in the solid state while in solution dimerization and irreversible oxidation of the complexes occur. Synthesizing these cobalt complexes inside the cage of a zeolite has the potential of eliminating these undesirable properties, and several zeolite-encapsulated metal complexes that reversibly bind dioxygen have been reported.[3] These compounds all involve neutral ligands, and though effective for separating oxygen from air, coordination of water as a sixth ligand or oxidation of the ligand limits their utility.[4] We have eliminated these problems by preparing an anionic cobalt cyanide complex within zeolite Y.[1] This complex is stable in the presence of water and can even be prepared in aqueous solutions. The cyanide ligand is very stable to oxidation and the zeolite prevents dimerization to form a μ-peroxo complex.

Experimental Section

Linde LZY-52 Na–Y zeolite was used as the starting material. It was slurried in 0.25 M NaCl solution, washed until no Cl$^-$ was present in the filtrate, and dried at 100 °C under vacuum (10^{-3} Torr) prior to use. Unless otherwise stated, all reactions were carried out without any precautions to exclude air or atmospheric moisture.

Preparation of Cobalt Cyanide Containing Zeolites. Co–Y samples were prepared by exchanging Na$^+$ ions for Co^{2+} ions in an aqueous solution of CoCl$_2$ at 70 °C. After exchange, the solids were washed with water until no Cl$^-$ was present in the filtrate. The resulting pink solids were dried at 150 °C under vacuum, yielding a deep blue solid. Ni–Y samples were prepared by using the same procedure. Co–Y(1) and Co–Y(2) contain 7.1 and 3.5 wt % cobalt, respectively. Ni–Y contains 3.4 wt % nickel.

Co(CN)–Y(1) and Co(CN)–Y(2) were prepared by reacting Co–Y(1) and Co–Y(2), respectively, with cyanide in a methanolic NaCN solution (CN:Co 10:1 minimum) at room temperature for 2–4 days. The resulting solids were washed with copious amounts of methanol and dried at 60 °C under vacuum. The resulting solids were gray–blue. The Ni(CN)–Y sample was prepared in the same way, resulting in a yellow solid after drying. Co(CN)–Y(3) was prepared from Co–Y(1) by using a much shorter reaction time and a minimum CN:Co ratio. Both Co(CN)–Y(1) and Co(CN)–Y(2) exhibit a single, sharp C–N stretching vibration at 2131 cm^{-1}. Co(CN)–Y(3) has an additional ν_{CN} at 2176 cm^{-1}. Ni(CN)–Y shows a single, sharp ν_{CN} at 2128 cm^{-1}.

Chelate treatment for removal of uncomplexed cobalt was carried out by stirring the samples with aqueous 0.1 M Na$_4$EDTA at 70 °C. The solids were then washed with water and dried at 60 °C under vacuum. The resulting solids are light yellow. This treatment also removes the ν_{CN} at 2176 cm^{-1} from Co(CN)–Y(3). The ν_{CN} at 2131 cm^{-1} remains unchanged.

Elemental Analysis. Cobalt concentrations were determined by ICP analysis of the dissolved zeolite. Typically, 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$_4$EDTA were added, and the mixture was refluxed to completely dissolve the solid. The solution was then diluted to 100 mL and analyzed by using ICP. 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$_2$O 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.

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IR and EPR Spectral Measurements. The IR spectra were obtained as Nujol mulls with a Nicolet DXB FTIR spectrophotometer. X-band (9.14 GHz) EPR spectra were recorded by using a Bruker ER 200D-SRC spectrometer. EPR spectral simulations were calculated by using the QPOW EPR simulation program.[5] Signal intensities were determined by numerical double integration of the first-derivative spectra. Spin concentrations were calculated by comparison with the integrated spectrum of $CuSO_4 \cdot 5H_2O$, and the uncertainty in the absolute value is estimated at 30%.

Gas-Uptake Measurements. The adsorption isotherms were determined by using a volumetric technique. A sample was placed in a container of known volume and exposed to a known volume of gas at a known pressure and temperature. From this the amount of gas adsorbed by the sample was determined by pressure differences. Pressure measurements were made by using an 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}–1000 Torr. The temperature was monitored during each experiment and did not vary more than ±1 °C.

Exclusion of Water and Oxygen. Schlenk techniques were used in an attempt to prepare samples in the absence of oxygen and water. Methanol used in this reaction was distilled from Mg turnings under nitrogen into activated 3A sieves. The argon used was passed through a NaOH column and an activated sieves column. The solution of NaCN in methanol was degassed by repeated evacuation and filling with dry argon. Co–Y(2) was dried at 400 °C under vacuum for several hours. The solid was cooled under vacuum and filled with dry argon. The NaCN solution was transferred into the flask under argon, and the mixture was allowed to stir under flowing, dry argon for 2 days. The solid was filtered under argon, washed with degassed methanol, and dried under vacuum at 60 °C. The resulting material showed the same IR and EPR spectra as seen in Co(CN)–Y(2).

Synthesis under Hydrogen. Co–Y(2) was reacted with a methanolic NaCN solution in a Parr pressure bottle under 50 psig hydrogen. The resulting solid showed the same IR and EPR spectra as did Co(CN)–Y(2).

Results and Discussion

Preparation of Co(CN)–Y Materials. We recently reported that cobalt(II) exchanged into zeolite Y reacts with cyanide solutions to form entrapped cobalt cyanide complexes[1] (CN/Co ratio of 4). This reaction is unique because it requires a negatively charged ligand to enter into a negatively charged framework and form an anionic complex. To our knowledge, all the previously reported transition-metal complexes synthesized inside a zeolite framework have been either cationic or neutral.[3,6] In our case, the driving force to overcome the charge repulsions between the ligand and framework is likely the large formation constant for the cobalt cyanide complexes. Cyanide does not enter the framework when stirred under our synthesis conditions with zeolites exchanged with group IA and IIA cations. Furthermore, cobalt cyanide complexes, such as $Co(CN)_5^{3-}$ and $Co(CN)_6^{3-}$ prepared in solution, do not enter into Na–Y under synthesis conditions.

Since charge balance inside the zeolite must be maintained during this reaction, a cation must also be incorporated into the zeolite when a cyanide enters. Elemental analysis of these Co(CN)–Y materials show that sodium ions are incorporated to maintain the balance of charge.

Solvent effects are important in the reaction of Co–Y with NaCN. When water (ϵ = 78.5, AN = 54.8) is the solvent, more than 80% of the cobalt is removed from the zeolite to form the cobalt cyanide complexes in solution. When, however, methanol (ϵ = 32.5, AN = 41.3) is the solvent, very little cobalt is lost from the zeolite during the reaction with cyanide. Formamide (ϵ = 109.5, AN = 39.8) gives results similar to methanol. When dimethyl sulfoxide (DMSO, ϵ = 46.6, AN = 19.3), *N*,*N*-dimethylformamide (DMF, ϵ = 37.8, AN = 16.0), and *N*,*N*-dimethylacetamide (DMA, ϵ = 37.8, AN = 13.6) are used as the reaction media, very little cobalt is lost during the cyanide reaction but very little cyanide is coordinated to the cobalt in the zeolite. The effectiveness of the solvent is dependent on its ability to solvate the cyanide ion and correlates well with the acceptor numbers, AN, listed for each solvent.[7] Water is good at solvating ions but extracts cobalt from the zeolite to form complexes in solution. The best solvent for the formation of cobalt cyanide complexes inside zeolite Y must have a balance between the ability to solvate cyanide and to extract cobalt.

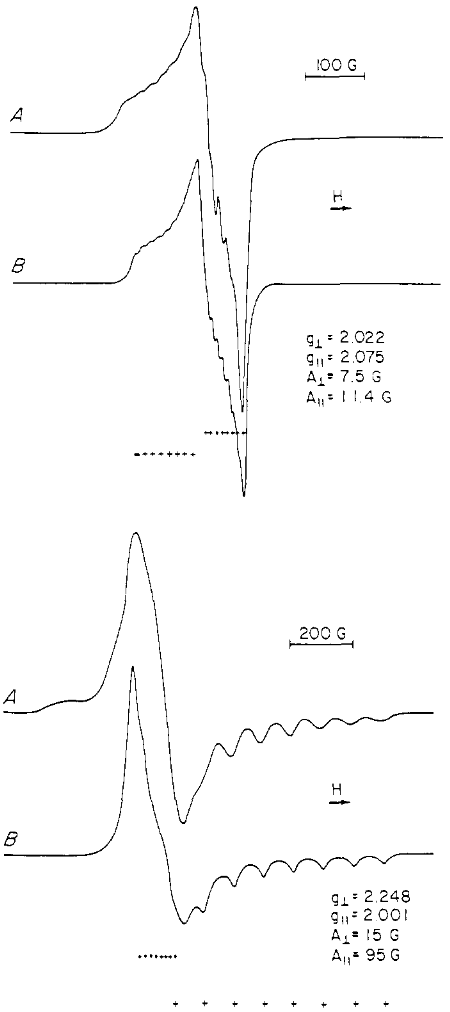

Figure 1. X-band EPR spectrum of $[Co(CN)_4(O_2)^{2-}]$–Y (above) and $[Co(CN)_4{}^{2-}]$–Y (below): (A) experimental; (B) simulated.[5]

Table I. IR Data for Cobalt Cyanide Complexes

compound	ν_{CN}, cm^{-1}
Co(CN)–Y	2131
$(Et_4N)_3Co(CN)_5$[a]	2080
$(Et_4N)_3Co(CN)_5(O_2)$[a]	2120
$(PNP)_3Co(CN)_5$[b]	2072
$(PNP)_2Co(CN)_4$[b]	2095
$Co(CN)_2$[c]	2138, 2172
$K_3Co(CN)_6$[b]	2131
$K_6[(CN)_5Co–Co(CN)_5]$[d]	2130 (m), 2100 (s), 2073 (vs)
$K_6[(CN)_5Co–O_2–Co(CN)_5]$[e]	2146, 2132, 2125, 2120

[a] Reference 11. [b] Reference 12a. [c] Prepared by: *Inorg. Synth. 3*, 225. [d] Reference 8a. [e] Reference 8b.

IR and EPR Characterization of Co(CN)–Y. The IR spectrum of the Co(CN)–Y material exhibits a C–N stretching vibration, ν_{CN}, at 2131 cm^{-1}. Table I lists IR data for complexes prepared here as well as for several known metal cyanide complexes. These results suggest that the major species formed in the zeolite is $Co(CN)_6^{3-}$; however, the zeolite lattice may influence the fre-

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[5] The EPR simulations were done with the QPOW EPR simulation program copyrighted by R. L. Belford.

[6] (a) Scherzer, J.; Fort, D. *J. Catal.* **1981**, *71*, 111. (b) Lunsford, J. H. Molecular Sieves—II. *ACS Symp. Ser.* **1977**, *40*, 473. (c) Lunsford, J. H. *Rev. Inorg. Chem.* **1987**, *9*, 1. (d) Klier, K. *Langmuir* **1988**, *4*, 136.

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Table II. Selected EPR Parameters

IIA: Co–O_2 adducts	g_z	g_y	g_x	a_z, G	a_y, G	a_x, G
$Co(CN)_4(O_2)$–Y	2.075	2.022		11.4	7.5	
$(Et_4N)_3Co(CN)_5(O_2)^a$ (solid)	2.02–2.03					
$(Et_4N)_3Co(CN)_5(O_2)^a$ (acetone)	2.02			10.5		
$Co(CN)_5(O_2)^{3-c}$ (water)	2.007			9.8		
$Co(NH_3)_5(O_2)$–Y^d	2.084	2.010	2.000	17.8	12.0	12.5
$Co(en)_2(O_2)$–Y^b	2.084	1.998	1.992	20	10	13
Co(SALEN)(O_2)–Y^f	2.078	2.020	2.020	21.0	11.3	11.3
Co(bpy)(terpy)(O_2)–Y^e	2.063	2.007	1.998	15.6	11.0	11.0

IIB: nonadducts	$g_\perp$	$g_\parallel$	$a_\perp$, G	$a_\parallel$, G
$Co(CN)_4$–Y	2.248	2.001	15	95
$Co(CN)_5^{3-h}$	2.157	1.992	28	87
$Co(CN)_5^{3-c}$	2.20	2.00		
$Co(CN)_5^{3-a}$	2.18	2.00	29	87
$Co(CN)_3(NCH_3)^{-a}$	2.28	2.00	14	112
$Co(CNCH_3)_6$–Y^g	2.087	2.000	72	68
$Co(CNCH_3)_5$–Y^g	2.163	2.003	32	89
Co(bpy)(terpy)–Y^e	2.250	2.012	15	101

[a] Reference 11. [b] Reference 3a. [c] Reference 16. [d] Reference 3b. [e] Reference 3d. [f] Reference 3e. [g] Reference 17. [h] Reference 10.

quency, and other complexes with similar ν_{CN} may be masked by this large peak. The species formed are not cobalt dimers or oxygen bridged dimers, both of which have multiple cyanide stretching frequencies.[8]

The EPR spectrum of the Co(CN)-Y material consists of a broad signal near $g = 2$ (see Figure 1). The EPR parameters (Table IIA) are characteristic of a wide variety of low-spin Co–O_2 adducts, including several cationic and neutral adducts that have been synthesized in zeolite Y.[3] Hyperfine splitting resulting from ^{59}Co ($S = {}^7/_2$) is small, as predicted by the spin-pairing model for Co–O_2 adducts in which the unpaired electron resides predominately on the dioxygen molecule.[3a,9] The spin-pairing model of binding dioxygen to a low-spin cobalt(II) can be viewed as a free-radical reaction in which the lone unpaired electron on cobalt(II) combines with one of the π^* electrons of the dioxygen molecule to form a σ bond. The other π^* electron remains unpaired and resides essentially on the oxygen with cobalt hyperfine splitting arising from spin polarization of the cobalt–oxygen σ bond.[9]

This model allows an interpretation of the EPR parameters that produce the cobalt(II) contribution to the σ-bonding molecular orbital, α'^2_{Co-O}:

$$\alpha'^2_{Co-O} = \frac{[A_{aniso}(CoO_2) + 1.0 \times 10^{-4}\ cm^{-1}]}{2.44 \times 10^{-3}\ cm^{-1}}$$

The partial negative charge on the bound O_2 is referred to as the extent of electron transfer from cobalt(II), ET, and is given by the formula

$$ET = 2(1 - \alpha'^2) - 1$$

Such an analysis produces an electron transfer value of 0.7 e^- for the cyano complex trapped in the zeolite.

The spin concentrations for the Co–O_2 adduct in Co(CN)-Y(1) and Co(CN)-Y(2) are 4.8×10^{18} and 1.8×10^{18} spins/g, respectively. These correspond to less than 1% of the total cobalt present.

The Co–O_2 adduct can be deoxygenated under vacuum yielding a species with an EPR spectrum that is quite different from that of the original Co–O_2 adduct (see Figure 1). The much larger ^{59}Co hyperfine coupling and reversal in magnitude of $g_\parallel$ and $g_\perp$ indicates that the unpaired electron density is located mostly in the d_{z^2} orbital of the cobalt(II) ion[10] (see Table IIB). The g values are close to those of the four-coordinate complex formed in a 3:1 mixture of CN^- to Co^{2+} in acetonitrile solvent.[11] The relatively large anisotropy in the g tensors supports the contention that the complex is not $Co(CN)_5{}^{3-}$ but rather square-planar $Co(CN)_4{}^{2-}$ with axial coordination positions occupied by zeolite framework oxygens.

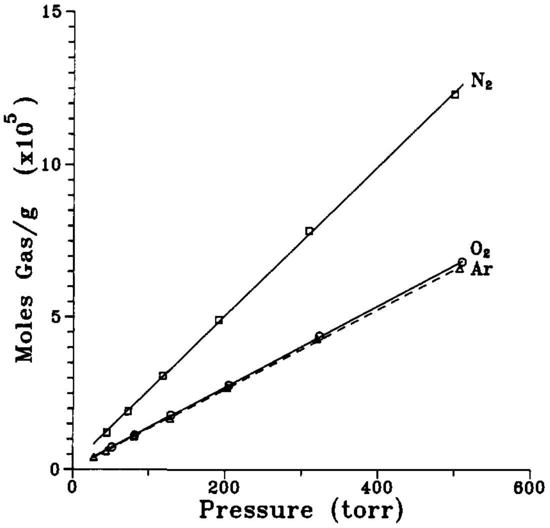

Figure 2. Gas adsorption isotherms for Na-Y measured at 298 K: —, □ nitrogen; —, ○ oxygen; ---, △, argon.

The IR spectrum for square-planar $(PNP)_2[Co(CN)_4]$ (PNP = bis(triphenylphosphine)nitrogen(+)) cation is reported to contain a ν_{CN} at 2096 cm^{-1}, but the oxygen adduct of this square-planar complex has not been reported.[12] By assuming the same shift upon oxygenation as seen when $Co(CN)_5{}^{3-}$ (2080 cm^{-1}) forms $Co(CN)_5(O_2)^{3-}$ (2120 cm^{-1}),[11] we can estimate ν_{CN} for $Co(CN)_4(O_2)^{2-}$ to be about 2136 cm^{-1}. The ν_{CN} frequency for metal cyanide complexes is reported to increase as the oxidation state of the metal increases,[13] and this increase due to the formation of the oxygen adducts is consistent with the removal of electron density for cobalt(II) when the oxygen binds.[9] Due to the low concentration of the O_2 adduct and the presence of the intense ν_{CN} (2131 cm^{-1}) for $Co(CN)_6{}^{3-}$ in the sample, the ν_{CN} for the $Co(CN)_4(O_2)^{2-}$ is not observed.

Stability of the Active Complex. The active species appears very stable to repeated cycling experiments in the presence of

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(13) Nakamoto, K.; *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley: New York, 1970; p 178.

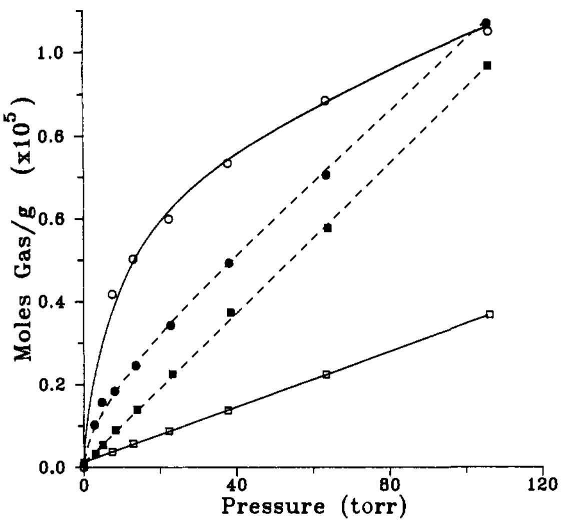

Figure 3. Comparison of O_2 and Ar gas adsorption isotherms for Co(CN)–Y materials: —, ○ Co(CN)–Y(1), O_2; —, □, Co(CN)–Y(1), Ar; ---, ● Co(CN)–Y(2), O_2; ---, ■ Co(CN)–Y(2), Ar.

atmospheric levels of moisture. A sample of Co(CN)–Y(1) was alternately oxygenated (atmospheric oxygen) and deoxygenated at room temperature through 510 cycles over a 6-week period without losing its oxygen absorption capacity. Analysis by EPR performed at the end of the experiment indicated that no decomposition had occurred.

Quantitative Gas-Uptake Measurements. The gas adsorption properties of these Co(CN)–Y materials were studied by volumetric gas-uptake measurements. Figure 2 shows the equilibrium adsorption isotherms for N_2, O_2, and Ar obtained for 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.[14] Gases for which these interactions are minimal, such as O_2 and Ar, show very similar adsorption 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 3 shows the adsorption isotherms for O_2 and Ar on Co(CN)–Y(1) and Co(CN)–Y(2). From this we see that at 100 Torr, more than twice as much O_2 is adsorbed as Ar on Co(CN)–Y(1). This increase in O_2 uptake relative to Ar is attributed to the presence of the active oxygen-binding complex. A similar increase for O_2 over Ar uptake is shown for Co(CN)–Y(2); however, it is not as large as in the Co(CN)–Y(1) sample due to the lower concentration of active complex in the former. The decreased uptake of Ar for Co(CN)–Y(1) and Co(CN)–Y(2) compared with Na–Y is due to the presence of $Co(CN)_6^{3-}$. This species, which occupies space in the zeolite, decreases the pore volume available for gas absorption.[15]

A second approach that demonstrates an increased uptake of O_2 in the Co(CN)–Y material involves a comparison of its adsorption isotherm with that of a Ni(CN)–Y material that has the same metal concentration. Square-planar nickel cyanide is inert to oxygen. As shown in Figure 4, the Ni(CN)–Y adsorbs the same amount of O_2 as it does Ar and the same amount of Ar as Co(CN)–Y(2). When, however, the adsorption isotherm for O_2 in Ni(CN)–Y is compared with that of Co(CN)–Y(2), increased O_2 uptake is clearly established.

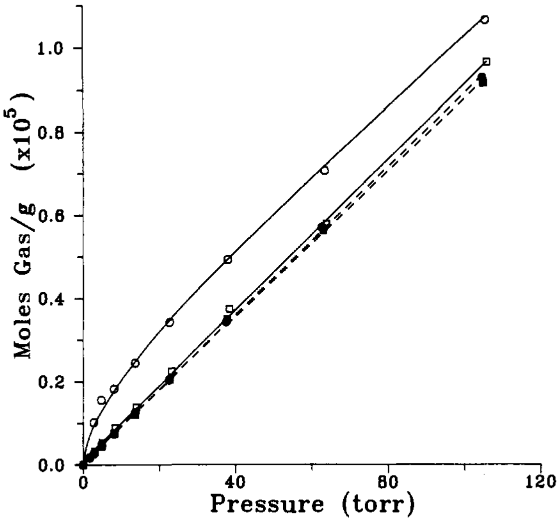

Figure 4. Comparison of Co(CN)–Y and Ni(CN)–Y gas adsorption isotherms: ---, ● Ni(CN)–Y, O_2; ---, ■ Ni(CN)–Y, Ar; —, ○ Co(CN)–Y, O_2; —, □ Co(CN)–Y, Ar.

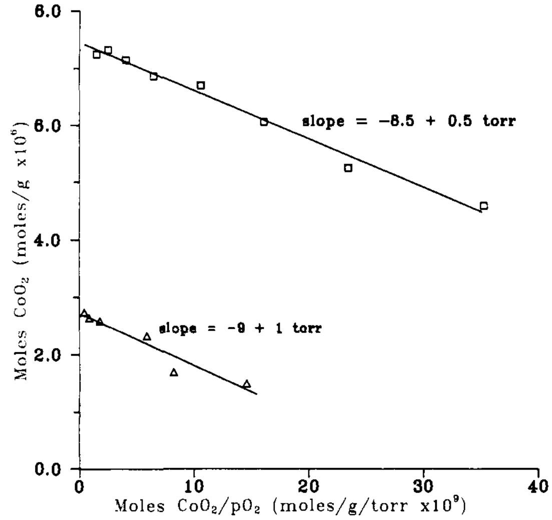

Figure 5. Plot of eq 2 for Co(CN)–Y(1), □, determined from gas-uptake data and Co(CN)–Y(2), △, determined from EPR data.

Equilibrium Constant for Oxygen Binding. The observed equilibrium constant for the binding of O_2 to the active cobalt can be expressed as follows:

$$K_{obs} = [CoO_2]/[Co]p(O_2) \qquad (1)$$

where $[CoO_2]$ 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. Since the total concentration of active cobalt, $[Co]_T$, is the sum of [Co] and $[CoO_2]$, eq 1 can be rearranged to give

$$[CoO_2] = [Co]_T - K_{obs}^{-1}[CoO_2]/p(O_2) \qquad (2)$$

The volume for each concentration term is the same; therefore, a plot of the amount of CoO_2 formed at $p(O_2)$ divided by $p(O_2)$ versus the amount of CoO_2 yields a straight line, assuming K_{obs} is constant. The equation of this line gives K_{obs} and the amount of active cobalt present.

The amount of CoO_2 formed at a known pressure above the zeolite can be determined from the data shown in Figure 3. The difference between the oxygen and argon adsorption isotherms at the same gas pressure above the zeolite corresponds to the amount of CoO_2 formed at that pressure. The same information can be obtained by determining the amount of CoO_2 formed at

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(14) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974.

(15) An estimate of the pore volume for the Co(CN)–Y materials can be made by comparing the adsorption isotherms for an inert gas such as argon for Na–Y and Co(CN)–Y. The pore volume for Na–Y is reported to be 6700 Å (4.0 L/mol).[14] Assuming that both Na–Y and Co(CN)–Y have the same affinity for argon and the amount of Ar adsorbed is determined only by the available pore volume, a comparison of the Ar adsorption isotherms for Na–Y with Co(CN)–Y(1) and Co(CN)–Y(2) give pore volumes of 1.1 and 2.5 L/mol, respectively.

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Table III. $P_{1/2}$ Values for Co–O_2 Adducts

complex	$P_{1/2}$, Torr
Co(CN)–Y	9 ± 1
CoSALEN·py^{2+} in Na–Y[a]	306
CoSALEN^{2+} in pyridine[a]	10.5
CoSALEN^{2+} in DMSO[b]	333
Co(3-FSALEN)$^{2+}$ solid[c]	2
Co(terpy)(bpy)$^{2+}$ in Na–Y[b]	0.59
Co(terpy)(bpy)$^{2+}$ in Li–Y[c]	0.34

[a] Reference 3e. [b] Reference 3d. [c] Reference 4.

a pressure of O_2 above the zeolite by using the intensity of its EPR signal.

Figure 5 shows a plot of eq 2 for Co(CN)–Y(1) and Co(CN)–Y(2). The slopes of these lines are −8.5 ± 0.5 and −9 ± 1 Torr, respectively, and indicate the active species in both materials have the same observed equilibrium constant for binding oxygen, K_{obs}, of 0.12 ± 0.01 Torr^{-1}.

If plots of eq 2 are extended to lower pressures, K_{obs} appears to change significantly. This can be explained by the fact that at lower pressures the distribution coefficient, K_d, for gas inside versus outside the zeolite increases significantly (eq 3 and 4). This

$$[O_2]_{out} \overset{K_d}{=} [O_2]_{in} \tag{3}$$

$$K_d = [O_2]_{in}/[O_2]_{out} \tag{4}$$

phenomenon is known as the sieving effect. Equation 5 can be used to relate K_{obs} to the true K_{eq} and K_d:

$$K_{obs} = K_d K_{eq} \tag{5}$$

From eq 5 it is seen that when K_d increases, K_{obs} increases and the magnitude of the slope in Figure 5 will decrease. This sieving effect has been described as the ability of the zeolite to "pump" oxygen to the complex, and results comparable to ours are observed at lower pressures.[3e] The distribution coefficient for Ar on Co(CN)–Y(1) and Co(CN)–Y(2) at 25 °C was determined to be 10 ± 1 for pressures of gas above the zeolite greater than 8 Torr. The K_d for O_2 and Ar are the same for Na–Y and Ni(CN)–Y and determined to be 8 ± 1 for Na–Y and 10 ± 1 for Ni(CN)–Y.

If the concentration of oxygen inside the zeolite, $[O_2]_{in}$, is substituted for $p(O_2)$ in eq 2, K_{obs} becomes K_{eq}, and the influence of K_d on the measured equilibrium constant is corrected. The amount of argon absorbed by Co(CN)–Y at a designated pressure can be assumed to be the amount of uncomplexed oxygen present in the zeolite at that pressure during oxygen absorption. A plot of eq 2 can be made with $[O_2]_{in}$ replacing $p(O_2)$ to produce a K_{eq} of 240 ± 10 M^{-1}. Converting the K_{obs} in units of Torr^{-1} (Figure 5) to molarity^{-1} gives a value for K_{obs} of 2200 ± 100 M^{-1}. With $K_d = 10$ and eq 5, we see that a value of $K_{eq} = 220$ M^{-1} results.

It can be seen from this study that the sieving effect of zeolites will make the complete removal of O_2 from the active cobalt more difficult than that expected from the K_{obs} measured at near atmospheric pressures.

Table III summarizes the $P_{1/2}$ values for several cobalt(II) complexes inside zeolites and in solution. Consistent with the spin-pairing model,[9] the $P_{1/2}$ value for the complex reported here is less than that reported for CoSALEN·py (SALEN = *N*,*N*′-bis(salicylidene)ethylenediamine, py = pyridine) prepared in Na–Y.[3e] The cyanide ligands produce a stronger ligand field than SALEN, raising the energy of the d_{z^2} orbital containing the unpaired electron. The higher the d_{z^2} energy, the more energy gained when the complex forms a Co–O_2 bond and this electron drops down into the σ-bonding orbital. This results in a lower $P_{1/2}$ value.

Comparing the active complex in Co(CN)–Y with Co(terpy)(bpy)–Y[3d,4] (bpy = bipyridine, terpy = terpyridine) we see that our complex has a larger $P_{1/2}$ value, indicating a weaker overall ligand field. The active cyanide species is a low-spin $Co(CN)_4^{2-}$ ion with the axial position occupied by a lattice oxygen, as suggested by the EPR parameters. In the case of Co(terpy)(bpy)–Y, the axial position is occupied by the stronger nitrogen donor ligand. The weaker axial base in our material results in a lower energy d_{z^2} orbital and a correspondingly larger $P_{1/2}$. This is consistent with our conclusion that the active species is not $Co(CN)_5^{3-}$, which would give a much smaller $P_{1/2}$ due to the stronger axial ligand. The dramatic influence of the axial base can be seen in comparing CoSALEN^{2+} in solution with pyridine ($P_{1/2}$ = 10.5 Torr) and DMSO ($P_{1/2}$ = 333 Torr) as the axial ligands.[3(e)]

Table IV. Elemental Analysis for Co(CN)–Y Materials

	Co content		N content		
material	wt %	per unit cell	wt %	per unit cell	N/Co
Co(CN)–Y(1)	5.9	15	4.5	48	3.2
CT–Co(CN)–Y(1)[a]	4.2	11	4.4	48	4.4
Co(CN)–Y(2)	3.1	7.6	3.0	30	4.1
CT–Co(CN)–Y(2)[a]	2.4	5.8	3.0	31	5.2
Co(CN)–Y(3)	5.9	15	3.2	33	2.3
CT–Co(CN)–Y(3)[a]	2.5	6.1	2.9	30	4.9

[a] CT prefix indicates results after chelate treatment.

Elemental Analysis Data for Co(CN)–Y. Table IV lists the elemental analyses for the Co(CN)–Y materials prepared here. If the major species formed is $Co(CN)_6^{3-}$, then a N/Co ratio of 6 is expected. We see from the low N/Co ratios that even after extended reaction times with cyanide there is still uncomplexed cobalt present. This is not surprising in Co(CN)–Y(1) since each large cavity (eight large cavities per unit cell zeolite Y) contains one $Co(CN)_6^{3-}$ complex, leaving no room for further complex formation.

In an attempt to remove this uncomplexed cobalt, the Co(CN)–Y samples were treated with a chelating reagent (aqueous Na_4EDTA). When Co–Y samples are treated with this chelate solution, all the cobalt is removed from the zeolite and exchanged for Na$^+$. When, however, a Co(CN)–Y sample is given the same treatment, only part of the cobalt is removed. For Co(CN)–Y(1) and Co(CN)–Y(2) the N content and IR spectrum for the major complex remain unchanged by this treatment. This removal of uncomplexed cobalt results in an increase in the N/Co ratio approaching, in some cases, a value of 6. In the case of Co(CN)–Y(3) the chelate treatment removes the lower coordinate species responsible for the CN band at 2176 cm^{-1} but leaves the major $Co(CN)_6^{3-}$ species with CN at 2131 cm^{-1}. We also note a corresponding decrease in the nitrogen content due to the removal of this lower coordinate species.

As further proof that the major species formed is indeed a Co^{3+} complex, the Co(CN)–Y materials were reacted with several oxidizing reagents (H_2O_2, $Na_2S_2O_8$, and NaOCl). This resulted in no change in color or ν_{CN} for the material, suggesting the major complex is $Co(CN)_6^{3-}$.

Varying Synthesis Conditions. Many reactions of Co–Y with cyanide were carried out in the absence of oxygen. Samples of Co–Y were evacuated (10^{-2} Torr) and filled with argon for several cycles. Even at very low cobalt concentrations (<0.5 wt %) and short reaction times (1 h) the major complex formed in the absence of O_2 but in the presence of the excess cyanide needed to drive the reaction to completion is $Co(CN)_6^{3-}$. This suggests that water plays a role in the oxidation of the cobalt(II) in this system.

In several attempts water has also been excluded from the reaction. Even when Co–Y samples were dried at 400 °C and the reaction was carried out in dry methanol under flowing, dry argon, no increase in the concentration of the active complex is obtained as shown by IR and EPR.

Attempts were made to prepare the cobalt cyanide complexes in a reducing environment to retard the oxidation process. When the cyanide reaction was carried out in the presence of reducing agents such as sodium borohydride or hydrazine, the major species formed was still $Co(CN)_6^{3-}$. In other attempts Na–Y was prewashed with a reducing agent and kept under inert atmosphere during the cobalt exchange and cyanide reaction. Again only the oxidized species was seen in the IR spectrum. Since reactions of $Co(CN)_5^{3-}$ with H_2 are known to form hydride species in solution, the Co–Y/cyanide reaction was carried out under H_2. When Co–Y was stirred with a NaCN/methanol solution under

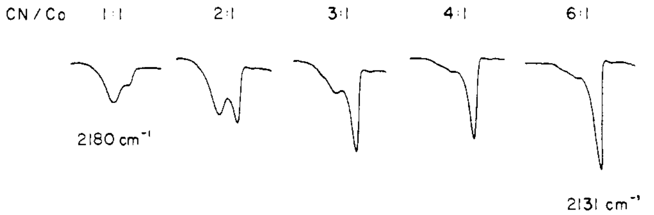

Figure 6. IR spectra for Co(CN)–Y samples prepared by varying the CN^-/Co ratio during preparation.

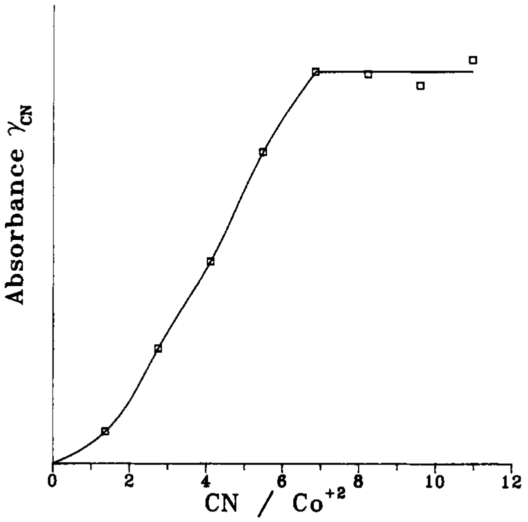

Figure 7. Plot of CN/Co ratio used during preparation of Co(CN)–Y versus the intensity of the ν_{CN} absorbance at 2131 cm^{-1}.

50 psig H_2, no new ν_{CN} bands were seen in the IR spectrum for the resulting material.

Up to this point no reaction conditions that inhibit oxidation of the cobalt and increase the concentration of the active cobalt species have been found.

Titration of Co-Y with Cyanide. Stuhl and co-workers have reported the formation of several cobalt cyanide complexes in solution by varying the CN/Co ratio during preparation.[12] Figure 6 shows selected IR spectra of samples prepared here by reacting the same Co–Y material with solutions containing different cyanide concentrations. These spectra show the initial formation of a lower coordinated species with a ν_{CN} at 2180 cm^{-1}. This lower coordinate species is formed in low concentration, is EPR silent, and is believed to be the neutral $Co(CN)_2$. As the concentration of cyanide increases, this species is converted to $Co(CN)_6^{3-}$. Figure 7 shows that the intensity of the ν_{CN} band for $Co(CN)_6^{3-}$ increases steadily as the concentration of cyanide increases until the CN/Co ratio exceeds 6. Above this valve the absorbance remains constant, indicating no more complex formation.

Conclusion

We believe the major species formed in the reaction of Co–Y with cyanide is the $Co(CN)_6^{3-}$ ion, which shows a characteristic ν_{CN} at 2131 cm^{-1}. At high cobalt loading a complex can be formed in every large cavity. This species seems to form even under conditions that exclude oxygen and minimize water. At short reaction times and low CN:Co ratios, a lower coordinate species believed to be $Co(CN)_2$ also forms. This species can be removed by EDTA treatment.

The most interesting species formed in this reaction is a low-spin cobalt(II) complex capable of reversibly binding oxygen. This species represents less than 1% of the total cobalt present. The EPR parameters and equilibrium constant for oxygen binding suggest that this active complex is a square-planar $Co(CN)_4^{2-}$ ion that is coordinated to the zeolite framework through a lattice oxygen. This species is stable to repeated cycling in air. Even in such low concentrations, this species increased the amount of oxygen absorbed by 100% over the amount of argon at 100 Torr. Attempts to increase the concentration of the active species are under investigation.

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Registry No. O_2, 7782-44-7; Ar, 7440-37-1; $Co(CO)_6^{3-}$, 14897-04-2.