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Tetrabutylammonium Tetracyanocobaltate(II) Dioxygen Carriers

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The second example of a low-spin, square-planar Co(II)L_4 species (L = unidentate ligand), $(Bu_4N)_2Co(CN)_4$ (**1**), and a new family of tetrabutylammonium tetracyanocobaltate(II) complexes have been isolated and characterized. All of the solid compounds react reversibly with dioxygen to form 1:1 cobalt(III)−superoxo complexes. Since a variety of neutral bases react readily with **1** and the complexes can be obtained as solids, the effects of different axial bases on the dioxygen-binding behavior of the solids could also be studied. Interestingly, reversible phase changes occur on oxygenation/deoxygenation for $(Bu_4N)_2[Co(CN)_4{\cdot}C_5H_5N]$ (**2**) and $[(Bu_4N)_2Co(CN)_4]_2{\cdot}(C_{10}H_8N_2)$ (**3**). Presumably this happens because the crystal lattices of the unoxygenated materials do not contain enough room for the dioxygen. Complex **2** crystallizes in the orthorhombic space group *Pbcm* with the following cell parameters at 25 °C: $a = 9.024(3)$ Å, $b = 21.886(8)$ Å, $c = 23.184(6)$ Å, $V = 4578.6(27)$ Å^3, and $Z = 4$. From the molecular packing, it is apparent that the $[Co(CN)_4{\cdot}C_5H_5N]^{2-}$ anions are aligned parallel to the *a* axis, with the pyridine of each anionic unit pointing toward the vacant site on the cobalt of the adjacent anion. The tetrabutylammonium cations completely surround the anions, forming hydrophobic casings that also run parallel to the *a* axis. Thus, it is clear that the bulky tetrabutylammonium cations are capable of separating the cobalt centers so that μ-peroxo dimers cannot form.

Introduction

Considerable work has been devoted to the study of the reversible reactions of dioxygen with transition metal complexes because such complexes can be used to model biological systems and have the potential to be used in separating dioxygen from other gases or liquids.[1] A stable, solid state O_2-binding material containing a high concentration of active cobalt sites could be attractive as a sorbent for air separation applications.[1d] We describe here a new class of solid complexes that reversibly bind O_2 and approach these desirable properties. They have the general formula $(Bu_4N)_2Co(CN)_4{\cdot}B$, where B represents a neutral axial base.

In order for a solid compound to reversibly bind O_2, it must be stable to oxygenation/deoxygenation and it must have the appropriate amount of electron density on the cobalt center. It has been known for some time that, if two metal centers are able to form a μ-peroxo dimer complex, irreversible oxidation may occur; therefore, a common approach to designing stable materials has been to try to separate the cobalt centers from one another. Many researchers have attempted to do this, and the most stable complexes have been obtained through the use of clever ligand design in cobalt(II) systems. These successful approaches include anchoring the cobalt complex to a solid support through one of its ligands,[2] encapsulating the cobalt complex inside the cage of a zeolite,[3] and using sterically encumbered ligand systems such as the “picket fence” porphyrins[4] and “lacunar” Schiff bases.[5] Unfortunately, the most robust complexes that have been made are not very practical for air separation because these materials either have low O_2-binding capacities, in the case of supported or encapsulated species, or difficult ligand syntheses, as in the case of sterically encumbered ligands.

Recent work in our laboratories has shown that $Li_3[Co(CN)_5]{\cdot}2DMF$ (DMF is *N,N′*-dimethylformamide) is stable to repeated oxygenation/deoxygenation and has the appropriate cobalt electron density to react reversibly with dioxygen.[6] The structure of $Li_3[Co(CN)_5]{\cdot}2DMF$ shows it to be a polymeric lithium cyanocobaltate(II) complex: Co−C≡N−Li(DMF) bridges form an infinite three-dimensional network in which the cobalt sites are effectively separated from one another and fixed in the coordination polymer. This is the first instance in which cations have been used to separate the cobalt centers in a solid state reversibly O_2-binding complex. In this particular cyanocobaltate complex, the concentration of active cobalt centers remains high and no ligand syntheses are required. Ramprasad *et al.* have hypothesized that reversible oxygen binding occurs in the lithium pentacyanocobaltate(II) systems because the lithium cations act as Lewis acids toward the cyanide ligands, removing electron density from the cobalt center and weakening the Co−O_2 interaction.

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The concept that five cyanide ligands provide so much electron density to cobalt that oxygen binding is irreversible, but that removing some of that electron density enables reversible oxygen binding to occur, suggested to us that tetracyanocobaltate(II) complexes might also reversibly bind oxygen without requiring the use of Lewis acid cations. This would allow a wider variety of cations and axial bases to be used in the tetracyanocobaltate(II) systems.

Solid state compositions of the formula $(R_4N)_3Co(CN)_5$ were successfully isolated by White *et al.*,[7] and their structures were studied by Brown and Raymond.[8] Although the cobalt centers are effectively separated by the bulky cations in these monomeric complexes, the compounds do not reversibly bind O_2 (*vide supra*). In contrast, we have been able to use the bulky, noncoordinating tetrabutylammonium cations to prepare stable tetracyanocobaltate(II) complexes which do reversibly bind O_2. The cobalt centers in these complexes are isolated from one another because of the packing arrangement of the monomeric cyanocobaltate units in the salt lattice. Relative to $(R_4N)_3Co(CN)_5$, less electron density resides on cobalt, allowing these solids to reversibly bind O_2. We were also able to study the effects of different axial ligands on the O_2 affinity of these complexes. Many studies have been done to probe the effects of different axial bases on reversible O_2 binding and the electron density on cobalt using *solutions* of O_2 complexes.[9] This is the first time that these effects have been seen in a series of solid state complexes.

Results and Discussion

Earlier $[Co(CN)_4]^{2-}$ Systems. Prior to this study, only three tetracyanocobaltate(II) complexes had been isolated in the solid state: monomeric $(PNP)_2Co(CN)_4{\cdot}4DMF$ and $(PNP)_2Co(CN)_4$[10] (PNP is the bis(triphenylphosphine)nitrogen(1+)) and polymeric $K_2Co(CN)_4$.[11] None of the complexes had been reported to react with O_2, but $(PNP)_2Co(CN)_4$ was described as "air-sensitive". Solvent-free $(PNP)_2Co(CN)_4$ was also the first known example of a low-spin, square-planar Co(II)L$_4$ species (L = unidentate ligand). The solution spectroscopic studies that Carter *et al.* performed using $[CN^-]/[Co]$ ratios of 4:1 indicate that the $[Co(CN)_4]^{2-}$ anion becomes involved in a dynamic equilibrium when coordinating solvents are used:[10,12]

$$[Co(CN)_2(S)_2] \rightleftharpoons [Co(CN)_3S]^- \rightleftharpoons [Co(CN)_4]^{2-} \rightleftharpoons [Co(CN)_5]^{3-}$$

Because the presence of several species in solution makes it difficult or impossible to isolate pure $[Co(CN)_4]^{2-}$ complexes, the paucity of well-characterized solid state $[Co(CN)_4]^{2-}$ complexes was understandable.

The $(PNP)_2Co(CN)_4$ complex was prepared by the literature method.[10] Thermal gravimetric analysis studies demonstrated that $(PNP)_2Co(CN)_4$ gained weight under an oxygen-containing atmosphere at 30 °C and lost weight under nitrogen at 80 °C over several cycles. A large $(PNP)^+$ peak at 1115 cm^{-1} with a shoulder at 1074 cm^{-1} masked the region in which cobalt(III)–superoxo oxygen stretches should occur, and the nature of oxygen binding in this material was not established. However, this initial result suggested that a solid state monomeric $[Co(CN)_4]^{2-}$ complex might be able to reversibly bind O_2. The inconvenience of preparing (PNP)CN[13] prompted us to investigate synthesizing tetracyanocobaltate(II) complexes from other cyanide salts containing bulky cations.

$(Bu_4N)_2Co(CN)_4$ System. Carter *et al.* also studied the infrared spectra of acetonitrile and DMF solutions containing $CoCl_2$ and 4 equiv of $(Bu_4N)CN$.[10] Five cyanide bands between 2112 and 2015 cm^{-1} were observed in the IR spectrum of the acetonitrile solution, but only two cyanide stretches at 2099 (s) and 2082 (m) cm^{-1} were seen in the IR spectrum of the DMF solution. These results, as well as our own, suggested that disproportionation of the tetracyanocobaltate(II) anion occurred in acetonitrile, but that the $[Co(CN)_4]^{2-}$ species was more stable in DMF. When cobalt(II) concentrations of ~0.3 M were used, $(Bu_4N)_2Co(CN)_4$ (**1**) could be isolated as a solid from DMF solutions by adding diethyl ether as a nonsolvent. A simpler and cleaner synthesis of **1** was achieved by using tetrahydrofuran (THF) as the solvent, because compound **1** precipitated from the THF solution as a white, microcrystalline solid while the $(Bu_4N)Cl$ remained in solution.

The infrared data for compound **1** indicate that it is a monomeric $[Co(CN)_4]^{2-}$ complex, since only terminal cyanide groups are observed (ν_{CN} = 2114 (sh), 2095 (s), 2072 (sh), and 2056 (w) cm^{-1}),[14] and there is no evidence for solvent in the infrared spectrum. Visible and near-infrared spectra of **1** in dichloromethane show bands at 607 (35) and 1153 (68) nm (ϵ). Very little data are available on the electronic spectra of square-planar cobalt(II) complexes. Bands at 563 (28), 594 (50), and 1095 (12) nm (ϵ) have been reported for $(PNP)_2Co(CN)_4$ in dichloromethane,[10b] and spectra of low-spin Co–N$_2$O$_2$ complexes such as *N*,*N'*-bis(salicylidene)ethylenediaminato(2−)-cobalt(II) have been found to contain characteristic bands at approximately 500 nm (strong but broad) and 1100–1200 nm (relatively narrow but weaker).[15]

Literature precedent suggests that a square-pyramidal arrangement, in which the d_{z^2} orbital is raised in energy above the d_{xy} orbital to yield the configuration $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^1$, is required for cobalt(II) complexes to react readily with dioxygen.[1] Thus, four-coordinate cobalt(II) complexes bind dioxygen very poorly, but addition of an axial base to these systems results in compounds that easily bind dioxygen at ambient pressures of the gas. We were surprised to find that, although **1** is a low-spin, square-planar complex and contains no solvent that could serve as an axial ligand, it is still capable of reversibly binding dioxygen at ambient temperature. In 80 min under an O_2-containing atmosphere, compound **1** picks up 31.4 cm^3/g of oxygen (91% of the stoichiometric amount for a 1:1 Co–O$_2$ complex), but the material loses only 56% of the oxygen on purging with nitrogen for 240 min at 30 °C.

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(14) $(PNP)_2Co(CN)_4$ has cyanide stretches at 2100 (sh, s) and 2095 (s) cm^{-1} (terminal cyanides)[10], and $K_2Co(CN)_4$ is reported to have cyanide bands at 2100 and 2080 cm^{-1} (terminal cyanides) and 2170 and 2122 cm^{-1} (bridging cyanides).[11]

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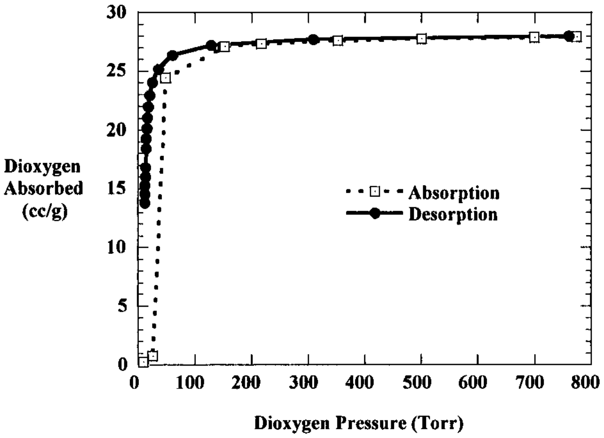

Figure 1. Dioxygen absorption and desorption isotherms of $(Bu_4N)_2Co(CN)_4\cdot$(pyridine) (**2**).

Although some irreversible oxygenation occurs, **1** is able to reversibly bind dioxygen for more than 15 cycles. New cyanide stretching bands appear at 2211 (m), 2196 (sh, m), 2153 (sh, w), 2118 (sh, m), and 2106 (s) cm^{-1} in the infrared spectrum of the material after repeated oxygen/nitrogen cycling; the highest frequency bands (ν_{CN} = 2211 and 2196 cm^{-1}) could be due to bridging cyanide[11] or cobalt cyanato[16] compounds. A new band at 1122 cm^{-1}, which could be due to a Co(III)-O_2^- complex, is also observed in the infrared spectrum of the oxygenated material. A bridged species (Co−C≡N−Co) would result in five-coordinate cobalt centers, which should react readily with dioxygen. X-ray powder diffraction data of $(Bu_4N)_2Co(CN)_4$ under N_2 and O_2 indicate that the material, which is crystalline while under nitrogen, becomes amorphous on dioxygenation. Although purging the dioxygenated material with nitrogen for 2 d restores approximately half of the material's O_2-binding capacity, it does not restore its crystallinity.

Pyridine Adduct of $(Bu_4N)_2Co(CN)_4$. It is well-known in the literature that the amount of electron density on the cobalt(II) center determines the strength of dioxygen binding in cobalt(II) complexes.[9c,17] The fact that $(Bu_4N)_2Co(CN)_4$ could reversibly bind dioxygen suggested that there is sufficient electron density on the cobalt center in this complex. It seemed reasonable to expect that the electron density on cobalt could be further tuned by adding neutral axial bases of differing strengths. Thus, $(Bu_4N)_2Co(CN)_4$ was reacted with several axial bases to synthesize a family of tetracyanocobaltate(II) complexes.

The compound $(Bu_4N)_2Co(CN)_4\cdot$(pyridine) (**2**) was prepared by simply dissolving **1** in pyridine and precipitating the product *via* addition of a nonsolvent. Compound **2** was also found to reversibly bind dioxygen, readily forming the cobalt(III)−superoxo complex at room temperature; its maximum oxygen capacity was 27.8 cm^3/g at 30 °C and 760 Torr of O_2 (29.7 cm^3/g at 25 °C and 760 Torr of O_2). No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors.

In contrast to the Type I (Langmuir) oxygen absorption/desorption isotherm that was seen for $Li_3[Co(CN)_5]\cdot 2DMF$,[6] the oxygen absorption/desorption isotherms of **2** (Figure 1) appeared to be more S-shaped, indicating that a phase change occurred upon oxygenation at a pressure of 50−70 Torr at 25 °C.[18a] Considerable hysteresis was observed in the desorption isotherm, most likely because a restructuring of the crystal lattice occurs. X-ray diffraction pattern studies (Figure 2) also showed that **2** exists in one crystalline phase under nitrogen and a completely different phase while under an atmosphere of oxygen. Purging the oxygenated phase with nitrogen converted it back to the first phase, and this process could be repeated 25 times with very little loss in oxygen-binding activity. Similar phase changes occur when *N,N′*-bis(salicylidene)ethylenediaminatocobalt(II) and *N,N′*-bis(3-fluorosalicylidene)ethylenediaminatocobalt(II) react with dioxygen.[18]

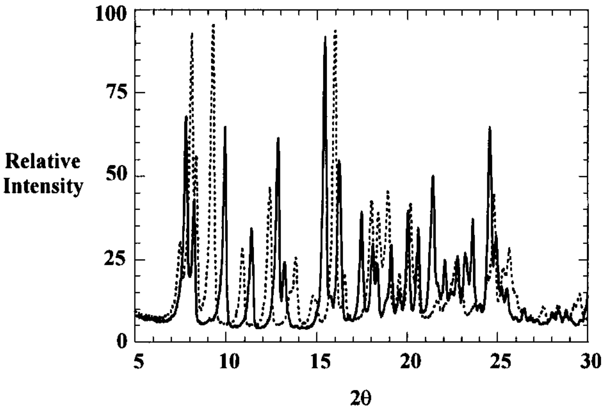

Figure 2. X-ray powder diffraction patterns of $(Bu_4N)_2Co(CN)_4\cdot$(pyridine) (**2**) under nitrogen (solid line) and oxygen (dotted line).

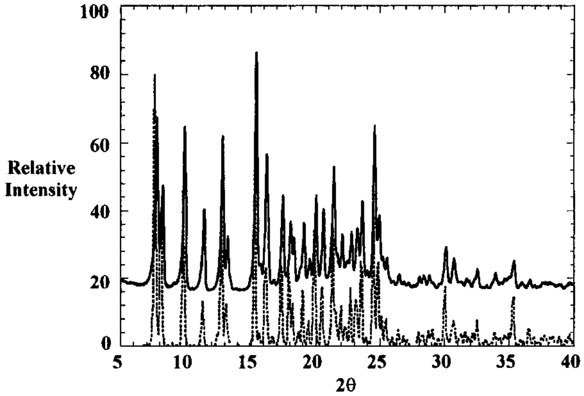

Figure 3. X-ray powder diffraction pattern of $(Bu_4N)_2Co(CN)_4\cdot$(pyridine) (**2**) under nitrogen (solid line) and the calculated powder pattern of **2** using the single-crystal results (dotted line).

Single-crystal X-ray structural analysis was attempted for **2**, but the analysis could not be satisfactorily refined due to either a high degree of thermal motion or static disorder of the butyl groups.[19] However, the structure at its current resolution (R_w = 11.53%) is adequate to ascertain the molecular packing and the cobalt coordination. We were also able to confirm that the calculated powder pattern generated from the single-crystal data matched the observed powder diffraction data (Figure 3). Crystallographic information and the data collection and refinement information are reported in Table 1. Selected bond lengths and angles are listed in Table 2. The $[Co(CN)_4\cdot C_5H_5N]^{2-}$ anion was found to be square pyramidal with the cobalt slightly elevated above the plane formed by the carbon atoms of the four cyanide ligands (Figure 4). From the molecular packing (Figure 5), it is apparent that the anions are aligned parallel to the *a* axis, with the pyridine of each anionic unit pointing toward

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Table 1. Crystallographic Information for $(Bu_4N)_2Co(CN)_4\cdot$(pyridine) (**2**)

empirical formula	$C_{41}H_{77}CoN_7$
formula weight	727.05
space group	*Pbcm* (No. 57)
a (Å)	9.024(3)
b (Å)	21.886(8)
c (Å)	23.184(6)
V (Å^3)	4578.6(27)
Z	4
ρ_{calcd} (g/cm^3)	1.055
temp (K)	298
λ (Å)	0.71073
no absorption correction	
final *R* indices (observed data)[a]	$R = 10.13\%$, $R_w = 11.53\%$

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum(|F_o|)$, where F_o and F_c are respectively the observed and calculated structure factors; $R_w(F) = \sum(w(|F_o| - |F_c|)^2)/\sum(wF_o{}^2)^{1/2}$, where $w^{-1} = \sigma^2(F_o) + g(F_o)^2$ and $g = 0.0008$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(Bu_4N)_2Co(CN)_4\cdot$(pyridine) (**2**)

Co−N(3)	2.148(15)	Co−C(1)	1.945(13)
Co−C(2)	1.910(13)	Co−C(1A)	1.945(13)
Co−C(2A)	1.910(13)	N(1)−C(1)	1.115(17)
N(2)−C(2)	1.131(18)	N(3)−C(3)	1.312(19)
N(3)−C(3A)	1.312(19)	N(4)−C(6)	1.489(18)
N(4)−C(10)	1.534(17)	N(4)−C(6A)	1.489(18)
N(4)−C(10A)	1.534(17)	N(5)−C(14)	1.478(24)
N(5)−C(18)	1.512(22)	N(5)−C(22)	1.493(16)
N(5)−C(22A)	1.493(16)	C(3)−C(4)	1.333(23)
C(4)−C(5)	1.351(26)	C(5)−C(4A)	1.351(26)
C(6)−C(7)	1.495(26)	C(7)−C(9)	1.555(31)
C(8)−C(9)	1.380(36)	C(10)−C(11)	1.507(24)
C(11)−C(12)	1.509(31)	C(12)−C(13)	1.359(34)
C(14)−C(15)	1.550(31)	C(15)−C(16)	1.560(34)
C(16)−C(17)	1.571(36)	C(16)−C(17A)	1.571(36)
C(18)−C(19)	1.516(26)	C(19)−C(20)	1.580(28)
C(20)−C(21)	1.522(32)	C(22)−C(23)	1.518(20)
C(23)−C(24)	1.533(27)	C(24)−C(25)	1.171(31)
N(3)−Co−C(1)	93.2(5)	N(3)−Co−C(2)	97.5(5)
C(1)−Co−C(2)	89.2(5)	N(3)−Co−C(1A)	93.2(5)
C(1)−Co−C(1A)	90.5(7)	C(2)−Co−C(1A)	169.3(6)
N(3)−Co−C(2A)	97.5(5)	C(1)−Co−C(2A)	169.3(6)
C(2)−Co−C(2A)	89.0(8)	C(1A)−Co−C(2A)	89.2(5)
Co−N(3)−C(3)	122.8(9)	Co−N(3)−C(3A)	122.8(9)
C(3)−N(3)−C(3A)	114.1(18)	C(6)−N(4)−C(10)	112.1(8)
C(6)−N(4)−C(6A)	109.5(15)	C(10)−N(4)−C(6A)	105.5(8)
C(6)−N(4)−C(10A)	105.5(8)	C(10)−N(4)−C(10A)	112.2(14)
C(6A)−N(4)−C(10A)	112.1(8)	C(14)−N(5)−C(18)	105.6(13)
C(14)−N(5)−C(22)	112.6(10)	C(18)−N(5)−C(22)	111.0(9)
C(14)−N(5)−C(22A)	112.6(10)	C(18)−N(5)−C(22A)	111.0(9)
C(22)−N(5)−C(22A)	104.2(14)	Co−C(1)−N(1)	177.8(12)
Co−C(2)−N(2)	177.4(12)	N(3)−C(3)−C(4)	124.0(17)
C(3)−C(4)−C(5)	122.4(20)	C(4)−C(5)−C(4A)	112.9(25)
N(4)−C(6)−C(7)	116.5(13)	C(6)−C(7)−C(9)	114.6(18)
C(7)−C(9)−C(8)	110.4(20)	N(4)−C(10)−C(11)	115.5(12)
C(10)−C(11)−C(12)	111.3(16)	C(11)−C(12)−C(13)	103.4(20)
N(5)−C(14)−C(15)	113.7(16)	C(14)−C(15)−C(16)	108.5(19)
C(15)−C(16)−C(17)	103.1(15)	C(15)−C(16)−C(17A)	103.1(15)
C(17)−C(16)−C(17A)	151.3(29)	N(5)−C(18)−C(19)	114.8(14)
C(18)−C(19)−C(20)	106.2(16)	C(19)−C(20)−C(21)	108.7(17)
N(5)−C(22)−C(23)	116.4(11)	C(22)−C(23)−C(24)	117.7(14)
C(23)−C(24)−C(25)	113.2(22)		

the vacant site on the cobalt of the adjacent anion. The tetrabutylammonium cations completely surround the anions, forming hydrophobic casings that also run parallel to the *a* axis. Since there are no strong interionic forces in this packing arrangement, a low density (1.055 g/cm^3) is seen. These results made it clear that the bulky tetrabutylammonium cations are capable of adequately separating the cobalt centers so that they could not interact with one another.

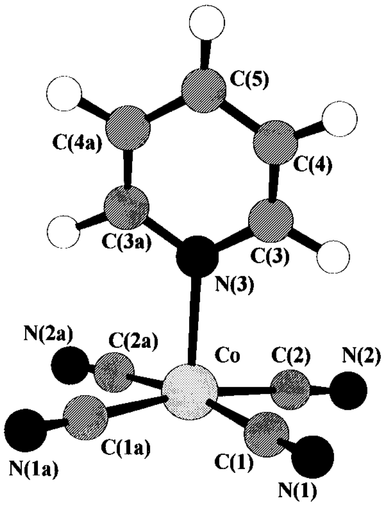

Figure 4. Cobalt coordination in $(Bu_4N)_2Co(CN)_4\cdot$(pyridine) (**2**).

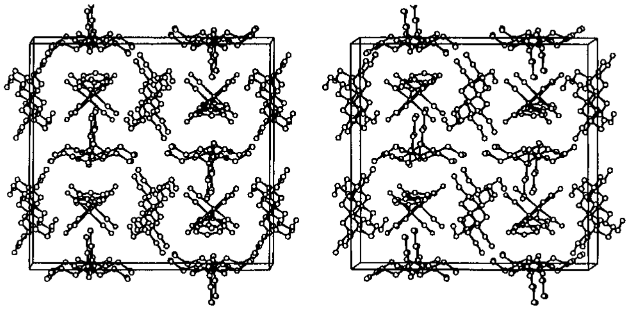

Figure 5. Stereoview of the molecular packing in $(Bu_4N)_2Co(CN)_4\cdot$(pyridine) (**2**) as viewed down the *a* axis (*b* is vertical and *c* is horizontal).

Since **2** undergoes a phase change when it reacts with oxygen, there is probably not enough room between the cobalt of one anionic unit and the pyridine in the next anionic unit to accommodate an oxygen molecule without a structural reorganization. Because the phase change that occurs on oxygenation is reversible over multiple cycles, this structural change might not be very dramatic.

Dimeric 4,4′-Dipyridyl Adduct, $[(Bu_4N)_2Co(CN)_4]_2\cdot(C_{10}H_8N_2)$. A DMF solution of **1** was added to a DMF solution containing 2 equiv of 4,4′-dipyridyl, and the product was precipitated through addition of a nonsolvent; in this way, a complex which contained two cobalt units per axial base was prepared. Because 4,4′-dipyridyl is a weaker base than pyridine, $[(Bu_4N)_2Co(CN)_4]_2\cdot$(4,4′-dipyridyl) (**3**) required a higher partial pressure of O_2 than did compound **2** in order to form the stoichiometric 1:1 dioxygen adduct. Compound **3** also formed the corresponding cobalt(III)−superoxo complex.

Compound **3** picked up 27.9 cm^3/g (90% of the stoichiometric amount for a 1:1 Co−O_2 complex) at 30 °C under 760 Torr of O_2. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors. The dioxygen absorption isotherm was rather complex (Figure 6), and hysteresis was seen on desorption. X-ray diffraction powder pattern studies also showed that compound **3** under nitrogen was a different phase than the same compound under O_2. The isotherm shape is very likely due to an anticooperative effect[20] between the two cobalt centers. When the first cobalt center binds a molecule of dioxygen, it probably causes electron density to be removed from the second cobalt in the dimer, making the second cobalt center bind dioxygen more weakly.

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(20) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley Interscience: New York, 1988; pp 1346−1348.

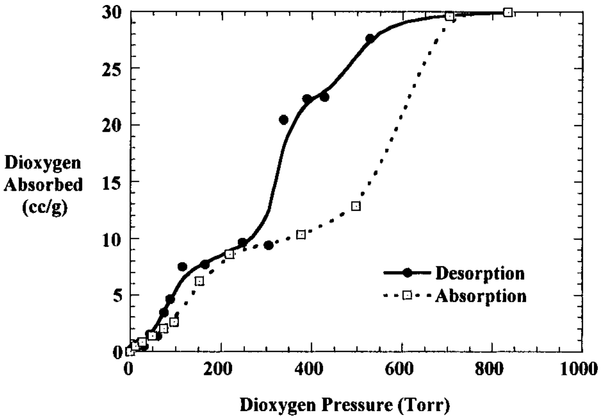

Figure 6. Dioxygen absorption and desorption isotherms of [$(Bu_4N)_2Co(CN)_4]_2\cdot$(4,4′-dipyridyl) (**3**).

Table 3. Dioxygen Affinity for Tetrabutylammonium Tetracyanocobaltate(II) Complexes at 25 °C

compd	axial base	pK_a of conjugate acid[22]	$P_{1/2}(O_2)$ (Torr)[a]
4	1-methylimidazole	7.05	*b*
2	pyridine	5.24	50−70[c]
7	TEDA[d]	8.10, 4.14	80[c]
3	4,4′-dipyridyl[e]	4.77, 2.69	500−700[c]
8	HMT[f]	4.89, <2[23]	4595[g]

[a] Oxygen pressure at half-saturation. [b] Oxygen binding was too strong to obtain an isotherm (see text). [c] Observed from the isotherm. [d] TEDA is 1,4-diazabicyclo[2.2.2]octane. [e] Bidentate. [f] HMT is hexamethylenetetraamine. [g] Calculated from the isotherm.

Effects of Other Axial Bases on Oxygen Binding. Compound **1** was reacted with 1-methylimidazole, 4-picoline, methyl isonicotinate, 1,4-diazabicyclo[2.2.2]octane (TEDA), and hexamethylenetetraamine (HMT). The corresponding solid complexes were isolated: $(Bu_4N)_2Co(CN)_4\cdot$(1-methylimidazole) (**4**), $(Bu_4N)_2Co(CN)_4\cdot$(4-picoline) (**5**), $(Bu_4N)_2Co(CN)_4\cdot$(methyl isonicotinate) (**6**), $(Bu_4N)_2Co(CN)_4\cdot$(TEDA) (**7**), and $(Bu_4N)_2Co(CN)_4\cdot$(HMT) (**8**). All of the compounds reacted reversibly with dioxygen at room temperature to form the cobalt(III)−superoxo species. The electron density on the cobalt center varied, depending upon the strength of the axial base (Table 3). Cobalt complexes containing weaker bases like methyl isonicotinate required more than 760 Torr of O_2 for stoichiometric uptake to occur. However, with strong axial bases, the cobalt complex was completely dioxygenated at lower partial pressures of O_2 than were required for complexes with weaker axial bases. With the cobalt complex containing the strongest π-donor base, 1-methylimidazole, dioxygen binding was almost irreversible at room temperature, and the complex had to be heated in order to remove the oxygen. Interestingly, although TEDA has the highest pK_a of all the bases studied, the TEDA complex **7** binds oxygen more weakly than the pyridine complex **2** does. This is consistent with the results of solution studies in which 1-methylimidazole was found to promote O_2 coordination and Co(L)(B) oxidation to a greater extent than was anticipated from its pK_a; this was attributed to its π-donor ability, which indirectly destabilizes the d_{z^2} electron.[9c,17b] Therefore, the π-donor ability of the base must also be important in the tetracyanocobaltate systems.

Although different axial bases substantially altered the reactivity of the cobalt center, very little change was seen in the infrared stretching frequencies of the equatorial cyanides in the various compounds. For example, the 1-methylimidazole complex **4** had a cyanide stretching band at 2078 cm^{-1}, while the methyl isonicotinate complex **6** had a cyanide stretching band at 2083 cm^{-1}.

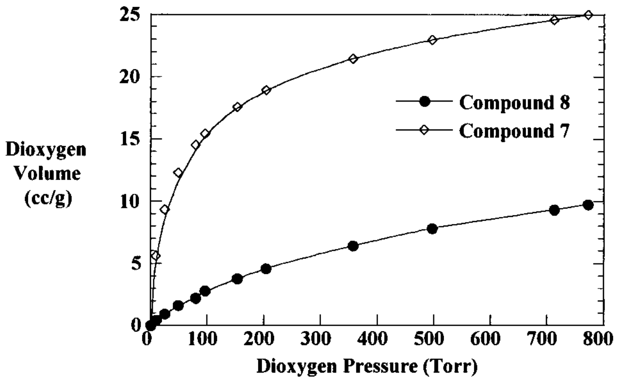

Figure 7. Dioxygen absorption/desorption isotherms of [$(Bu_4N)_2Co(CN)_4]\cdot$(TEDA) (**7**) and [$(Bu_4N)_2Co(CN)_4]\cdot$(HMT) (**8**).

We attempted to obtain oxygen absorption and desorption isotherms for all the materials that appeared to reversibly bind oxygen at room temperature (compounds **2**, **3**, **5**, **6**, **7**, and **8**). While compounds **2** and **3** experienced reversible phase changes on oxygenation and deoxygenation, compounds **7** and **8** displayed Type I isotherms[21] (Figure 7). Presumably, the phase changes observed with compounds **2** and **3** occurred because the unoxygenated phases did not provide enough room for dioxygen to reach all of the cobalt sites; therefore, the absence of phase changes in the isotherms of compounds **7** and **8** probably reflects a situation in which the axial bases TEDA and HMT are bulky enough to expand the structures, providing room for the bound oxygen. In other words, no structural rearrangement is necessary for compounds **7** and **8** to bind dioxygen, so Type I isotherms result. X-ray powder diffraction studies of **7** also indicate that no phase change occurs on oxygenation.

Compounds **5** and **6** only degrade slowly over several days when subjected to repetitive oxygen/nitrogen cycling; however, they decomposed to give off volatiles under low partial pressures of oxygen for the long equilibration times needed to obtain meaningful isotherms for these systems (several hours per data point at each pressure). Therefore, no oxygen absorption/desorption isotherms could be measured for these materials. Infrared spectra of compounds **5** and **6**, after they had suffered some decomposition under oxygen, both showed new bands that could be due to either bridging cyanides[11] or cobalt cyanato[16] compounds: 2210 (m) and 2197 (m) cm^{-1} for **5** and 2211 (w) and 2193 (w) cm^{-1} for **6**.

The relative strengths of oxygen binding in these tetrabutylammonium tetracyanocobaltate(II) complexes could be determined by comparing the maximum oxygen uptakes observed by gravimetric analysis at two different oxygen pressures (540 and 760 Torr). The stronger oxygen-binding materials (**2**, **4**, and **5**) absorbed nearly stoichiometric amounts of oxygen while under only 540 Torr of oxygen. Weaker oxygen-binding materials (**3** and **7**) were only partially oxygenated at 540 Torr but were completely oxygenated under 760 Torr of oxygen. At 760 Torr of oxygen, the weakest oxygen-binding materials (**6** and **8**) were still only partially oxygenated. Thus, we were able to qualitatively rank the base adducts of $(Bu_4N)_2Co(CN)_4$ in order from the strongest to the weakest oxygen binders:

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(21) Perry, R. H.; Chilton, C. H. *Chemical Engineers' Handbook*, 5th ed.; McGraw-Hill: New York, 1973; pp 16−14.

(22) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1975; Vol. 2.

(23) Cooney, A. P.; Crampton, M. R.; Golding, P. *J. Chem. Soc., Perkin Trans. II* **1986**, 835.

1-methylimidazole, 4-picoline, pyridine > 4,4′-dipyridyl > TEDA > methyl isonicotinate > HMT (see Table 3).

Conclusions

With the isolation of the low-spin, square-planar $(Bu_4N)_2Co(CN)_4$, the door has been opened to a new family of solid state tetrabutylammonium tetracyanocobaltate(II) complexes that reversibly bind dioxygen. Because of the bulky, noncoordinating cations, the cobalt centers are effectively separated and 1:1 cobalt(III)−superoxo complexes can form. These materials are, thus, relatively stable to repeated oxygen/nitrogen cycling.

Since the axial ligand can be changed readily and the complexes isolated as solids, the effects of different axial bases on the oxygen-binding behavior of the solids could be determined. Interesting reversible phase changes occur on oxygenation/deoxygenation for compounds **2** and **3**. Presumably this happens because the crystal lattices of the unoxygenated materials must expand to accommodate dioxygen.

Experimental Section

All reactions were performed under an inert atmosphere (nitrogen or argon) using standard Schlenk line or drybox techniques. Solvents were distilled under nitrogen from the appropriate drying agents, or anhydrous Aldrich Sure/Seal solvents were used. $^{18}O_2$ (97.7 at. % ^{18}O, MSD Isotopes) and all other reagents (Aldrich) were used as received unless otherwise noted. Methyl isonicotinate (Pfaltz & Bauer) and 4-picoline (Aldrich) were dried over 3 Å molecular sieves (previously activated at 400 °C overnight) under a blanket of nitrogen for at least 16 h and degassed prior to use. Solid bases were dried under vacuum at room temperature for at least 16 h prior to use.

Thermal gravimetric analyses were performed on either a DuPont 951, a DuPont 2950, a Perkin-Elmer TGS2, or a TA Instruments 2950 thermal gravimetric analyzer; samples were loaded onto the instruments under a nitrogen atmosphere unless otherwise noted. Oxygen/nitrogen cycling experiments were typically performed at 30 °C. The sample was first purged with nitrogen for 30 min, then purged with an oxygen-containing atmosphere (at either 540 or 760 Torr of O_2) for 10−60 min, and finally purged with nitrogen for 30−60 min. When the higher oxygen partial pressure was used, longer desorption times (60−100 min) were used.

Infrared spectra were obtained using either a Nicolet 510 or a Perkin-Elmer 1600 Series FTIR spectrometer. UV−visible spectra were performed using a Beckman DU-70 spectrophotometer, while an NIRSystems 6500 spectrometer was used to obtain the visible and near-infrared spectra. X-ray powder diffraction pattern data were obtained using a controlled-atmosphere cell with a beryllium window (Blake Industries) which was loaded and sealed under nitrogen. The cell could be purged with oxygen to obtain data for the oxygen adducts. A Siemens D-500 powder diffractometer was used to collect the data over the range $5° \leq 2\theta \leq 60°$ using Cu $K\alpha_{1,2}$ radiation; SRM-640a (the NBS silicon standard) was used as an internal standard. Room temperature magnetic susceptibilities were measured using a Johnson Matthey MSB-1 magnetic susceptibility balance.

The oxygen isotherm measurements were made using a Micromeritics ASAP 2000 static volumetric adsorption unit with the sample immersed in a thermostat bath. The pressure was measured with a capacitance transducer having an accuracy of ±0.15%. The samples were evacuated to a pressure of 10^{-4}−10^{-5} Torr overnight at ambient temperature prior to analysis. The instrument was programmed to take a pressure reading every 90 s until ten consecutive measurements were within ±0.1% of each other. At this point, the instrument recorded the pressure measurement.

Preparation and Reversible Oxygen-Absorbing Properties of $(PNP)_2Co(CN)_4$. The procedure recorded by Carter *et al.* was followed.[10] The solvent was removed by heating the solvated material to 80 °C under vacuum for 24 h to yield $(PNP)_2Co(CN)_4$ as a light blue powder, mp 227 °C dec. FTIR (Nujol, N_2): 2102 (sh, m), 2098 (m) cm^{-1} (CN). FTIR (Nujol, air, 24 h): 2120 (m), 2100 (m) cm^{-1} (CN).

The development of a cyanide stretch at higher wavenumber has also been observed upon oxygenation of other cyanocobaltate(II) complexes.[3f,7] A large $(PNP)^+$ peak at 1115 cm^{-1} with a shoulder at 1074 cm^{-1} masked the region in which cobalt(III)−superoxo oxygen stretches would occur, and the nature of oxygen binding in this material was not established.

A sample of $(PNP)_2Co(CN)_4$ was loaded onto a DuPont 951 thermal gravimetric analyzer in air. Initially, the sample was heated to 80 °C under nitrogen to remove any absorbed oxygen; a weight loss of 0.5% was observed. Cycling (one cycle consisted of 20 min under oxygen at 30 °C followed by being heated to 80 °C under nitrogen for 20 min) resulted in reversible weight gains and losses of 0.2% by weight. When the sample was kept under oxygen for 720 min, a weight gain of 1.20% was observed. After 20 min at 80 °C under nitrogen, a weight loss of 1.0% was observed. The length of oxygenation time was increased to 4250 min after which a 2.62% weight increase (from the completely deoxygenated material) was seen. This corresponded to approximately a Co:O_2 ratio of 1:1. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors. Upon the sample being heated to to 80 °C under nitrogen, a weight loss of 1.77% occurred after 3 h. The fact that the weight loss had reached a plateau at this point indicated that some irreversible oxidation had probably occurred.

Preparation of $(Bu_4N)_2Co(CN)_4$ (1) in THF. A filtered solution of $(Bu_4N)CN$ (8.437 g, 31.42 mmol, 4 equiv) in THF (95 mL to dissolve plus 55 mL to rinse frit) was added to a filtered solution of $CoCl_2$ (1.020 g, 7.856 mmol) in THF (395 mL) at room temperature. Additional THF (5 mL) was used to ensure complete transfer. Upon addition, the reaction mixture became emerald green and clear, but over a period of 5−10 min, white precipitate began to come out of the solution. The solution was then stirred at room temperature for 10 min before it was filtered. A white crystalline solid (with a faint greenish tint) was obtained; it was washed with THF (3 × 20 mL) and hexane (3 × 20 mL) and suction filtered dry to yield 3.510 g (5.42 mmol, 69% yield) of $(Bu_4N)_2Co(CN)_4$. FTIR (Nujol, N_2): 2114 (sh), 2095 (s), 2072 (sh), 2056 (w) cm^{-1} (CN). FTIR (Nujol, air): 2163 (w), 2124 (sh), 2105 (s) cm^{-1} (CN). FTIR after repeated O_2/N_2 cycling (Nujol, N_2): 2211 (m), 2196 (sh, m), 2153 (sh, w), 2118 (sh, m), and 2106 (s) cm^{-1} (CN); 1122 cm^{-1} (Co(III)−O_2^-). $\mu_{eff} = 2.7\ \mu_B$ at $T = 298.5$ K. Anal. Calcd for $C_{36}H_{72}N_6Co$: Co, 9.10; C, 66.73; H, 11.20; N, 12.97. Found: Co, 9.14; C, 66.65; H, 10.88; N, 12.70.

Maximum oxygen uptake observed by gravimetric analysis: 4.49 wt % (540 Torr of O_2). This corresponds to 91% of the stoichiometric uptake expected for a 1:1 Co−O_2 complex. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors.

Preparation of $(Bu_4N)_2Co(CN)_4$·(pyridine) (2). $(Bu_4N)_2Co(CN)_4$ (0.242 g, 0.373 mmol) was dissolved in anhydrous pyridine (3 mL); a light green solution resulted. After 5 min at room temperature, anhydrous hexane (10 mL) was added to precipitate a greenish-yellow solid. The solid was filtered and washed thoroughly with hexane (3 × 10 mL) before it was suction filtered dry. $(Bu_4N)_2Co(CN)_4$·(pyridine) was obtained as a light yellowish-green powder (0.235 g, 86% yield). FTIR (Nujol, N_2): 2099 (w), 2079 (s), 2054 (sh), 2040 (w) cm^{-1} (CN); 1589 (m) cm^{-1} (pyridine). FTIR (Nujol, air): 2124 (w), 2098 (w), 2093 (w), 2078 (s), 2055 (sh), 2041 (w) cm^{-1} (CN). FTIR (Nujol, $^{16}O_2$): 1138 (m), 1126 (m) cm^{-1} (Co(III)-O_2^-). FTIR (Nujol, $^{18}O_2$): 1080 (m), 1066 (m) cm^{-1} (Co(III)−O_2^-). $\mu_{eff} = 2.7\ \mu_B$ at $T = 297.0$K. Anal. Calcd for $C_{41}H_{77}N_7Co$: Co, 8.10; C, 67.73; H, 10.68; N, 13.48. Found: Co, 7.72; C, 67.62; H, 10.51; N, 13.79.

Maximum oxygen uptake observed by gravimetric analysis: 3.97 wt % (540 Torr of O_2). This corresponds to 90% of the stoichiometric uptake expected for a 1:1 Co−O_2 complex. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors.

X-ray Data Collection and Structure Determination for Compound 2. Crystals of **2** were grown by allowing slow vapor diffusion of THF (nonsolvent) into a pyridine solution of $(Bu_4N)_2Co(CN)_4$ at room temperature over approximately 1 month's time. A yellow, parallelpiped-shaped single crystal of **2**, with approximate dimensions 0.36 × 0.36 × 0.42 mm, was sealed in a capillary tube under nitrogen.

Diffraction data were collected at 298 K using a Siemens P4 diffractometer in the range of $4.0° \leq 2\theta \leq 45.0°$ with Mo Kα radiation. A total of 3422 (3087 independent, $R_{int} < 0.01\%$) reflections were collected; of these 1334 had $F > 4.0\sigma(F)$. The structure was solved by direct methods. The non-hydrogen atoms of the anion were refined with anisotropic displacement parameters; other displacement parameters were constrained to be isotropic. Hydrogen atom contributions were determined using a riding model with fixed isotropic U and a fixed bond length of 0.95 Å. All computations were done using the Siemens SHELXTL PLUS (VMS) system.[19]

Preparation of [(Bu$_4$N)$_2$Co(CN)$_4$]$_2$·(4,4′-dipyridyl) (3). $(Bu_4N)_2Co(CN)_4$ (0.774 g, 1.19 mmol) was dissolved in anhydrous DMF (10 mL), and a deep blue-green solution resulted. A solution of 4,4′-dipyridyl (0.373 g, 2.39 mmol) in DMF (15 mL) was added to the cobalt-containing solution with stirring. The color of the reaction mixture immediately changed to orange. After 15 min at room temperature, the product was precipitated by adding diethyl ether (75 mL) to the DMF solution. An orange solid was filtered and washed thoroughly with fresh ether (3 × 20 mL) before it was suction filtered dry. $[(Bu_4N)_2Co(CN)_4]_2$·(4,4′-dipyridyl) was isolated as an orange powder (0.663 g, 77% yield). FTIR (Nujol, N_2): 2101 (w), 2081 (s), 2043 (w) cm^{-1} (CN); 1599 (w), 1530 (w) cm^{-1} (4,4′-dipyridyl). FTIR (Nujol, air): 2113 (m), 2102 (w), 2081 (s), 2042 (vw) cm^{-1} (CN); 1127 (m) cm^{-1} (Co(III)−superoxo). $\mu_{eff} = 2.05\ \mu_B$ per cobalt at $T = 293.0$ K. Anal. Calcd for $C_{82}H_{152}N_{14}Co_2$: Co, 8.12; C, 67.83; H, 10.55; N, 13.50. Found: Co, 8.14; C, 67.59; H, 10.19; N, 13.55.

Maximum oxygen uptake observed by gravimetric analysis: 3.99 wt % (760 Torr of O_2). This corresponds to 90% of the stoichiometric uptake expected for a 1:1 $Co-O_2$ complex. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure or other factors.

Preparation of [(Bu$_4$N)$_2$Co(CN)$_4$]·(1-methylimidazole) (4). $(Bu_4N)_2Co(CN)_4$ (0.313 g, 0.483 mmol) was dissolved in anhydrous 1-methylimidazole (5 mL), and a greenish-yellow solution resulted. After 5 min at room temperature, anhydrous THF (20 mL) and anhydrous hexane (20 mL) were added to precipitate the product as a green oil. When the mixture was vigorously stirred for 10 min, a light green powder resulted. The powder was filtered and washed thoroughly with hexane (10 mL) and diethyl ether (2 × 10 mL); then it was suction filtered dry. $[(Bu_4N)_2Co(CN)_4]$·(1-methylimidazole) was isolated as a light green powder (0.281 g, 80% yield). FTIR (Nujol, N_2): 2170 (vw), 2100 (w), 2088 (sh), 2078 (s), 2053 (sh), 2039 (w) cm^{-1} (CN); 1515 (w) cm^{-1} (1-methylimidazole). FTIR (Nujol, air): 2110 (w), 2089 (sh), 2078 (s), 2053 (sh), 2039 (w) cm^{-1} (CN); 1135 (m) cm^{-1} (Co(III)−O_2^-). Anal. Calcd for $C_{40}H_{78}N_8Co$: Co, 8.07; C, 65.81; H, 10.77; N, 15.35. Found: Co, 7.81; C, 66.14; H, 10.39; N, 15.56.

Maximum oxygen uptake observed by gravimetric analysis: 3.15 wt % (540 Torr of O_2). This corresponds to 72% of the stoichiometric uptake expected for a 1:1 $Co-O_2$ complex. Desorption of oxygen is poor at 30 °C. If oxygenated **4** is heated under nitrogen to 100 °C for 60 min and temperature swing cycling is done (O_2, 10 min at 30 °C; N_2, 5 min at 30 °C, 5 °C/min to 70 °C, 70 °C for 30 min, 10 °C/min to 30 °C, 30 °C for 20 min), completely reversible cycling can be attained. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors.

Preparation of (Bu$_4$N)$_2$Co(CN)$_4$·(4-picoline) (5). $(Bu_4N)_2Co(CN)_4$ (0.633 g, 0.977 mmol) was dissolved in anhydrous DMF (5 mL). To this solution was added a solution of 4-picoline (1.079 g, 11.58 mmol) in DMF (5 mL). The reaction mixture turned light green in color. After the mixture was stirred for approximately 5 min at room temperature, diethyl ether (60 mL) was added to completely oil out the product. The supernatant liquid was decanted, and the light green oil was triturated with additional ether (30 mL) to yield a light green powder. The powder was then filtered, washed with fresh diethyl ether (2 × 10 mL), and suction filtered dry. A 63% yield (0.458 g) of **5** was obtained. FTIR (Nujol, N_2): 2079 (s), 2095 (s) cm^{-1} (CN); 1612 (m) cm^{-1} (4-picoline). FTIR (Nujol, air): 2158 (vw), 2117 (m), 2107 (sh), 2095 (s), 2080 (m) cm^{-1} (CN); 1129 (m) cm^{-1} (Co(III)−O_2^-).

FTIR (Nujol, after O_2/N_2 cycling for 2 d): 1581 (m) cm^{-1} (C═C and C═N bands), 2211 (w) and 2194 (w) cm^{-1} (bridging cyanide[11] or cobalt cyanato[16] species), and 2113 (s) and 2107 (sh) cm^{-1} (Co(III)−CN). Anal. Calcd for $C_{42}H_{79}N_7Co$: Co, 7.95; C, 68.07; H, 10.74; N, 13.23. Found: Co, 8.12; C, 67.93; H, 10.75; N, 13.19.

Maximum oxygen uptake observed by gravimetric analysis: 3.34 wt % (540 Torr of O_2) and 3.53 wt % (760 Torr of O_2). These uptakes correspond to 78% (at 540 Torr) and 82% (at 760 Torr) of the stoichiometric uptake expected for a 1:1 $Co-O_2$ complex. No significant change in the amount of oxygen uptake occurs between 540 and 760 Torr of oxygen partial pressure. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors.

Preparation of (Bu$_4$N)$_2$Co(CN)$_4$·(methyl isonicotinate) (6). $(Bu_4N)_2Co(CN)_4$ (0.417g, 0.644 mmol) was dissolved in anhydrous dichloromethane (14 mL). To this blue-green solution was added a solution of dry methyl isonicotinate (1.648 g, 12.02 mmol) in 4 mL of dichloromethane. The reaction mixture turned dark brown in color. After approximately 10 min of the mixture being stirred at room temperature, it was then added to THF (100 mL) and a powder precipitated. After 30 min, the powder was filtered, washed with fresh THF (3 × 10 mL) and diethyl ether (2 × 15 mL), and suction filtered dry to yield 0.326 g (64% yield) of rusty orange powder. FTIR (Nujol, N_2): 2103 (w), 2094 (sh), 2083 (s) cm^{-1} (CN); 1730 (s) cm^{-1} (methyl isonicotinate). FTIR (Nujol, air): 2123 (sh), 2116 (m), 2106 (w), 2095 (sh), 2088 (s), 2084 (sh) cm^{-1} (CN); 1129 (m) cm^{-1} (Co(III)−O_2^-). FTIR (Nujol, after O_2/N_2 cycling): 2211 (w) and 2193 (w) cm^{-1} (bridging CN[11] or OCN[16]), 2114 (s) and 2085 (s) cm^{-1} (CN), and 1624 (s) cm^{-1} (C═C, C═N, or carboxylate). Anal. Calcd for $C_{43}H_{79}N_7O_2Co$: Co, 7.51; C, 65.79; H, 10.14; N, 12.49; O, 4.08. Found: Co, 7.46; C, 65.62; H, 10.00; N, 12.53. Unsatisfactory carbon analyses were obtained when V_2O_5 was used as a combustion aid; however, satisfactory analyses were obtained for the same sample when powdered tin was used as a combustion aid.

Maximum oxygen uptake observed by gravimetric analysis: 0.77 wt % (540 Torr of O_2) and 3.23 wt % (760 Torr of O_2). The latter corresponds to 79% of the stoichiometric uptake expected for a 1:1 $Co-O_2$ complex. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors.

Preparation of [(Bu$_4$N)$_2$Co(CN)$_4$]·(TEDA) (7). 1,4-Diazabicyclo[2.2.2]octane (TEDA) was dried on a vacuum line at 45 °C overnight before it was taken into the drybox. In the drybox, it was recrystallized from diethyl ether at −20 °C to yield white needles which were used in the following reaction.

$(Bu_4N)_2Co(CN)_4$ (0.517 g, 0.798 mmol) was dissolved in anhydrous DMF (5 mL). To this solution was added a solution of TEDA (0.182 g, 1.62 mmol) in DMF (3 mL). The reaction mixture turned yellow-green in color. After approximately 5 min of the mixture being stirred at room temperature, THF (30 mL) was added in 10 mL increments to precipitate out the product as a light green powder. After the product was washed with fresh THF (3 × 10 mL) and suction filtered dry, 0.438 g (72% yield) of $[(Bu_4N)_2Co(CN)_4]\cdot(C_6H_{12}N_2)$ was obtained. FTIR (Nujol, N_2): 2100 (m), 2090 (sh), 2079 (s) cm^{-1} (CN); 1153 (m), 1061 (m), 996 (w), 888 (s), 833 (w) cm^{-1} (TEDA). No DMF was visible in the IR spectrum. FTIR (Nujol, air): 2127 (sh), 2110 (m), 2102 (sh), 2080 (s) cm^{-1} (CN); 1132 (m) cm^{-1} (Co(III)−O_2^-). Anal. Calcd for $C_{42}H_{84}N_8Co$: Co, 7.75; C, 66.37; H, 11.14; N, 14.74. Found: Co, 7.68; C, 65.79; H, 11.09; N, 13.69.

Maximum oxygen uptake observed by gravimetric analysis: 3.18 wt % (760 Torr of O_2). This corresponds to 75% of the stoichiometric uptake expected for a 1:1 $Co-O_2$ complex. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors.

Preparation of [(Bu$_4$N)$_2$Co(CN)$_4$]·(HMT) (8). $(Bu_4N)_2Co(CN)_4$ (0.559 g, 0.863 mmol) was dissolved in anhydrous DMF (10 mL). To this solution was added a solution of hexamethylenetetraamine (0.257 g, 1.83 mmol) in DMF (50 mL). The reaction mixture turned light green in color. After approximately 5 min of the mixture being stirred at room temperature, diethyl ether (150 mL) and hexane (150 mL) were added to precipitate out the product as a light green powder. After the product was washed with fresh hexane (2 × 20 mL) and ether (3 × 20 mL), the material was suction filtered dry. $[(Bu_4N)_2Co(CN)_4]$·(HMT) was isolated as a light green powder (0.438 g, 72% yield). FTIR (Nujol,

N_2): 2102 (m), 2091 (sh), 2080 (s), 2042 (w) cm^{-1} (CN); 1246, 1232, 1052, 1043, 1023, 1002, 824, 811, 694, 666 cm^{-1} (HMT). FTIR (Nujol, air): 2123 (w), 2108 (sh), 2102 (m), 2081 (s), 2043 (w) cm^{-1} (CN); 1143 (m) cm^{-1} (Co(III)$-O_2^-$). Anal. Calcd for $C_{42}H_{84}N_{10}Co$: Co, 7.48; C, 64.01; H, 10.74; N, 17.77. Found: Co, 7.57; C, 63.66; H, 10.64; N, 17.44.

Maximum oxygen uptake observed by gravimetric analysis: 1.09 wt % (760 Torr of O_2). This corresponds to 27% of the stoichiometric uptake expected for a 1:1 Co$-O_2$ complex. No attempt was made to determine the dependence of the rate of oxygen uptake on particle size, temperature, O_2 partial pressure, or other factors.

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Supporting Information Available: Experimental details for the structure determination (2 pages). An X-ray crystallographic file, in CIF format, for compound **2** is available. Access and ordering information is given on any current masthead page.

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