Solid state cyanocobaltates that reversibly bind dioxygen: synthesis, structure and reactivity relationships

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Abstract

New pentacyanocobaltate compositions, $Li_3Co(CN)_5 \cdot 1.42DMF \cdot 0.48DMAC$ (**3**) (DMF = N,N-dimethylformamide, DMAC = N,N-dimethylacetamide) and $Mg_{1.5}Co(CN)_5 \cdot 2DMF$ (**4**) were prepared and as solids were found to reversibly bind dioxygen. Compound **3** was found to be more stable to repeated cycling between O_2 and N_2 atmospheres than the previously reported $Li_3Co(CN)_5 \cdot 2DMF$ (**2**). The cyanide stretching frequencies of **3** and **4** are significantly higher than for $(Et_4N)_3Co(CN)_5$, an irreversible O_2 sorbent. This is ascribed to a loss of electron density from cobalt due to interaction of cyanide with the cations $Li(1+)$ and $Mg(2+)$ resulting in reversible O_2 binding.

Keywords: Cyanide ligand; Cobalt; Oxygen complex

1. Introduction

The reversible binding of dioxygen on to metal complexes is a subject of continuing academic and industrial interest [1]. It has been a long sought practical goal by many investigators to arrive at metal complex oxygen carriers of sufficient O_2 capacity, reaction kinetics and stability for use in absorption processes for the non-cryogenic separation of air [2]. Recently, work in our laboratories resulted in the discovery of a new family of solid state reversible O_2 carriers [3]. The first two members of this family are the polymeric lithium cyanocobaltates $Li_3Co(CN)_5 \cdot 4DMF$ (**1**), and $Li_3Co(CN)_5 \cdot 2DMF$ (**2**). Although both compounds reversibly absorb O_2 forming superoxo com-

plexes, **2** reacts more rapidly and has a remarkable O_2 capacity (55 std cm^3/g). We attempted to extend this chemistry by using DMAC instead of DMF as the $Li(1+)$ coordinating ligand. A structural analog of **2** with the composition $Li_3Co(CN)_5 \cdot 1.42DMF \cdot 0.48DMAC$ (**3**) was isolated. While **3** has a lower O_2 capacity (~ 40 std cm^3/g) than **2**, it is much more stable to repeated O_2/N_2 cycling. This paper also discusses a new composition, $Mg_{1.5}Co(CN)_5 \cdot 2DMF$ (**4**) which reversibly binds O_2.

2. Results and discussion

2.1. Synthesis of $Li_3Co(CN)_5 \cdot 1.42DMF \cdot 0.48DMAC$ (3) and studies of its O_2 reactivity

The reaction of lithium cyanide with cobalt chloride in DMF in a 5.2:1 M ratio gives a

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green precipitate [4] which we have previously shown by single crystal X-ray analysis to have the composition $Li_3Co(CN)_5 \cdot 4DMF$ (1) [3]. The structure of this material comprises $Co(CN)_5$ units crosslinked by various $(Li \cdot DMF)^+$ groups into a polymeric lattice. By heating 1 to 160°C under flow of N_2 a new crystalline composition of the formula $Li_3Co(CN)_5 \cdot 2DMF$ (2) was obtained. Both 1 and 2 reversibly bind O_2 in a pressure reversible mode, with the latter displaying faster reaction kinetics and a higher O_2 capacity.

Attempts were made to reproduce this chemistry using DMAC as the reaction medium instead of DMF. When an excess of lithium cyanide was reacted with cobalt chloride in DMAC, a green precipitate was obtained as in the reaction performed in DMF. Its infrared spectrum showed a strong cyanide band at 2099 cm^{-1}, similar to that of 1. This solid was heated to 160°C under N_2 in the hope of generating a reversible O_2 sorbent. Unfortunately, the resulting blue material did not react with O_2.

In order to obtain a reversible O_2 sorbent, the synthesis was done in essentially a mixed solvent by adding a solution of cobalt chloride in DMAC to 5.2 equivalents of lithium cyanide in DMF. A green solid was isolated which displayed an X-ray powder pattern that is very similar to 1, as shown in Fig. 1. When heated on a TGA instrument to 160°C under flow of N_2 a weight loss of 31% was observed. This weight loss is similar to that seen upon heating 4. Elemental analyses on a larger (1 g) sample, prepared and heat treated the same way, are consistent with the formula $Li_3Co(CN)_5 \cdot$ 1.42DMF $\cdot$ 0.48DMAC (3). An infrared spectrum of 3 showed the same three characteristic cyanide stretching frequencies at 2087, 2102, and 2117 cm^{-1} that were seen for 2 [3]. Also, bands seen in the carbonyl region at 1652 and 1613 cm^{-1} in a 3:1 ratio of intensities are ascribed to the presence of two different amides.

A sample of 3 was examined for reactivity with O_2. Upon introduction of O_2 for 5 min at 25°C, a weight gain corresponding to an absorp-
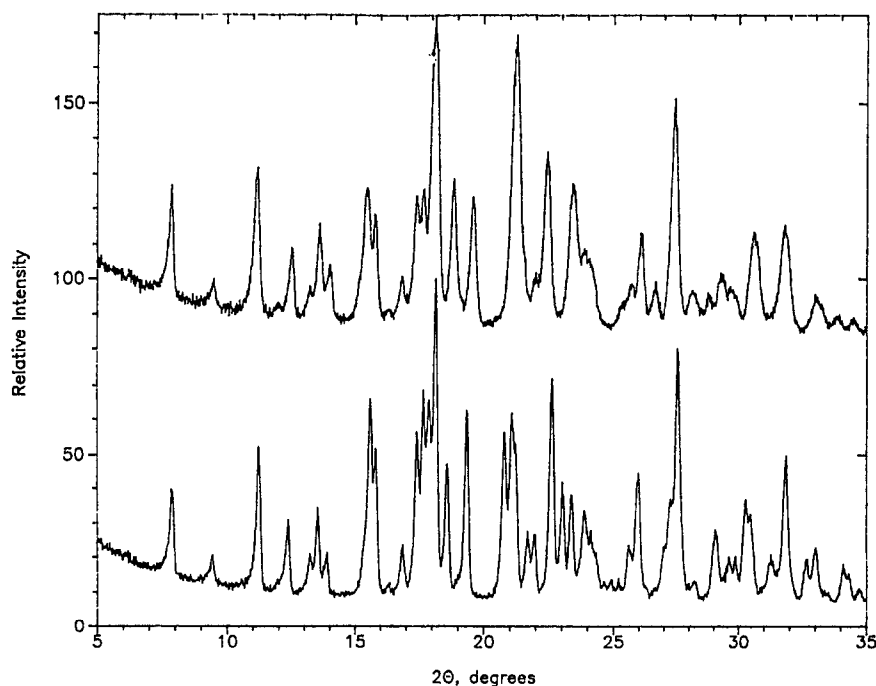

Fig. 1. X-ray powder patterns of $Li_3Co(CN)_5 \cdot 4DMF$ (1) (upper curve), and of product from 1:1 DMF/DMAC reaction (lower curve)

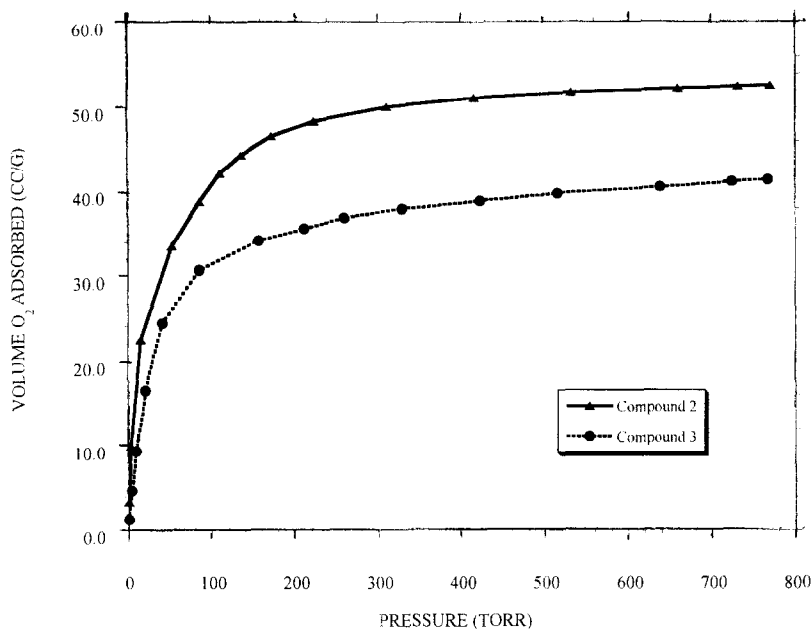Fig. 2. Dioxygen equilibrium absorption isotherms at 25°C for $Li_3Co(CN)_5 \cdot 2$ DMF (**2**), and $Li_3Co(CN)_5 \cdot 1.42$DMF $\cdot 0.48$DMAC (**3**).

tion of 1.5 mmol O_2/g was seen. Approximately 95% of this O_2 was desorbed by flushing with N_2 for 20 min. Equilibrium dioxygen absorption isotherms for **2** and **3** are shown together for comparison in Fig. 2. These volumetric O_2 measurements on **3** showed an over-
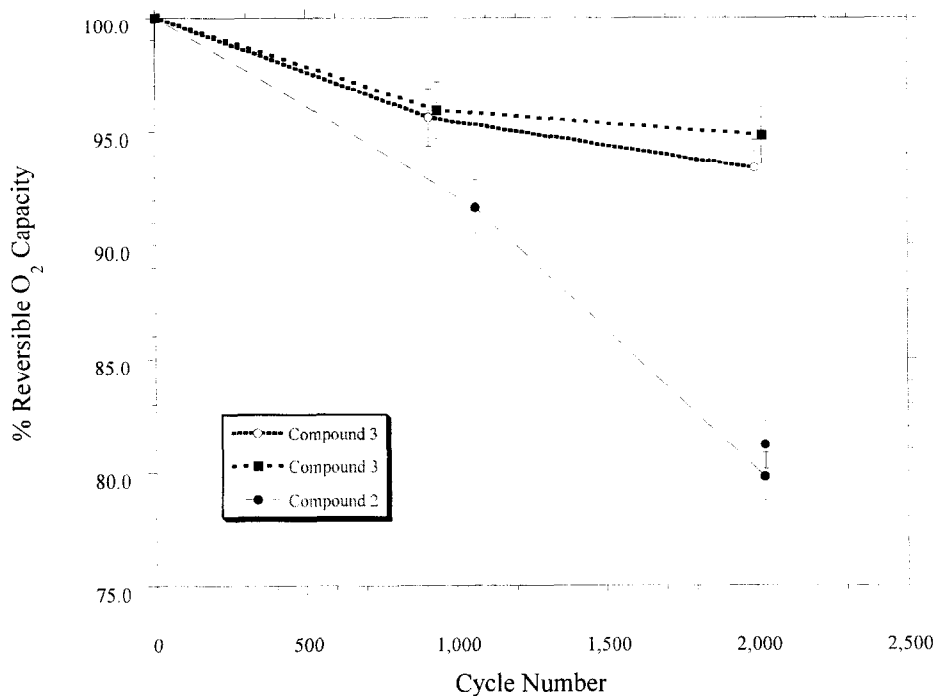
Fig. 3. Stability studies on two samples of compounds **3** and one sample of compound **2** under cycling conditions of 4 min dry air/4 min N_2 at 30°C.

all uptake of ∼ 40 cc O_2/g (1.78 mmol O_2/g) at one atmosphere of O_2 as compared to ∼ 55 cc O_2/g (2.4 mmol O_2/g) for compound **2** under the same conditions. Significantly however, **3** proved to be more stable than **2** under repeated O_2/N_2 cycling. This is evident in Fig. 3 which shows the reversible O_2 capacity of **2** and **3** when cycled in a TGA apparatus with alternate 4 min flows of dry air and N_2. The decomposition of **2** and **3** under O_2/N_2 cycling is accompanied by a decrease in crystallinity for the samples, and is more evident for the less stable compound **2**.

2.2. Synthesis of $Mg_{1.5}Co(CN)_5 \cdot \sim 2DMF$ (4) and studies of its O_2 reactivity

Having demonstrated that the O_2 binding properties could be altered by changing the coordination sphere around Li(1 +), we considered whether Li(1 +) might be replaced by Mg(2 +) to give reversibly O_2 reactive solids. Tetraethylammonium pentacyanocobaltate $(Et_4N)_3Co(CN)_5$ [5], was reacted with 1.6 equivalents of magnesium triflate in DMF to give a green solution. Addition of a large excess of diethyl ether afforded a green precipitate. The same solid could also be obtained by reacting the lithium salts **2** or **3** with an excess of magnesium triflate. These products were amorphous solids which consistently analyzed for Mg:Co atom ratios of ∼ 1.5:1. Total elemental analyses on a representative sample gave the formula; $Mg_{1.5}Co(CN)_5 \cdot \sim 2DMF$ (4). The solid state visible/near infrared spectrum of **4** displays a weak band at 611 nm, and a stronger broad band at ∼ 1050 nm, similar to the fea-

tures seen for **2** and other pentacyanocobaltates [3–5].

The infrared spectrum of **4** displays a strong cyanide stretch at ∼ 2120 cm^{-1}. On exposure to dry air the compound turns from green to red; the CN stretch is blue shifted by 40 cm^{-1} and a new absorption peak characteristic of a bound superoxo species is seen at 1128 cm^{-1} [6]. A sample of **4** was transferred without air exposure to a TGA instrument. Upon admission of O_2, there was a rapid increase in weight, which could be reversed by flushing with N_2. The sample was cycled alternately between 5 min O_2/40 min N_2 for 50 cycles. The initial O_2 uptake was 0.78 mmol O_2/g, however, this diminished to 0.36 mmol O_2/g at the end of 50 cycles. Thus, while **4** acts as a reversible O_2 sorbent its lifetime under O_2/N_2 cycling is less than that of **2** and **3**.

2.3. Correlation of cyanide stretching frequency with dioxygen reversibility

In our work on cyanometallates we have found that the position of the cyanide stretching frequency is directly related to the ability of the compound to reversibly bind dioxygen. Table 1 displays the cyanide stretching frequencies of the new materials **1** to **4** which can be compared with that for the irreversible O_2 sorbent, $(Et_4N)_3Co(CN)_5$. The higher cyanide stretching frequency for the new materials is attributed to the interaction of Li(1 +) or Mg(2 +) with cyanide. This leads to a reduction of electron density at the cobalt thus permitting reversible O_2 binding.

Table 1
Correlation of the cyanide stretching frequency for specific cyanocobaltates with dioxygen reversibility

Cyanocobaltate	Cyanide stretching frequency (cm^{-1})	Reversible O_2 binding
$(Et_4N)_3Co(CN)_5$	2066	no
$Li_3Co(CN)_5 \cdot 4DMF$ (1)	2100	yes
$Li_3Co(CN)_5 \cdot 2DMF$ (2)	2087, 2102, 2117	yes
$Li_3Co(CN)_5 \cdot 1.42DMF \cdot 0.48DMAC$ (3)	2087, 2102, 2117	yes
$Mg_{1.5}Co(CN)_5 \cdot \sim 2DMF$ (4)	2120	yes

2.4. Conclusion

The irreversible binding of O_2 to penta-cyanocobaltate is well documented in the literature [5]. We previously reported on the preparation of $Li_3Co(CN)_5 \cdot 2DMF$ (2) which as a solid reversibly binds O_2 [3]. Attempts to prepare a material with similar properties by simply replacing DMF with DMAC were unsuccessful. However, by using a mixed DMF/DMAC reaction solvent, a new complex $Li_3Co(CN)_5 \cdot$ 1.42DMF · 0.48DMAC (3) was prepared, which is isostructural with 2. Compound 3 is much more stable to O_2/N_2 cycling than 2, which we attribute to its having a more rigid lattice. Our hypothesis that the O_2 reversibility in these solids is due to a reduction of charge on cobalt by Li(1 +) interacting with cyanide is now further supported by the synthesis of the new reversible sorbent, $Mg_{1.5}Co(CN)_5 \cdot \sim 2DMF$ (4). This reduction in electron density leads to the higher cyanide stretching frequencies seen for 1, 2, 3, and 4 relative to $(Et_4N)_3Co(CN)_5$, an irreversible O_2 sorbent.

3. Experimental

3.1. General methods

All chemical synthesis and O_2 sorbent operations were performed using standard Schlenck line or inert atmosphere dry box techniques. Reaction solvents such as DMF or DMAC were purchased from Aldrich Chemicals as 'sure seal' reagents and used as received. Thermogravimetric analysis (TGA) experiments were carried out by using a Perkin Elmer TGS2 and TA2950 instruments equipped for use with controlled atmospheres (O_2 and or N_2). Infrared spectra were taken using a Nicolet 510 FTIR spectrometer. Vis–near IR spectra were recorded with a Perstorp Model 2400 near IR spectrometer. Routine X-ray powder diffraction measurements were made with a Siemen's D-500 powder diffractometer using a controlled atmosphere cell. The O_2 isotherm measurements were mea-

sured on a static volumetric apparatus with the sample immersed in a thermostat bath. The pressure was measured with a capacitance transducer having an accuracy of 0.15%.

3.2. Synthesis of $Li_3Co(CN)_5 \cdot 1.42DMF \cdot 0.48DMAC$ (3)

Anhydrous cobalt chloride (0.24 g, 1.92 mmol) dissolved in ~ 25 ml of DMAC was added to ~ 21 ml of 0.5 M LiCN (Aldrich) in DMF. The yellow solution was allowed to stand overnight giving a green very finely crystalline product. This was filtered, washed with 2×20 ml of ether and dried in vacuum for 12 h. A small sample was loaded on a TGA analyzer without exposure to air. Upon heating the sample at $5°/min$ to 160°C under 100 cc N_2/min and holding at that temperature for 20 min, a weight loss of 31.2% was seen. Elemental analyses on a larger (1 g) sample prepared and heat treated the same way were consistent with the formula: $Li_3Co(CN)_5 \cdot 1.42DMF \cdot 0.48DMAC$. Calcd (%): C, 37.76; H, 6.01; N, 27.19; Li, 5.85; Co, 16.58. Found (%): C, 37.59; H, 6.02; N, 27.09; Li, 5.81; Co, 16.51.

3.3. Preparation of $Mg_{1.5}Co(CN)_5 \cdot \sim 2DMF$ (4)

The compound $(Et_4N)_3Co(CN)_5$ [5] (0.997 g, 1.7 mmol) was stirred in ~ 40 ml of DMF for 5 min. In a separate vessel, $Mg(CF_3SO_3)_2$ (0.829 g, 2.57 mmol) was dissolved in 40 ml of DMF with warming. After cooling to room temperature this solution was added to the $(Et_4N)_3Co(CN)_5$ in DMF. The mixture was swirled once and filtered through a medium porosity frit. A large excess of diethyl ether (250 ml) was poured into the green filtrate thus precipitating a light green solid. This was collected by filtration, washed with 50 ml of ether, 50 ml of acetonitrile and then by 50 ml of ether again to yield a yellow green powder. This powder was dried in vacuum overnight. Calcd. for $Mg_{1.5}Co(CN)_5 \cdot 2.17DMF$. Calcd. (%): Mg, 9.49; Co, 15.34; C, 35.96; H, 3.95; N, 26.14.

Found (%): Mg, 10.04, Co, 15.35; C, 35.99; H, 4.20; N, 25.17.

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