424 *Inorg. Chem.* **1999,** *38,* 424−425

The First Structurally Characterized Discrete Dinuclear μ-Cyano Hexacyanoferrate Complex

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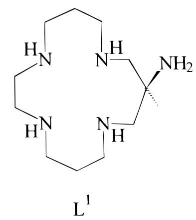
Received August 25, 1998

The complex anions hexacyanoferrate(II) and hexacyanoferrate(III) are among the oldest known coordination compounds. The reaction of Fe^{3+}_{aq} and $[Fe(CN)_6]^{4-}$ to form the intensely colored Prussian Blue (or Fe^{2+}_{aq} with $[Fe(CN)_6]^{3-}$ to give the same products) was employed almost 300 years ago to generate pigments for use in inks and paints. In Prussian Blue, the main structure comprises arrays of high-spin Fe^{3+} centers bridged by $[Fe(CN)_6]^{4-}$ units,[2] where a metal-to-metal charge transfer (MMCT, intervalence) transition from $[Fe(CN)_6]^{4-}$ to Fe^{3+} gives rise to its intense blue color. If the mixed valence Prussian Blue is oxidized to its $Fe^{3+}/[Fe(CN)_6]^{3-}$ analogue (Prussian Brown) or reduced to the $Fe^{2+}/[Fe(CN)_6]^{4-}$ relative (Prussian White), the intense blue color is lost. This feature has found application in electrochromic materials,[3] where a system may be switched, reversibly, between two contrasting colored states by a simple electrochemical reaction. The strong coupling between metal centers bridged by cyano ligands has also been exploited in the development of molecular magnetic materials based on ferricyanide and other transition metal analogues.[4]

Despite the multitude of cyano complexes in the literature,[5] and the intense degree of interest in the field of hexacyanoferrate complexes in particular, control over the assembly of oligonuclear arrays based on $[Fe(CN)_6]^{4-/3-}$ anions still presents a major challenge. There are six potentially bridging sites at each $[Fe(CN)_6]^{4-}$ unit, and polymeric arrays comprising linear (1D), square (2D), or cubic (3D) structures will generally result if either ferro- or ferricyanide is mixed with a labile metal ion or complex. Kinetic[6] and spectroscopic[7] studies of *discrete* dinuclear, cyano-bridged complexes of hexacyanoferrates have been reported, but remarkably none has been structurally characterized. In several cases, mixed valence complexes containing ferro- or ferricyanide are thermodynamically unstable toward comproportionation[8] or exhibit photolability.[9] This has perhaps hampered attempts to produce X-ray-quality single crystals of these compounds.

In order to make discrete dinuclear μ-cyano complexes of ferro- or ferricyanide, one must employ a metal complex bearing a *single* reactive coordination site. We have achieved this goal through reaction[10] of the *trans*-chloropentaaminecobalt(III) complex of a known[11] macrocycle L^1 with $[Fe(CN)_6]^{4-}$. The proposed mechanism for the formation of $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ is given in steps (i)−(iv); and is based on the fairly well understood reactions between pentaaminecobalt(III) complexes and ferrocyanide.[12] Typically, in the reactions of acyclic pentaamine analogs, the Co^{II} complex formed in step (iii) dissociates and a precipitate of $Co^{II}_3[Fe^{III}(CN)_6]$ forms unless a scavenging ligand such as EDTA is present. However, the Co^{II} intermediate in the present system is stabilized by strong binding with the macrocycle L^1.[13]



L^1

$$[Co^{III}L^1Cl]^{2+} + [Fe^{II}(CN)_6]^{4-} \rightleftharpoons \{[Co^{III}L^1Cl];[Fe^{II}(CN)_6]\}^{2-} \quad \text{(i)}$$

$$\{[Co^{III}L^1Cl];[Fe^{II}(CN)_6]\}^{2-} \rightarrow \{[Co^{II}L^1Cl];[Fe^{III}(CN)_6]\}^{2-} \quad \text{(ii)}$$

$$\{[Co^{II}L^1Cl];[Fe^{III}(CN)_6]\}^{2-} \rightarrow [L^1Co^{II}\text{-NC-}Fe^{III}(CN)_5]^- + Cl^- \quad \text{(iii)}$$

$$[L^1Co^{II}\text{-NC-}Fe^{III}(CN)_5]^- \rightarrow [L^1Co^{III}\text{-NC-}Fe^{II}(CN)_5]^- \quad \text{(iv)}$$

The solid state infrared spectrum of $Na[L^1Co(\mu\text{-NC})Fe(CN)_5]$ exhibits three distinct cyano stretching vibrations at 2042, 2078, and 2122 cm^{-1}, with the lowest-frequency band being the most intense. By comparison with $K_4[Fe(CN)_6]$ ($\bar{\nu}_{CN}$ 2033 cm^{-1}) the low-frequency vibration is assigned to the four equivalent "equatorial" cyano ligands. The high-frequency vibration is then assigned as the μ-cyano ligand and the middle band as the axial CN ligand trans to the bridging ligand. This assignment is also consistent with vibrational spectroscopic studies of similar CN-

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(10) To a solution of *trans*-$[CoL^1Cl](ClO_4)_2$ (2.0 g, 3.7 mmol) in water (200 mL, pH 5.6) was added $K_4[Fe(CN)_6]$ (1.08 g, 2.9 mmol), which gave an immediate darkening of the solution. The mixture was then stirred at 60 °C for 24 h. Column chromatography (Cellex D anion exchange, 0.1 M $NaClO_4$) gave a broad red band, which was concentrated to a small volume (*ca.* 5 mL). Precipitation was achieved by vapor diffusion of acetone into the concentrated solution to afford crystals suitable for X-ray work (0.4 g, 18%). Elem. anal. calcd for $C_{18}H_{53}CoFeN_{11}NaO_{12}$: C, 28.69; H, 7.09; N, 20.45. Found: C, 29.0; H, 6.1; N, 20.5. ^{13}C NMR (50.3 MHz, D_2O, 23 °C): δ 21.9, 26.4, 49.9, 51.1, 54.7, 61.5, 66.6, 177.9, 179.2, and 192.1 ppm. Electronic spectrum (H_2O) λ_{max} 528 nm (ϵ 420 M^{-1} cm^{-1}), 462 (ϵ 370), 326 (ϵ 410), and 218 (ϵ 32 300). Infrared (KBr disc) $\bar{\nu}_{CN}$ (cm^{-1}): 2042, 2078, and 2122.

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(13) It is unlikely that hydrolysis of the chloro ligand to form $[CoL^1(OH_2)]^{3+}$ as the reactive species precedes step (ii) (k_{OH} $[CoL^1Cl]^{2+}$ = 8000 M^{-1} s^{-1} at 25 °C) , as the hydrolysis reaction at pH 5.6 ($t_{1/2} \approx 6$ h), is considerably slower than the observed reaction between the Co^{III} and Fe^{II} species (see ref 12c).

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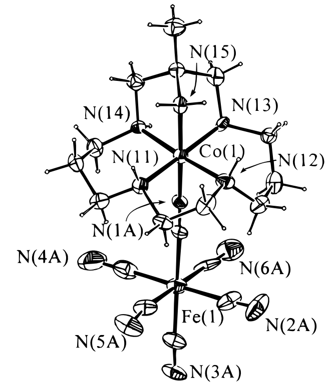

Figure 1. View of the $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ anion (30% probability ellipsoids shown). Selected bond lengths (Å): Co(1)−N(11), 1.97(2); Co(1)−N(12), 1.97(2); Co(1)−N(13), 1.95(2); Co(1)−N(14), 1.94(1); Co(1)−N(15), 1.93(2); Co−N(1A), 1.88(2); Fe−C, 1.82(2)−1.98(2).

bridged complexes.[14] The ^{13}C NMR resonances of the cyano ligands are also sensitive to their environment. The bridging CN ligand is furthest downfield (192.1 ppm), and well separate from the trans CN (179.2 ppm) and four equatorial CN ligands (177.9 ppm).

The X-ray crystal structure[15] of $Na[L^1Co(\mu\text{-NC})Fe(CN)_5]\cdot 4H_2O$ has been determined. The asymmetric unit comprises the three independent complex anions, three counter ions and twelve water molecules. There are no significant differences between the three complex anions, and one of these is shown in Figure 1. Pentadentate coordination by the pendent arm macrocycle in a *trans-III* (*RSSR*) configuration is apparent, with the sixth coordination site of the Co atom being occupied by a μ-CN ligand (N-bound).

Cyclic voltammetry on $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ identified one-electron oxidation ($Fe^{III/II}$) and reduction ($Co^{III/II}$) processes. The $Fe^{III/II}$ couple ($E_{1/2}$ +0.39 V *vs* Ag/AgCl) is totally reversible (Figure 2, inset) and *ca.* 0.2 V more positive than for $[Fe(CN)_6]^{3-/4-}$ measured under the same conditions, illustrating the significant influence of the bound cationic Co^{III} complex on the redox couple. The $Co^{III/II}$ couple ($E_{1/2}$ −0.78 V *vs* Ag/AgCl) is irreversible, with almost complete loss of the anodic wave at a scan rate of 100 mV s^{-1}). High scan rates (>5 V s^{-1}) allow the observation of an anodic ($Co^{II} \rightarrow Co^{III}$) peak of comparable intensity to the forward wave, but peak distortion is seen because electron transfer kinetics become rate limiting.

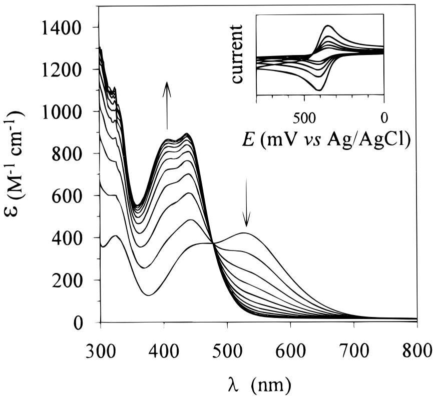

Figure 2. Aqueous UV−vis spectra of $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ upon addition of excess $K_2S_2O_8$. Spectra measured at 2 min intervals. Inset: cyclic voltammograms of $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ between 0 and 800 mV; scan rates 50, 100, 200, 400, and 1000 mV s^{-1}. Experimental conditions: glassy carbon working, Pt auxiliary, and Ag/AgCl reference electrodes, aqueous 0.1 M $NaClO_4$, scan rate 100 mV s^{-1}.

The solution electronic spectrum of $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ (Figure 2) exhibits relatively intense transitions in the visible region, by comparison with mononuclear Co^{III} analogues and $[Fe(CN)_6]^{4-}$, the latter being effectively transparent in the visible region. The maximum at 528 nm (ϵ 420 M^{-1} cm^{-1}) is assigned as a $Fe^{II} \rightarrow Co^{III}$ MMCT transition. According to theory,[16] the energy of the MMCT transition (E_{op}) in an asymmetric mixed valence complex is related to the reorganizational energy χ and the energy difference between the two redox isomers ΔE, *i.e.* $Co^{III}-Fe^{II}$ and $Co^{II}-Fe^{III}$ as shown by eq 1.

$$E_{op} = \Delta E + \chi \qquad (1)$$

Using the experimentally determined $Fe^{III/II}$ and $Co^{III/II}$ redox potentials of the dinuclear complex, we obtain a value of χ = 114.7 kJ mol^{-1} (9588 cm^{-1}). The bandwidth at half-height $\Delta\bar{\nu}_{1/2}$ of the MMCT transition at 300 K is also related to the reorganizational energy (in units of cm^{-1}) by eq 2.

$$\Delta\bar{\nu}_{1/2} = 48.06\,\chi^{1/2} \qquad (2)$$

Using this relationship, we calculate a theoretical bandwidth of 4706 cm^{-1}, which compares well with that found experimentally (4550 cm^{-1}).

Quantitative oxidation of $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ to the $Co^{III}-Fe^{III}$ analogue $[L^1Co(\mu\text{-NC})Fe(CN)_5]$ has been achieved both chemically with $K_2S_2O_8$ and electrochemically by bulk electrolysis at +0.6 V *vs* Ag/AgCl. In both cases, a bright yellow complex is obtained. The spectral changes accompanying this oxidation are shown in Figure 2. The isosbestic point at *ca.* 480 nm is indicative of a clean redox process involving only two absorbing species. Disapperance of the maximum at 528 nm upon oxidation is further supporting evidence for this band being an intervalence transition of the precursor $Co^{III}-Fe^{II}$ complex. The ligand field stregth of a μ-cyano group is comparable with that of NH_3,[9] so we would expect the lower energy d−d maximum of the $Co^{III}L^1(NC)$ chromophore ($^1A_{1g} \rightarrow {}^1T_{1g}$, O_h) to be around 460 nm by comparison with hexaaminecobalt(III) analogues. The maximum at 462 nm in the spectrum of $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ is likely to be the first d−d maximum of the $Co^{III}N_6$ chromophore.

We have demonstrated that the novel dinuclear complex $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ exhibits redox bistability. If we can stabilize the $Co^{II}-Fe^{II}$ form by avoiding rearrangement of the Co^{II} centre upon reduction, then a *tristable* redox switch may be accessible. We are currently pursuing this goal by employing Co^{III} complexes of other macrocyclic ligands of different ring sizes and containing donor atoms other than nitrogen.

Acknowledgment. Financial support of the Univeristy of Queensland and the Direccion General de Investigacion Cientifica y Tecnica is gratefully ackowledged.

Supporting Information Available: Crystallographic data, in CIF format, and a multiple scan cyclic voltammogram of $[L^1Co(\mu\text{-NC})Fe(CN)_5]^-$ are available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystal data for $Na[L^1Co(\mu\text{-NC})Fe(CN)_5]\cdot 4H_2O$: $C_{18}H_{37}CoFeN_{11}NaO_4$, M_r = 609.4, monoclinic space group $P2_1$, a = 21.224(5) Å, b = 10.7537(8) Å, c = 22.723(5) Å, β = 116.76(1)°, V = 4631(2) Å^3, Z = 6 (three independent formula units), ρ = 1.311 g cm^{-3}, μ = 10.61 cm^{-1}, $F(000)$ = 1908. Of 8598 independent reflections collected on an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, $\omega-2\theta$ scans, $2 < \theta < 25°$), 4158 were observed ($F > 2\sigma(F)$). Absorption correction (ψ scans) was performed with XTAL3.2. The structure was solved by direct methods with SHELXS86 and refined by full matrix least squares with SHELXL93. Alkyl and amine H atoms were included at estimated positions, water H atoms were not modeled. At convergence, R1 = 0.0924 and wR2 = 0.2463 for 943 refined parameters, goodness-of-fit = 1.005. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre.

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