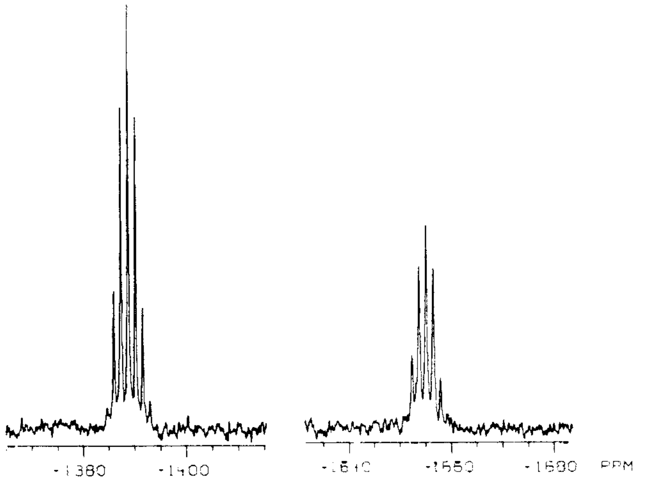

Figure 1. ^{49}Ti and ^{47}Ti NMR spectrum of a 0.05 M solution of 99% ^{13}C enriched $[K(2.2.2)]_2[Ti(^{13}CO)_6]$ in $CH_3CN:CD_3CN$ = 10:1 at 23 °C: ^{49}Ti (δ −1389, $J_{^{49}Ti-^{13}C}$ = 23 Hz), ^{47}Ti (δ −1655, $J_{^{47}Ti-^{13}C}$ = 23 Hz).

of $TiCl_4(DME)$ and 6 equiv of $KC_{10}H_8$ were mixed, stirred for 5 h while warming to room temperature under argon, and then filtered. To the resulting red-brown solution, containing presently uncharacterized intermediate(s), was added 4 equiv of 15-C-5, and stirring was resumed for 2 h. The solution was then cooled to −60 °C, argon was removed by evacuation, and ≥99.9% carbon monoxide was introduced at near atmospheric pressure. After stirring for 40 h at −60 °C a bright red slurry had formed. This was filtered, and the resulting solid was washed with DME, dried in vacuo, and recrystallized from acetonitrile–DME. A 38% yield (3.2 g) of deep red and thermally robust crystalline product (dec 180–182 °C) was isolated. This material provided satisfactory analyses (C, H, K, Ti) for the composition $[K(15\text{-}C\text{-}5)_2]_2[Ti(CO)_6]$ (**2**).[7] Product **2** was also obtained from $Ti(CO)_3(dmpe)_2$ in 56% yield as a pure substance. This procedure is summarized in Scheme II.

Spectroscopic properties of **1** and **2** in acetonitrile are consistent with the presence of discrete octahedral $Ti(CO)_6^{2-}$ units. For example, a single intense ν(CO) band at 1745–1750 cm^{-1} is observed in the infrared region which is reasonable for a dianionic mononuclear binary carbonyl of this symmetry.[8] A single ^{13}C resonance is found at δ 245.8 ppm which compares well with previously reported ^{13}C resonance positions of carbonylmetallate dianions (e.g., $HV(CO)_5^{2-}$, δ 250.3[9] and $W(CO)_5^{2-}$, δ 247.4 ppm[6]). The very narrow ^{49,47}Ti NMR resonances observed for **1** [δ −1388 ($W_{1/2}$ = 3 Hz), −1654 ($W_{1/2}$ = 7 Hz) ppm, respectively] and **2** [δ −1386 ($W_{1/2}$ = 5 Hz), −1652 ($W_{1/2}$ = 12 Hz) ppm, respectively] indicate the presence of relatively unperturbed cubic or octahedral titanium species.[10] By comparison our attempts to observe the ^{49,47}Ti NMR resonances of the much less symmetrical $(C_5H_5)_2Ti(CO)_2$ were unsuccessful. The only other carbonyl of titanium examined for which a Ti NMR spectrum could be obtained was $[Et_4N][C_5H_5Ti(CO)_4]$[11] which exhibited much broader ^{49}Ti and ^{47}Ti resonances at −1269 ($W_{1/2}$ = 93 Hz) and −1536 ($W_{1/2}$ = 224 Hz) ppm, respectively, due to the lower symmetry of $C_5H_5Ti(CO)_4^-$ relative to that of $Ti(CO)_6^{2-}$.[12] Proof for the formulation of $Ti(CO)_6^{2-}$ has been obtained by the ^{49,47}Ti NMR spectrum of 99% ^{13}C enriched $Ti(^{13}CO)_6^{2-}$ as the $K(2.2.2)^+$ salt.[13] Figure 1 shows the binominal septet of the ^{49}Ti resonance (δ −1389, $J_{^{49}Ti-^{13}C}$ = 23 Hz) due to coupling of six equivalent carbonyl groups to the central titanium and five bands of the expected seven band multiplet of the corresponding ^{47}Ti resonance (δ −1655, $J_{^{47}Ti-^{13}C}$ = 23 Hz). Significantly, there have been no previous reports of resolved ^{49,47}Ti–^{13}C coupling for any organotitanium species. The spectrum in Figure 1 qualitatively resembles that reported for TiF_6^{2-}.[14]

In summary, the first binary carbonyl anion of titanium, $Ti(CO)_6^{2-}$, has been synthesized by two independent methods, isolated, and fully characterized by multinuclear NMR spectroscopy. The importance of employing crown ethers and related alkali metal complexants in the synthesis of certain early transition metal carbonyl anions has been established for the first time.[15] This discovery may prove to be extremely important for future efforts in this emerging area of synthetic chemistry.

Acknowledgment. This research was supported by the National Science Foundation (CHE 85-06710) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(8) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(9) Warnock, G. F. P.; Philson, S. B.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1984**, 893.

(10) (a) Dechter, J. J. *Prog. Inorg. Chem.* **1984**, *32*, 393. (b) Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861.

(11) Kelsey, B. A.; Ellis, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 1344.

(12) Ti NMR spectra were obtained at 23 °C on a Nicolet WB-300 NMR spectrometer at 16.9 MHz; samples were referenced to ^{49}Ti in neat $TiCl_4$ (δ 0.00) and were sealed under argon as 0.05 M solutions in 10:1 V:V mixtures of $CH_3CN:CD_3CN$ or 1:1 $Me_2SO\text{–}Me_2SO\text{-}d_6$ for $C_5H_5Ti(CO)_4^-$ in 12-mm tubes.

(13) Prepared in 95% yield (unrecrystallized) from the reductive carbonylation of $Ti(^{13}CO)_3(dmpe)_2$ (ref 5b) under ^{13}CO: IR in CH_3CN (ν(CO), cm^{-1}) 1710; $^{13}C\{^1H\}$ NMR (CD_3CN) δ 245.8 (s and satellites due to ^{49,47}Ti–^{13}C coupling, J = 23 Hz); ^{49,47}Ti NMR, see Figure 1. Noteworthy is the ^{13}C isotope effect on the ^{49,47}Ti resonance positions of nearly 1 ppm. Similar isotope effects have been observed previously in the ^{51}V NMR spectra of $V(^{12}CO)_6^-$ and $V(^{13}CO)_6^-$: Ihmels, K.; Rehder, D.; Pank, V. *Inorg. Chim. Acta* **1985**, *96*, L69. See, also: ref 9.

(14) Hao, N.; Sayer, B. G.; Denes, G.; Bickley, D. G.; Detellier, C.; McGlinchey, M. J. *J. Magn. Reson.* **1982**, *50*, 50.

(15) Stabilization of unusual anions in metal salts by crown ethers and cryptands has been recognized for many years. Two spectacular examples include the electride, $[Cs(18\text{-}crown\text{-}6)_2]^+e^-$, and the sodide, $[K(2.2.2)]^+Na^-$: Dye, J. L. *Sci. Am.* **1987**, *257(3)*, 66. Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 329.

Entrapment of an Anionic, Stable, Moisture-Resistant Oxygen Carrier in Zeolite Y

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Cobalt(II)–cyanide complexes, such as $Co(CN)_5^{3-}$, are known to bind dioxygen and function as homogeneous catalysts.[1] We have succeeded in preparing an anionic cobalt(II)–cyanide complex within the large cavity of zeolite Y. The species present is a low-spin $Co(CN)_4^{2-}$ ion and is probably coordinated to the zeolite framework through a lattice oxygen. The complex combines reversibly with dioxygen, forming a six-coordinate monoadduct, with the zeolite cage inhibiting the formation of the μ-peroxo dimer. This feature, and the stability of the cyanide ligand to oxidation, has resulted in a reversible oxygen carrier that is thermally stable to oxidation at temperatures as high as 250 °C. Both IR and EPR spectroscopy have been used to characterize this material. To our knowledge, this represents the first case in which a large, negative ion has been synthesized within a zeolite cavity,[2] opening the possibility for preparing a whole new class of trapped anionic complexes.

Several Co^{II}–Y zeolites with cobalt contents ranging from 2 to 19 cobalts per mole of zeolite were prepared from Linde LZY-52 zeolite with conventional ion exchange methods. A sample of the Co^{II}–Y zeolite, dried at 160 °C under vacuum (10^{-3} Torr), is stirred for a minimum of 24 h at room temperature in

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(1) Kwiatek, K. *Catal. Rev.* **1967**, *1*, 37.

(2) Scherzer, J.; Fort, D. *J. Catal.* **1981**, *71*, 111.

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Table I. Selected EPR Parameters

(A) Co–O_2 Adducts

	g_z	g_y	g_x	a_z	a_y	a_x
$Co(CN)_4(O_2)$–Y	2.075	2.022		11.4	7.5	
$Co(CN)_5(O_2)^{3-}$[a] (water)	2.007	isotropic		9.8		
$Co(NH_3)_5(O_2)$–Y[b]	2.084	2.010	2.000	17.8	12.0	12.5
$Co(en)_2(O_2)$–Y[c]	2.084	1.998	1.992	20	10	13
$Co(SALEN)(O_2)$–Y[d]	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

(B) Non-Adducts

	$g_\perp$	$g_\parallel$	$a_\perp$	$a_\parallel$
$Co(CN)_4$–Y	2.248	2.001	15	95
$Co(CN)_5^{3-}$[f]	2.18	2.00	29	87
$Co(CN)_3(NCCH_3)^-$[f]	2 28	2.00		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 17. [b] Reference 11c. [c] Reference 11a. [d] Reference 11e. [e] Reference 11d. [f] Reference 6. [g] Reference 15. [h] Reference 16.

a methanolic sodium cyanide solution containing a ten to one ratio of CN^-/Co.[3] The zeolite sample containing the Co–O_2 adduct is collected and dried at 60 °C under vacuum. Elemental analysis for Co and N has shown a N/Co ratio of 3.8.[4] At cobalt concentrations less than 8 cobalts per mole of zeolite (i.e., one cobalt per large cavity) very little cobalt loss is detected during preparation.

The IR spectrum of the Co–O_2 adduct contains a C–N stretching vibration, ν_{CN}, at 2131 cm^{-1}.[5] This peak decreases in intensity as the sample is deoxygenated and a new peak appears at 2096 cm^{-1}. The new peak disappears when the sample is exposed to dioxygen. A similar decrease in ν_{CN} is observed in the IR spectrum of $Co(CN)_5(O_2)^{3-}$ (2120 cm^{-1}) and $Co(CN)_5^{3-}$ (2080 cm^{-1}).[6] The increase in frequency for the O_2 adduct results from the removal of electron density from the cobalt(II) when oxygen binds. The ν_{CN} frequency is reported to increase in metal cyanide complexes as the oxidation state of the metal increases or as the number of cyanide ions coordinated decreases.[7,8] The value we observed for ν_{CN}, 2096 cm^{-1}, is much closer to that of the $Co(CN)_4^{2-}$ ion in $(PNP)_2Co(CN)_4$ (2095 cm^{-1})[9] than to that of the well-characterized $Co(CN)_5^{3-}$ ion (2080 cm^{-1}).[6,7,9]

The EPR spectrum of the Co–O_2 adduct at 77 K consists of a broad signal near $g = 2$[10] (Figure 1). The EPR parameters are similar to those of a wide variety of low-spin Co–O_2 adducts, including several cationic and neutral adducts in zeolite Y[11] (Table IA). The hyperfine splitting resulting from ^{59}Co ($S = {}^7/_2$) is small, as expected for Co–O_2 adducts in which the unpaired electron density resides predominantely on the dioxygen molecule.[11a,12]

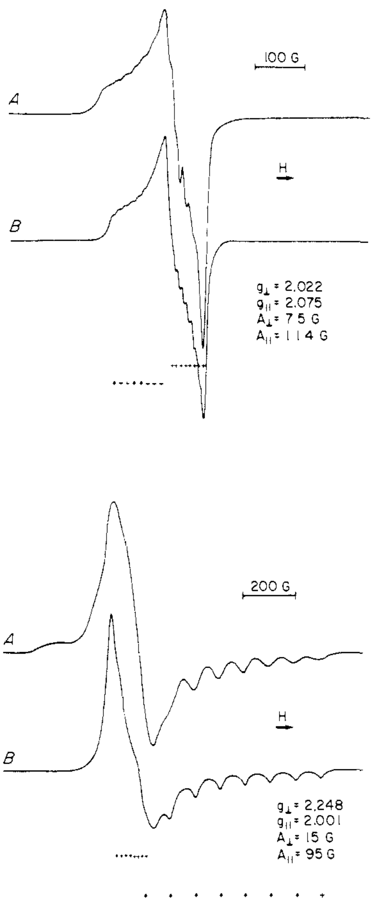

Figure 1. X-Band EPR spectrum of $[Co(CN)_4(O_2)^{2-}]$–Y (above) and $[Co(CN)^{2-}{}_4]$–Y (below) [(A) experimental and (B) simulated[16]].

The EPR spectrum of a deoxygenated sample is quite different from that of the O_2 adduct[13] (Figure 1). The much larger ^{59}Co hyperfine coupling indicates that the unpaired electron density is located mostly in the d_{z^2} orbital of the cobalt(II) ion.[14] Our values for $g_\perp$ and $g_\parallel$ differ significantly from those of 5-coordinate cobalt(II) complexes reported in solution[6,14] and inside zeolite cages.[15] They are much closer to those of the 4-coordinate complex formed in a 3:1 mixture of CN^- to Co^{2+} in acetonitrile[6] (Table IB). 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 the axial position probably occupied by a zeolite framework oxygen.

A sample of $Co(CN)_4^{2-}$–Y zeolite was alternately oxygenated (atmospheric oxygen) and partially deoxygenated (at 10^{-3} Torr) at room temperature through 510 cycles over a 6-week period without change. Analysis by EPR and IR spectroscopy performed at the end of the experiment indicated that no chemical decomposition had occurred. The recycling ability, thermal stability, and resistance to moisture make this material a unique oxygen carrier. At present we are undertaking a quantitative study of the dioxygen absorption process.

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(3) (a) This procedure has been used to prepare cyanide complexes with Mn^{II}–Y, Fe^{II}–Y, Co^{II}–Y, Ni^{II}–Y, Cu^{I}–Y, and Zn^{II}–Y. In addition, metal cyanide complexes have been prepared with zeolite A and zeolite X. (b) Drago, R. S.; Bresinska, I. U.S. Patent filed 2/20/87.

(4) Cobalt concentrations were determined by ICP analysis of the dissolved zeolite. Nitrogen concentrations were determined by Galbraith Laboratories, Inc., Knoxville, TN.

(5) The IR spectra were obtained as Nujol mulls with a Nicolet 5DXB FTIR spectrophotometer. A very weak peak which is sometimes observed near 2180 cm^{-1} probably arises from a complex having a low CN/Co ratio.

(6) White, D. A.; Solodar, A. J.; Baizer, M. M. *Inorg. Chem.* **1972**, *11*, 2160.

(7) Carter, S. J.; Foxman, B. M.; Stuhl, L. S. *Inorg. Chem.* **1986**, *25*, 2888.

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

(9) Carter, S. J.; Foxman, B. M.; Stuhl, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 4265.

(10) X-Band EPR spectra were recorded at 77 K on a Brucker ER 200D-SRC spectrometer.

(11) (a) Howe, R. F.; Lunsford, J. H. *J. Phys. Chem.* **1975**, *79*, 1836. (b) Vansant, E. F.; Lunsford, J. H. *Adv. Chem. Ser.* **1973**, *121*, 441. (c) Howe, R. F.; Lunsford, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 5156. (d) Mizuno, K.; Imamura, S.; Lunsford, J. H. *Inorg. Chem.* **1984**, *23*, 3510. (e) Herron, N. *Inorg. Chem.* **1986**, *25*, 4714.

(12) Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353.

(13) This sample contained 5.9% cobalt with a N/Co ratio of 3.8. It was deoxygenated by heating at 100 °C for 3 days under a vacuum less than 10^{-4} Torr.

(14) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1967**, *89*, 3356.

(15) Lunsford, J. H.; Vansant, E. F. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 1028.

(16) The EPR simulations were done with the "QPOW" EPR Simulation Program copyrighted by R. L. Belford.

(17) Bayston, J. H.; Looney, F. D.; Winfield, M. E. *Aust. J. Chem.* **1963**, *16*, 557.