# New Cyanometalate Building Units:
## Synthesis and Characterization of [Re(CN)$_7$]$^{3-}$ and [Re(CN)$_8$]$^{3-}$

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The past decade has witnessed an extraordinary revival of transition metal−cyanide chemistry, fueled largely by interest in the magnetic and photomagnetic properties of cyano-bridged solids[1] and molecules.[2] The preparations for many of these compounds rely upon the use of homoleptic cyanometalate complexes as building units. To give but two examples, octahedral [M(CN)$_6$]$^{n-}$ complexes are employed in the synthesis of cubic Prussian blue-type solids with adjustable magnetic properties,[1a−f,h,i] while [M(CN)$_8$]$^{3-}$ (M = Mo, W) complexes can be incorporated into high-nuclearity clusters with ground states of record high spin.[2e,f] Thus, the synthesis of new cyanometalate complexes stands as a potent means of extending the range of accessible properties in cyano-bridged compounds.[3] Moreover, second- and third-row transition-metal complexes, which have been less thoroughly investigated, can be expected to deliver stronger magnetic exchange coupling and greater magnetic anisotropy to the materials.[4] With these factors in mind, we chose to explore the synthesis of new homoleptic rhenium−cyanide complexes.

To date, only one such complex has been structurally verified: pentagonal bipyramidal [Re(CN)$_7$]$^{4-}$.[5] The most oft-cited preparation for this diamagnetic molecule is somewhat inconvenient, involving the reaction between K$_2$[ReCl$_6$] and KCN at 250 °C in a KSeCN melt.[6] Although the early literature contains many purported examples of other rhenium−cyanide complexes, nearly all of these formulations are now in doubt,[6] with the possible exception of [Re(CN)$_6$]$^{5-}$.[7] Here, we report the syntheses, structures, and spectral properties of two additional species: [Re(CN)$_7$]$^{3-}$ and [Re(CN)$_8$]$^{3-}$.

The synthesis of [Re(CN)$_7$]$^{3-}$ proceeds through a simple ligand exchange reaction. Under a pure dinitrogen atmosphere, solid (Bu$_4$N)CN (1.2 g, 4.5 mmol) was added to a solution of (Bu$_4$N)$_2$-[ReCl$_6$][8] (0.55 g, 0.62 mmol) in 2.0 mL of DMF. The mixture was stirred and heated at 85 °C for 3 days to give a yellow solid, which was collected by filtration and washed with successive aliquots of THF (3 × 10 mL) and ether (3 × 5 mL). Diffusion of THF vapor into a concentrated DMF solution of the solid afforded 0.52 g (76%) of (Bu$_4$N)$_3$[Re(CN)$_7$] (**1**) as yellow block-shaped crystals.[9] Compound **1** is stable in air both in the solid state and in nonprotic solvents, but gradually decomposes over the course of several days in oxygenated water. In contrast, [Re(CN)$_7$]$^{4-}$ rapidly oxidizes in air.[6] The cyclic voltammogram of **1** in acetonitrile displays a [Re(CN)$_7$]$^{3-/4-}$ redox couple centered at $E_{1/2} = -1.06$ V ($\Delta E_p =$ 140 mV) versus Cp$_2$Fe$^{0/1+}$.[10]

X-ray analysis[11] of a single crystal of **1** revealed [Re(CN)$_7$]$^{3-}$ to adopt the pentagonal bipyramidal geometry depicted in Figure 1. The complex closely approaches $D_{5h}$ symmetry, with the carbon atoms of the five equatorial cyanide ligands (C(3)−C(7)) forming a nearly perfect equilateral pentagon. Its Re−C distances, which fall within the range 2.064(10)−2.123(11) Å, are comparable to those observed for [Re(CN)$_7$]$^{4-}$ in K$_4$[Re(CN)$_7$]·2H$_2$O (2.077(3)− 2.099(6) Å).[5]
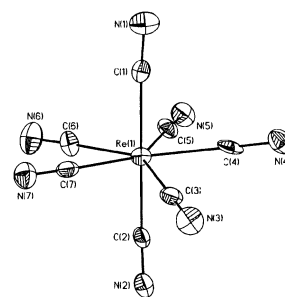


**Figure 1.** Structure of a pentagonal bipyramidal [Re(CN)$_7$]$^{3-}$ complex in **1**; ellipsoids are drawn at the 40% probability level. Selected mean interatomic distances (Å) and angles (deg) for two crystallographically independent complexes: Re−C 2.09(2), C−N 1.17(1), C$_{eq}$−Re−C$_{eq}$ 72.4(9), C$_{ax}$−Re−C$_{eq}$ 90(4), C$_{ax}$−Re−C$_{ax}$ 178.6(6), Re−C−N 177(1).

The spectral and magnetic properties of **1** are consistent with [Re(CN)$_7$]$^{3-}$ having the $^2E_1''$ ground state expected for a pentagonal bipyramidal complex with a low-spin d$^3$ electron configuration. As measured using a SQUID magnetometer, the effective magnetic moment of 2.02 $\mu_B$ at 298 K indicates an $S = ^1/_2$ ground state with an average $g$ value of 2.33. The X-band EPR spectrum of an undiluted powder of **1** at 20 K is axial with $g_{||} = 3.66$ and $g_\perp = 1.59$, and shows hyperfine splitting in the parallel component with $A_{||} = 129$ G. The electronic absorption spectrum of **1** dissolved in acetonitrile differs little from the diffuse reflectance spectrum of the solid, suggesting that the complex maintains its pentagonal bipyramidal geometry in solution. These spectra display a band centered at 25 300 cm$^{-1}$ (395 nm) that can potentially be assigned to the lowest-energy spin-allowed component of the e$_1''$ → e$_2'$ transition. The analogous transition in [Mo(CN)$_7$]$^{4-}$ occurs at the slightly lower energy of 24 900 cm$^{-1}$.[12]

Efforts to incorporate this new paramagnetic building unit into cyano-bridged solids are underway. As with [Mo(CN)$_7$]$^{4-}$, the anisotropy of the structure and **g** tensor of [Re(CN)$_7$]$^{3-}$ can be anticipated to lend such solids highly anisotropic magnetic behavior.[1g,4a] In aqueous solution, however, initial reactions led to a product in which the complex had spontaneously reduced to the diamagnetic 18-electron species [Re(CN)$_7$]$^{4-}$. Heating a solution of **1** (60 mg, 55 $\mu$mol) and MnCl$_2$·4H$_2$O (60 mg, 0.30 mmol) in 3 mL of water at 85 °C for 5 days afforded 23 mg (61%) of [*fac*-Mn(H$_2$O)$_3$][*cis*-Mn(H$_2$O)$_2$][Re(CN)$_7$]·3H$_2$O (**2**) as light purple trapezoidal plate-shaped crystals.[13] X-ray analysis[11] showed **2** to exhibit an intricate three-dimensional framework polymorphic to that in [*mer*-Mn(H$_2$O)$_3$][*cis*-Mn(H$_2$O)$_2$][Mo(CN)$_7$]·4H$_2$O.[1g] Interestingly, attempts to prevent reduction of the rhenium by adding a variety of noncoordinating oxidants to the aqueous reaction mixture resulted instead in formation of [Re(CN)$_8$]$^{3-}$.

Currently, [Re(CN)$_8$]$^{3-}$ is still best prepared via oxidation of [Re(CN)$_7$]$^{3-}$ in the presence of manganese. A mixture of **1** (62 mg, 0.056 mmol), KIO$_4$ (28 mg, 0.12 mmol), and MnCl$_2$·4H$_2$O

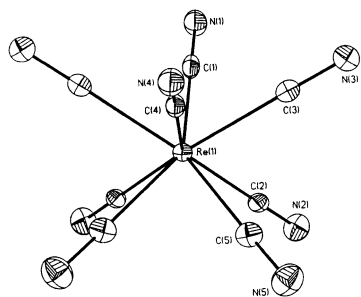**Figure 2.** Structure of the square antiprismatic [Re(CN)$_8$]$^{3-}$ complex in **4**·2MeCN; ellipsoids are drawn at the 50% probability level. Closely approaching $D_{4d}$ symmetry, the molecule resides on a crystallographic mirror plane that contains atoms N(4), C(4), Re(1), C(1), and N(1). Selected mean interatomic distances (Å) and angles (deg): Re−C 2.10(1), C−N 1.150(5), C−Re−C 76(3), 114.3(9), 142.5(3), Re−C−N 177.7(9).

(34 mg, 0.17 mmol) in 3 mL of deoxygenated water was heated at 85 °C for 24 h. The resulting solid was collected by filtration and washed with successive aliquots of water (3 × 10 mL) and THF (3 × 10 mL). The product was extracted into 2 mL of acetonitrile and, upon filtration, addition of 30 mL of ether gave 25 mg (35%) of (Bu$_4$N)$_3$[Re(CN)$_8$] (**3**) as a white precipitate.[14] Attempts to carry out the preparation in the absence of manganese left [Re(CN)$_7$]$^{3-}$ unreacted. Addition of K(CF$_3$SO$_3$) to a solution of **3** in acetonitrile afforded the water-soluble salt K$_3$[Re(CN)$_8$] (**4**) in essentially quantitative yield.[15]

Colorless rectangular plate-shaped crystals of **4**·2MeCN suitable for X-ray analysis[11] were obtained by layering a solution of **3** in acetonitrile onto a saturated solution of K(CF$_3$SO$_3$) in acetonitrile. Therein, [Re(CN)$_8$]$^{3-}$ adopts the square antiprismatic structure shown in Figure 2. Using a previously devised method for analyzing eight-coordinate geometries,[16] the minimal torsion angles, $\delta$, between adjacent triangular faces of the C$_8$ polyhedron were determined to be 0.0°, 2.6°, 51.5°, and 51.8°. For comparison, an ideal square antiprism exhibits $\delta_1 = \delta_2 = 0°$ and $\delta_3 = \delta_4 = 52.5°$. Thus, [Re(CN)$_8$]$^{3-}$ appears to be the most nearly perfect metal−octacyanide square antiprism yet encountered.[17]

The electronic absorption spectrum of **3** in acetonitrile is remarkably similar to spectra of the isoelectronic [M(CN)$_8$]$^{4-}$ (M = Mo, W) complexes, suggesting that [Re(CN)$_8$]$^{3-}$ converts to a dodecahedral geometry in solution.[18] Accordingly, the three bands centered at 436, 348, and 298 nm are tentatively assigned as spin-allowed d−d transitions. Like [Mo(CN)$_8$]$^{4-}$ and [W(CN)$_8$]$^{4-}$, [Re(CN)$_8$]$^{3-}$ is also photoactive upon exposure to UV radiation, presumably oxidizing to the paramagnetic 17-electron species [Re(CN)$_8$]$^{2-}$.[19] Indeed, the cyclic voltammogram of **3** in acetonitrile displays a [Re(CN)$_8$]$^{3-/2-}$ redox couple centered at $E_{1/2} = 0.999$ V ($\Delta E_p = 110$ mV) versus Cp$_2$Fe$^{0/1+}$. Thus, as observed for solids containing [Mo(CN)$_8$]$^{4-}$,[1j] cyano-bridged compounds incorporating [Re(CN)$_8$]$^{3-}$ could potentially exhibit a large photomagnetic response. Efforts are underway to probe this possibility in a [(MeOH)$_{24}$Mn$_9$Re$_6$(CN)$_{48}$] cluster, obtained simply by substituting [Re(CN)$_8$]$^{3-}$ for [Mo(CN)$_8$]$^{3-}$ in the preparation of the analogous high-spin molecule [(MeOH)$_{24}$Mn$_9$Mo$_6$(CN)$_{48}$].[2f]

Ultimately, it is hoped that the new cyanorhenate complexes disclosed here will be of utility in the design of magnetic materials with applications in information storage.[2g]

**Supporting Information Available:** Figures depicting the EPR spectrum of **1** and the structure of **2**, and tables for the structures of **1**, **2**, and **4**·2MeCN (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Characterization of **1**: Absorption spectrum (MeCN): $\lambda_{max}$ ($\epsilon_M$) 233 (8390), 258 (2280), 293 (2620), 315 (2030), 326 (1620, sh), 363 (899, sh), 378 (1200), 395 (1280) nm. IR: $\nu_{CN}$ 2112 (s), 2073 (s) cm$^{-1}$. $\mu_{eff}$ = 2.02 $\mu_B$ at 298 K. ES$^-$-MS (MeCN): $m/z$ 853.5 ({(Bu$_4$N)$_2$[Re(CN)$_7$]}$^-$). Anal. Calcd for C$_{55}$H$_{108}$N$_{10}$Re: C, 60.29; H, 9.94; N, 12.78. Found: C, 60.52; H, 9.73; N, 12.80.

(10) The analogous couple for a solution of K$_4$[Re(CN)$_7$]·H$_2$O in deoxygenated water occurs at $E_{1/2}$ = 0.643 V versus NHE: Marty, W.; Renaud, P.; Gampp, H. *Helv. Chim. Acta* **1987**, *70*, 375.

(11) Crystal and structure refinement parameters: **1**: C$_{55}$H$_{108}$N$_{10}$Re, $T$ = 152 K, $P2_1/c$, $Z$ = 8, $a$ = 22.9918(3) Å, $b$ = 23.0860(3) Å, $c$ = 23.0773(5) Å, $\beta$ = 90.755(1)°, $V$ = 12248.1(3) Å$^3$, $d_{calc}$ = 1.188 g/cm$^3$, $R_1$ = 0.0541, w$R_2$ = 0.1250. **2**: C$_7$H$_{16}$Mn$_2$N$_7$O$_8$Re, $T$ = 136 K, P1, $Z$ = 2, $a$ = 7.5397(3) Å, $b$ = 12.5924(6) Å, $c$ = 19.737(1) Å, $\alpha$ = 78.868(1)°, $\beta$ = 87.873(2)°, $\gamma$ = 88.026(2)°, $V$ = 1836.6(2) Å$^3$, $d_{calc}$ = 1.125 g/cm$^3$, $R_1$ = 0.0545, w$R_2$ = 0.1358. **4**·2MeCN: C$_{12}$H$_6$K$_3$N$_{10}$Re, $T$ = 134 K, *Pnma*, $Z$ = 4, $a$ = 17.2149(5) Å, $b$ = 10.5170(3) Å, $c$ = 9.3391(2) Å, $V$ = 1690.84(9) Å$^3$, $d_{calc}$ = 2.333 g/cm$^3$, $R_1$ = 0.0194, w$R_2$ = 0.0438. Data were collected on a Siemens SMART diffractometer using graphite monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation. Structures were solved by direct methods and refined against all data using SHELXTL 5.0.

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(13) Characterization of **2**. IR: $\nu_{CN}$ 2103 (s), 2058 (s) cm$^{-1}$. $\mu_{eff}$ = 8.35 $\mu_B$ at 298 K. Anal. Calcd for C$_7$H$_{16}$Mn$_2$N$_7$O$_8$Re: C, 13.48; H, 2.63; N, 16.03. Found: C, 13.79; H, 2.59; N, 16.03.

(14) Characterization of **3**. Absorption spectrum (MeCN): $\lambda_{max}$ ($\epsilon_M$) 196 (13200), 231 (sh), 252 (sh), 298 (168), 348 (76), 436 (22) nm. IR: $\nu_{CN}$ 2150 (s), 2135 (s) cm$^{-1}$. ES$^-$-MS (MeCN): $m/z$ 879.6 ({(Bu$_4$N)$_2$[Re(CN)$_8$]}$^-$). Anal. Calcd for C$_{56}$H$_{108}$N$_{11}$Re: C, 59.90; H, 9.70; N, 13.73. Found: C, 59.97; H, 9.81; N, 13.72.

(15) Characterization of **4**. IR: $\nu_{CN}$ 2155 (s), 2148 (s) cm$^{-1}$. ES$^-$-MS (MeCN): $m/z$ 472.9 ({(K)$_2$[Re(CN)$_8$]}$^-$). Anal. Calcd for C$_8$K$_3$N$_8$Re: C, 18.75; H, 0.00; N, 21.88. Found: C, 18.97; H, < 0.20; N, 21.51.

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