

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

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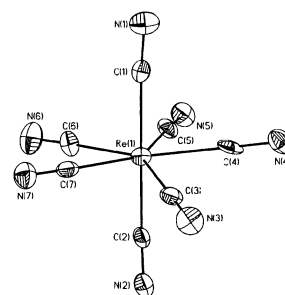
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The past decade has witnessed an extraordinary revival of transition metal–cyanide chemistry, fueled largely by interest in the magnetic and photomagnetic properties of cyano-bridged solids<sup>1</sup> and molecules.<sup>2</sup> The preparations for many of these compounds rely upon the use of homoleptic cyanometalate complexes as building units. To give but two examples, octahedral  $[\text{M}(\text{CN})_6]^{n-}$  complexes are employed in the synthesis of cubic Prussian blue-type solids with adjustable magnetic properties,<sup>1a–f,h,i</sup> while  $[\text{M}(\text{CN})_8]^{3-}$  ( $\text{M} = \text{Mo}, \text{W}$ ) complexes can be incorporated into high-nuclearity clusters with ground states of record high spin.<sup>2e,f</sup> Thus, the synthesis of new cyanometalate complexes stands as a potent means of extending the range of accessible properties in cyano-bridged compounds.<sup>3</sup> 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.<sup>4</sup> 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  $[\text{Re}(\text{CN})_7]^{4-}$ .<sup>5</sup> The most oft-cited preparation for this diamagnetic molecule is somewhat inconvenient, involving the reaction between  $\text{K}_2[\text{ReCl}_6]$  and KCN at 250 °C in a KSeCN melt.<sup>6</sup> Although the early literature contains many purported examples of other rhenium–cyanide complexes, nearly all of these formulations are now in doubt,<sup>6</sup> with the possible exception of  $[\text{Re}(\text{CN})_6]^{5-}$ .<sup>7</sup> Here, we report the syntheses, structures, and spectral properties of two additional species:  $[\text{Re}(\text{CN})_7]^{3-}$  and  $[\text{Re}(\text{CN})_8]^{3-}$ .

The synthesis of  $[\text{Re}(\text{CN})_7]^{3-}$  proceeds through a simple ligand exchange reaction. Under a pure dinitrogen atmosphere, solid  $(\text{Bu}_4\text{N})\text{CN}$  (1.2 g, 4.5 mmol) was added to a solution of  $(\text{Bu}_4\text{N})_2[\text{ReCl}_6]$ <sup>8</sup> (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 ( $3 \times 10$  mL) and ether ( $3 \times 5$  mL). Diffusion of THF vapor into a concentrated DMF solution of the solid afforded 0.52 g (76%) of  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_7]$  (**1**) as yellow block-shaped crystals.<sup>9</sup> 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,  $[\text{Re}(\text{CN})_7]^{4-}$  rapidly oxidizes in air.<sup>6</sup> The cyclic voltammogram of **1** in acetonitrile displays a  $[\text{Re}(\text{CN})_7]^{3-/4-}$  redox couple centered at  $E_{1/2} = -1.06$  V ( $\Delta E_p = 140$  mV) versus  $\text{Cp}_2\text{Fe}^{0/1+}$ .<sup>10</sup>

X-ray analysis<sup>11</sup> of a single crystal of **1** revealed  $[\text{Re}(\text{CN})_7]^{3-}$  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  $[\text{Re}(\text{CN})_7]^{4-}$  in  $\text{K}_4[\text{Re}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  (2.077(3)–2.099(6) Å).<sup>5</sup>

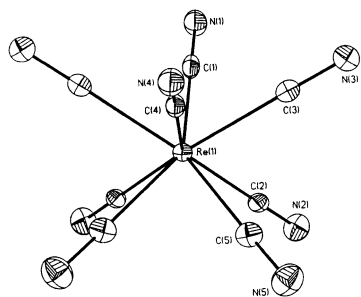


**Figure 1.** Structure of a pentagonal bipyramidal  $[\text{Re}(\text{CN})_7]^{3-}$  complex in **1**; ellipsoids are drawn at the 40% probability level. Selected mean interatomic distances (Å) and angles (deg) for two crystallographically independent complexes: Re–C 2.09(2), C–N 1.17(1),  $\text{C}_{\text{eq}}\text{–Re–C}_{\text{eq}}$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

The spectral and magnetic properties of **1** are consistent with  $[\text{Re}(\text{CN})_7]^{3-}$  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  $g_{\parallel} = 3.66$  and  $g_{\perp} = 1.59$ , and shows hyperfine splitting in the parallel component with  $A_{\parallel} = 129$  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  $25\,300 \text{ cm}^{-1}$  (395 nm) that can potentially be assigned to the lowest-energy spin-allowed component of the  $e_1'' \rightarrow e_2'$  transition. The analogous transition in  $[\text{Mo}(\text{CN})_7]^{4-}$  occurs at the slightly lower energy of  $24\,900 \text{ cm}^{-1}$ .<sup>12</sup>

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

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



**Figure 2.** Structure of the square antiprismatic  $[\text{Re}(\text{CN})_8]^{3-}$  complex in  $4 \cdot 2\text{MeCN}$ ; 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 ( $3 \times 10$  mL) and THF ( $3 \times 10$  mL). The product was extracted into 2 mL of acetonitrile and, upon filtration, addition of 30 mL of ether gave 25 mg (35%) of  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  (**3**) as a white precipitate.<sup>14</sup> Attempts to carry out the preparation in the absence of manganese left  $[\text{Re}(\text{CN})_7]^{3-}$  unreacted. Addition of  $\text{K}(\text{CF}_3\text{SO}_3)$  to a solution of **3** in acetonitrile afforded the water-soluble salt  $\text{K}_3[\text{Re}(\text{CN})_8]$  (**4**) in essentially quantitative yield.<sup>15</sup>

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

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

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.<sup>2g</sup>

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**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**· $2\text{MeCN}$  (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):  $\lambda_{\text{max}}$  ( $\epsilon_{\text{M}}$ ) 233 (8390), 258 (2280), 293 (2620), 315 (2030), 326 (1620, sh), 363 (899, sh), 378 (1200), 395 (1280) nm. IR:  $\nu_{\text{CN}}$  2112 (s), 2073 (s)  $\text{cm}^{-1}$ .  $\mu_{\text{eff}} = 2.02 \mu_{\text{B}}$  at 298 K. ES<sup>−</sup>-MS (MeCN):  $m/z$  853.5 ( $\{(\text{Bu}_4\text{N})_2[\text{Re}(\text{CN})_7]^{-}\}$ ). Anal. Calcd for  $\text{C}_{55}\text{H}_{108}\text{N}_{10}\text{Re}$ : 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  $\text{K}_4[\text{Re}(\text{CN})_7] \cdot \text{H}_2\text{O}$  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**:  $\text{C}_{55}\text{H}_{108}\text{N}_{10}\text{Re}$ ,  $T = 152$  K,  $P2_1/c$ ,  $Z = 8$ ,  $a = 22.9918(3)$  Å,  $b = 23.0860(3)$  Å,  $c = 23.0773(5)$  Å,  $\beta = 90.755(1)^\circ$ ,  $V = 12248.1(3)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.188$  g/cm<sup>3</sup>,  $R_1 = 0.0541$ ,  $wR_2 = 0.1250$ . **2**:  $\text{C}_7\text{H}_{16}\text{Mn}_2\text{N}_7\text{O}_8\text{Re}$ ,  $T = 136$  K,  $P1$ ,  $Z = 2$ ,  $a = 7.5397(3)$  Å,  $b = 12.5924(6)$  Å,  $c = 19.737(1)$  Å,  $\alpha = 78.868(1)^\circ$ ,  $\beta = 87.873(2)^\circ$ ,  $\gamma = 88.026(2)^\circ$ ,  $V = 1836.6(2)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.125$  g/cm<sup>3</sup>,  $R_1 = 0.0545$ ,  $wR_2 = 0.1358$ . **4**· $2\text{MeCN}$ :  $\text{C}_{12}\text{H}_8\text{K}_3\text{N}_{10}\text{Re}$ ,  $T = 134$  K,  $Pnma$ ,  $Z = 4$ ,  $a = 17.2149(5)$  Å,  $b = 10.5170(3)$  Å,  $c = 9.3391(3)$  Å,  $V = 1690.84(9)$  Å<sup>3</sup>,  $d_{\text{calc}} = 2.333$  g/cm<sup>3</sup>,  $R_1 = 0.0194$ ,  $wR_2 = 0.0438$ . Data were collected on a Siemens SMART diffractometer using graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  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:  $\nu_{\text{CN}}$  2103 (s), 2058 (s)  $\text{cm}^{-1}$ .  $\mu_{\text{eff}} = 8.35 \mu_{\text{B}}$  at 298 K. Anal. Calcd for  $\text{C}_7\text{H}_{16}\text{Mn}_2\text{N}_7\text{O}_8\text{Re}$ : 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):  $\lambda_{\text{max}}$  ( $\epsilon_{\text{M}}$ ) 196 (13200), 231 (sh), 252 (sh), 298 (168), 348 (76), 436 (22) nm. IR:  $\nu_{\text{CN}}$  2150 (s), 2135 (s)  $\text{cm}^{-1}$ . ES<sup>−</sup>-MS (MeCN):  $m/z$  879.6 ( $\{(\text{Bu}_4\text{N})_2[\text{Re}(\text{CN})_8]^{-}\}$ ). Anal. Calcd for  $\text{C}_{56}\text{H}_{108}\text{N}_{11}\text{Re}$ : C, 59.90; H, 9.70; N, 13.73. Found: C, 59.97; H, 9.81; N, 13.72.
- (15) Characterization of **4**: IR:  $\nu_{\text{CN}}$  2155 (s), 2148 (s)  $\text{cm}^{-1}$ . ES<sup>−</sup>-MS (MeCN):  $m/z$  472.9 ( $\{(\text{K})_2[\text{Re}(\text{CN})_8]^{-}\}$ ). Anal. Calcd for  $\text{C}_8\text{K}_2\text{N}_8\text{Re}$ : C, 18.75; H, 0.00; N, 21.88. Found: C, 18.97; H, < 0.20; N, 21.51.
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