Inorg. Chem. **2005**, *44*, 352–358

Inorganic Chemistry Article

Synthesis and Structural Characterization of Bi- and Trimetallic Octacyanometalate(IV) Complexes: $[\Delta,\Lambda\text{-}M^{II}(en)_3][cis\text{-}M^{II}(en)_2(OH_2)][M^{IV}(CN)_8]\cdot 2H_2O$ and $[cis\text{-}M^{II}(en)_2(OH_2)]_2[(\mu\text{-}NC)_2M^{IV}(CN)_6]\cdot 4H_2O$ (M^{II} = Mn, Co, Ni; M^{IV} = Mo, W)

Jeffrey R. Withers, Chad Ruschmann, Pasano Bojang, Sean Parkin, and Stephen M. Holmes*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

Received August 3, 2004

Treatment of $[M^{II}(en)_3][OTs]_2$ or methanolic ethylenediamine solutions containing transition metal *p*-toluenesulfonates (M^{II} = Mn, Co) with aqueous $K_4M^{IV}(CN)_8\cdot 2H_2O$ or $Cs_3M^{V}(CN)_8$ (M^{IV} = Mo, W; M^{V} = Mo) affords crystalline clusters of $[M^{II}(en)_3][cis\text{-}M^{II}(en)_2(OH_2)(\mu\text{-}NC)M^{IV}(CN)_7]\cdot 2H_2O$ (M^{IV} = Mo; M^{II} = Mn, **1**; Ni, **5**; M^{IV} = W; M^{II} = Mn, **2**; Ni, **6**) and $[cis\text{-}M^{II}(en)_2(OH_2)]_2[(\mu\text{-}NC)_2M^{IV}(CN)_6]\cdot 4H_2O$ (M^{IV} = Mo; M^{II} = Co, **3**; Ni, **7**; M^{IV} = W; M^{II} = Co, **4**) stoichiometry. Each cluster contains $cis\text{-}M^{II}(en)_2(OH_2)(\mu\text{-}NC)^{2+}$ units that likely result from dissociative loss of en from $[M^{II}(en)_3]^{2+}$, affording $cis\text{-}M^{II}(en)_2(OH_2)_2^{2+}$ intermediates that are trapped by $M^{IV}(CN)_8^{4-}$.

Introduction

The synthesis and characterization of molecule-based magnetic materials has experienced a resurgence of activity over the last 15 years.[1−5] Using a building block approach, a variety of cyanometalate networks and clusters can be prepared that exhibit interesting properties such as room temperature magnetism,[2−4] single molecule magnetism,[5−7] compensation,[8,9] electrochromism,[10,11] and photomagnetic[12−28] behavior. Cyanometalates are excellent building blocks for constructing molecule-based clusters and networks because cyanides generally form linear μ-CN linkages between two metal centers, stabilize a variety of transition metal centers

* To whom correspondence should be addressed. E-mail: smholm2@uky.edu.

(1) Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415−1417.
(2) Ferlay, S.; Mallah, T.; Ouahès, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701−703.
(3) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593−5594.
(4) Hatlevik, Ø.; Buschmann, W. E.; Zhang, J.; Manson, J. L.; Miller, J. S. *Adv. Mater.* **1999**, *11*, 914−918.
(5) Sokol, J. J.; Hee, A. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 7656−7657.
(6) Choi, H. J.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2004**, *43*, 1606−1608.
(7) Berlinguette, C. P.; Vaughn, D.; Cañada-Vilalta, C.; Galán-Mascarós, J. R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1523−1526.
(8) Ohkoshi, S.; Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Inorg. Chem.* **1997**, *36*, 268−269.
(9) Ohkoshi, S.; Abe, Y.; Fujishima, A.; Hashimoto, K. *Phys. Rev. Lett.* **1999**, *82*, 1285−1288.
(10) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *271*, 49−51.
(11) Ohkoshi, S.-I.; Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *J. Am. Chem. Soc.* **1998**, *120*, 5349−5350.
(12) Sato, O. *Acc. Chem. Res.* **2003**, *36*, 692−700.
(13) Arimoto, Y.; Ohkoshi, S.; Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hashimoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 9240−9241.
(14) Yokoyama, T.; Okamoto, K.; Ohta, T.; Ohkoshi, S.-I.; Hashimoto, K. *Phys. Rev.* **2001**, *65B*, 1−9.
(15) Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **1999**, *121*, 10591−10597.
(16) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704−705.
(17) Sato, O.; Einaga, Y.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Inorg. Chem.* **1999**, *38*, 4405−4412.
(18) Shimamoto, N.; Ohkoshi, S.; Sato, O.; Hashimoto, K. *Inorg. Chem.* **2002**, *41*, 678−684.
(19) Bleuzen, A.; Lomenech, C.; Escax, V.; Villain, F.; Varret, F.; Cartier dit Moulin, C.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 6648−6652.
(20) Cartier dit Moulin, C.; Villain, F.; Bleuzen, A.; Arrio, M.; Sainctavit, P.; Lomenech, C.; Escax, V.; Baudelet, F.; Dartyge, E.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 6653−6658.
(21) Ohkoshi, S.; Yorozu, S.; Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Appl. Phys. Lett.* **1997**, *70*, 1040−1042.
(22) Ohkoshi, S.; Einaga, Y.; Fujishima, A.; Hashimoto, K. *J. Electroanal. Chem.* **1999**, *473*, 245−249.
(23) Ohkoshi, S.; Mizuno, M.; Hung, G.; Hashimoto, K. *J. Phys. Chem.* **2000**, *40*, 9365−9367.
(24) Gu, Z.-Z.; Sato, O.; Iyoda, T.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem.* **1996**, *100*, 18289−18291.
(25) Gu, Z.-Z.; Sato, O.; Iyoda, T.; Hashimoto, K.; Fujishima, A. *Chem. Mater.* **1997**, *9*, 1092−1097.
(26) Ohkoshi, S.-I.; Hashimoto, K. *J. Photochem. Photobiol., C* **2001**, *2*, 71−88.
(27) Ohkoshi, S.; Machida, N.; Zhong, Z. J.; Hasimoto, K. *Synth. Met.* **2001**, *122*, 523−527.
(28) Rombaut, G.; Verelst, M.; Golhen, S.; Ouahab, L.; Mathonière, C.; Kahn, O. *Inorg. Chem.* **2001**, *40*, 1151−1159.

10.1021/ic048936m CCC: $30.25
© 2005 American Chemical Society
Published on Web 12/16/2004

and oxidation states, and efficiently communicate spin density information.[29-31]

The majority of cyanometalate networks and clusters generally contain hexacyanometalate or *fac*-$LM(CN)_3$ centers while far fewer contain octacyanometalates. The preparation of octacyanomolybdate(IV) networks of $M^{II}_2[Mo^{IV}(CN)_8]\cdot nH_2O$ ($2 \leq n \leq 9$) stoichiometry (M^{II} = Mn, Fe, Co, Ni, Cu, and Zn) was first reported in 1927, and the structures of several analogues have recently been determined.[28,32-35] Octacyanometalate materials are an interesting class of cyanometalates due to their propensity to photoeject electrons and form lattices that exhibit photoinduced magnetization changes; analogues containing $Cu^{II}/Mo(CN)_8^{n-}$ and $Co^{II/III}/W(CN)_8^{n-}$ units are reported to exhibit reversible photoinduced magnetization changes, and we anticipate that incorporation of such bistable materials into electronic circuitry may ultimately afford molecule-based nanoscale switchable devices.[13,26-28,36-39]

While limited success in crystallizing octacyanometalate networks via hydrothermal and slow diffusion methods was realized, we began to explore the utility of amine ligands to direct and limit the number of cyano linkages formed between transition metal centers. Bidentate amines such as ethylenediamine (en) and 1,3-propanediamine (tn) have been extensively used to prepare a variety of so-called "expanded Prussian blue solids",[40] but relatively few octacyanometalate derivatives are known;[41-48] octacyanometalate clusters containing such amines are also relatively rare.[49]

In the present contribution, we describe the synthesis and infrared, magnetic, and X-ray characterization of several unusual bi- and trimetallic octacyanometalate clusters containing $[cis\text{-}M^{II}(en)_2OH_2]^{2+}$ fragments that crystallize from aqueous mixtures of ethylenediamine, octacyanometalate, and transition metal *p*-toluenesulfonate salts.[48]

Experimental Section

Materials. All operations were conducted while dark in a vacuum or under an argon atmosphere by using standard Schlenk and drybox techniques. Transfers of solutions containing cyanide were carried out through stainless steel cannulas. Solvents were distilled under dinitrogen from CaH_2 (acetonitrile), Mg turnings (methanol), or sodium-benzophenone (diethyl ether) and sparged with argon before use. Deionized water was also sparged with argon before use. The preparation of $K_4[Mo(CN)_8]\cdot 2H_2O$,[50,51] $K_4[W(CN)_8]\cdot 2H_2O$,[52] $Mn(OTs)_2$,[53] $Fe(OTs)_2$,[53] $Co(OTs)_2$,[53] and $[Ni(en)_3][OTs]_2$[53] salts are described elsewhere. $[HBu_3N]_3[Mo(CN)_8]$, $[HBu_3N]_3[W(CN)_8]$, $Cs_3[W(CN)_8]$, and $Cs_3[Mo(CN)_8]$ were prepared via modifications to previously described procedures.[52,54,55] Transfers of solutions containing cyanide materials were carried out through stainless steel cannulas.

Physical Measurements. The IR spectra were recorded as Nujol mulls between KBr plates on a Mattson Galaxy 5200 FTIR instrument. Magnetic measurements were conducted on a Johnson-Matthey magnetic susceptibility balance. Diamagnetic corrections were estimated using Pascal's constants:[56,57] $\chi_{dia} = -419.5 \times 10^{-6}$ $cm^3\ mol^{-1}$ for **1**, -425.5×10^{-6} $cm^3\ mol^{-1}$ for **2**, -408.2×10^{-6} $cm^3\ mol^{-1}$ for **3**, -414.2×10^{-6} $cm^3\ mol^{-1}$ for **4**, -415.5×10^{-6} $cm^3\ mol^{-1}$ for **5**, -421.5×10^{-6} $cm^3\ mol^{-1}$ for **6**, -408.2×10^{-6} $cm^3\ mol^{-1}$ for **7**, and -414.2×10^{-6} $cm^3\ mol^{-1}$ for **8**. Microanalyses were performed by the University of Illinois Microanalysis Laboratory.

Synthesis of $[\Lambda\text{-}Mn^{II}(en)_3][cis\text{-}Mn^{II}(en)_2(OH_2)(\mu\text{-}NC)Mo^{IV}(CN)_7]\cdot 2H_2O$ (1). Solid $Mn(OTs)_2$ (1.05 g, 2.53 mmol) was

(29) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397−400.
(30) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283−291.
(31) Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Scuiller, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190−192*, 1023−1047.
(32) (a) McKnight, G. F.; Haight, G. P. *Inorg. Chem.* **1973**, *12*, 3007−3008. (b) Malik, W. U.; Ali, S. I. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1306−1310. (c) Malik, W. U.; Ali, S. I. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1310. (d) Bucknall, W. R.; Wardlaw, W. *J. Chem. Soc.* **1927**, 2981−2993.
(33) Herrera, J. M.; Armentano, D.; de Munno, G.; Lloret, F.; Julve, M.; Verdaguer, M. *New J. Chem.* **2003**, *27*, 128−133.
(34) (a) Herrera, J. M.; Bleuzen, A.; Dromzée, Y.; Julve, M.; Lloret, F.; Verdaguer, M. *Inorg. Chem.* **2003**, *42*, 7052−7059. (b) Willemin, S.; Larionova, J.; Clérac, R.; Donnadieu, B.; Henner, B.; Le Goff, X. F.; Guérin, C. *Eur. J. Inorg. Chem.* **2003**, 1866−1872.
(35) Sra, A. K.; Rombaut, G.; Lahitête, F.; Golhen, S.; Ouahab, L.; Mathonière, C.; Yakhmi, J. V.; Kahn, O. *New J. Chem.* **2000**, *24*, 871−876.
(36) Billing, R.; Vogler, A. *J. Photochem. Photobiol., A* **1997**, *103*, 239−247.
(37) Ali, S. I.; Majid, K. *Thermochim. Acta* **1998**, *317*, 141−149.
(38) Sra, A. K.; Andruh, M.; Kahn, O.; Golhen, S.; Ouahab, L.; Yakhmi, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 2606−2609.
(39) Rombaut, G.; Golhen, S.; Ouahab, L.; Mathonière, C.; Kahn, O. *J. Chem. Soc., Dalton Trans.* **2000**, 3609−3614.
(40) (a) Yuan, A.; Zou, J.; Li, B.; Zha, Z.; Duan, C.; Liu, Y.; Xu, Z.; Keizer, S. *Chem. Commun.* **2000**, 1297−1298. (b) Ohba, M.; Fukita, N.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1997**, 1733−1737. (c) Kou, H.; Bu, W.; Liao, D.; Jiang, Z.; Yan, S.; Fan, Y.; Wang, G. *J. Chem. Soc., Dalton Trans.* **1998**, 4161−4164. (d) Ohba, M.; Usuki, N.; Fukita, N.; Okawa, H. *Inorg. Chem.* **1998**, *37*, 3349−3354. (e) Fukita, N.; Ohba, M.; Okawa, H.; Matsuda, K.; Iwamura, H. *Inorg. Chem.* **1998**, *37*, 842−848. (f) Zhang, S.; Fu, D.; Sun, W.; Hu, Z.; Yu, K.; Tang, W. *Inorg. Chem.* **2000**, *39*, 1142−1146. (g) Usuki, N.; Yamada, M.; Ohba, M.; Okawa, H. *J. Solid State Chem.* **2001**, *159*, 328−335. (h) Ohba, M.; Okawa, H.; Fukita, N.; Mashimoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 1011−1019. (i) Thétiot, F.; Triki, S.; Pala, J. S. *New J. Chem.* **2002**, *26*, 196−198. (j) Zhang, S.; Fu, D.; Sun, W.; Hu, Z.; Yu, K.; Tang, W. *Inorg. Chem.* **2000**, *39*, 1142−1146. (k) Kou, H.-Z.; Tang, J.-K.; Liao, D.-Z.; Gao, S.; Cheng, P.; Jiang, Z.-H.; Yan, S.-P.; Wang, G.-L.; Chansou, B.; Tuchagues, J. *Inorg. Chem.* **2001**, *40*, 4839−4844.
(41) Meske, W.; Babel, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 51−56.
(42) Sieklucka, B.; Szklarzewicz, J.; Kemp, T. J.; Errington, W. *Inorg. Chem.* **2000**, *39*, 5156−5158.
(43) Li, D.; Zheng, L.; Wang, X.; Huang, J.; Gao, S.; Tang, W. *Chem. Mater.* **2003**, *15*, 2094−2098.
(44) Li, D.; Okamura, T.; Sun, W.; Ueyama, N.; Tang, W. *Cryst. Struct. Commun.* **2002**, *C58*, m280−m282.
(45) Li, D.; Okamura, T.; Sun, W.; Ueyama, N.; Tang, W. *Acta Crystallogr.* **2002**, *C58*, m280−m282.
(46) Li, D.; Yang, D.; Li, S.; Tang, W. *Inorg. Chem. Commun.* **2002**, *5*, 791−195.
(47) Podgajny, R.; Dromzée, Y.; Kruczala, K.; Sieklucka, B. *Polyhedron* **2001**, *20*, 685−694.
(48) Chang, F.; Sun, H.-L.; Kou, H.-Z.; Gao, S. *Inorg. Chem. Commun.* **2002**, *5*, 660−663.
(49) (a) Kania, R.; Lewinski, K.; Sieklucka, B. *Dalton Trans.* **2003**, 1033−1040. (b) Herrera, J. M.; Marvaud, V.; Verdaguer, M.; Marrot, J.; Kalisz, M.; Mathonière, C. *Angew. Chem., Int. Ed.* **2004**, ASAP.
(50) Leipoldt, J. G.; Bok, L. D.; Cilliers, P. J. *Z. Anorg. Allg. Chem.* **1974**, *409*, 343−344.
(51) Furman, N. H.; Miller, C. O.; Arvan, P. G.; Audrieth, L. F. *Inorg. Synth.* **1950**, *3*, 160−162.
(52) Bok, L. D.; Leipoldt, J. G.; Basson, S. S. *Z. Anorg. Allg. Chem.* **1975**, *415*, 81−83.
(53) Holmes, S. M.; McKinley, S. G.; Girolami, G. S.; Szalay, P. S.; Dunbar, K. R. *Inorg. Synth.* **2002**, *33*, 91−103.
(54) Saha, B.; Hung, M.; Stanbury, D. M. *Inorg. Chem.* **2002**, *41*, 5538−5543.
(55) Withers, J. R.; Triplett, J. S.; Parkin, S.; Holmes, S. M. Submitted.
(56) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: New York, 1986.
(57) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

dissolved into MeOH (15 mL) and ethylenediamine (0.98 mL, 14.6 mmol) was added over 15 s. The white suspension was evacuated to dryness under vacuum at room temperature, and the residue was suspended in water (25 mL). Aqueous (15 mL) $K_4Mo(CN)_8{\cdot}2H_2O$ (1.29 g, 2.60 mmol) was quickly added, and the amber mixture was allowed to stand 18 days. The yellow crystals were isolated by filtration, washed with EtOH (2 × 10 mL) and Et_2O (2 × 10 mL), and dried under vacuum for 2 h at room temperature. Yield: 0.624 g (62.7%). Anal. Calcd for $C_{18}H_{46}Mn_2N_{18}O_3Mo$: C, 28.11; H, 6.05; N, 32.79. Found: C, 28.25; H, 5.86; N, 32.27. IR (Nujol, cm^{-1}): 3484 (vs), 3219 (vs, br), 2134 (s), 2112 (vs), 2101 (vs), 2072 (s), 2061 (s), 1661 (m), 1621 (m, sh), 1592 (vs), 1569 (s, sh), 1394 (w), 1328 (m), 1279 (w), 1131 (w, sh), 1113 (w), 1057 (w), 1029 (s), 1015 (vs, sh), 999 (vs), 970 (s), 867 (w), 858 (w), 655 (m), 640 (m, sh), 610 (m), 594 (m), 509 (w, sh), 487 (m), 469 (m), 430 (w). μ_{eff} Calcd (μ_B): 8.37. μ_{eff} Found (μ_B): 8.47.

Synthesis of [Λ-Mn^{II}(en)$_3$][*cis*-Mn^{II}(en)$_2$(OH$_2$)(*μ*-NC)W^{IV}(CN)$_7$]·3H$_2$O (2). Solid $Mn(OTs)_2$ (0.72 g, 1.76 mmol) was dissolved into MeOH (15 mL) and ethylenediamine (0.40 mL, 5.98 mmol) was added over 15 s. The white suspension was evacuated to dryness under vacuum at room temperature and was suspended in water (25 mL). Aqueous (15 mL) $K_4Mo(CN)_8{\cdot}2H_2O$ (1.18 g, 2.02 mmol) was quickly added, and the amber mixture was allowed to stand overnight. The yellow crystals were isolated by filtration, washed with EtOH (2 × 10 mL) and Et_2O (2 × 10 mL), and dried under vacuum for 2 h at room temperature. Yield: 0.391 g (51.9%). Anal. Calcd for $C_{18}H_{46}Mn_2N_{18}O_3W$: C, 25.22; H, 5.42; N, 29.43. Found: C, 25.25; H, 5.37; N, 28.77. IR (Nujol, cm^{-1}): 3232 (vs, br) 2134 (s), 2111 (vs), 2098 (vs), 2077 (s), 2058 (s), 1659 (vs), 1480 (vs, sh), 1453 (vs), 1393 (s), 1328 (s), 1278 (s), 1128 (s, sh), 1113 (s), 1057 (s), 999 (vs), 960 (s), 866 (w), 655 (m, br), 510 (w, sh), 485 (m). μ_{eff} Calcd (μ_B): 8.37. μ_{eff} (μ_B) Found: 8.21.

Synthesis of [*cis*-Co^{II}(en)$_2$(OH$_2$)]$_2$[(*μ*-NC)$_2$$Mo^{IV}(CN)_6$] (3). Solid $Co(OTs)_2$ (1.003 g, 2.51 mmol) was dissolved into MeOH (15 mL) and ethylenediamine (0.90 mL, 13.5 mmol) was added over 15 s. The peach suspension was evacuated to dryness under vacuum at room temperature, and the residue was suspended in water (25 mL). Aqueous (25 mL) $K_4Mo(CN)_8{\cdot}2H_2O$ (1.29 g, 2.80 mmol) was quickly added, and the yellow solution was allowed to stand 18 days. The orange crystals were isolated by filtration, washed with EtOH (2 × 10 mL) and Et_2O (2 × 10 mL), and dried under vacuum for 2 h at room temperature. Yield: 0.750 g (74.4%). Anal. Calcd for $C_{16}H_{36}N_{16}O_2Co_2Mo$: C, 27.49; H, 5.21; N, 32.07. Found: C, 27.79; H, 5.96; N, 31.79. IR (Nujol, cm^{-1}): 3480 (vs), 3343 (vs, br), 3292 (vs, br), 2140 (s), 2126 (s), 2112 (vs), 2100 (vs), 2072 (s), 2059 (s), 1778 (w), 1755 (w), 1752 (w), 1664 (vs), 1641 (w), 1620 (s), 1593 (vs), 1572 (vs), 1514 (w), 1501 (w), 1464 (vs), 1392 (s), 1377 (s), 1277 (s), 1126 (s), 1112 (s), 1074 (m), 1065 (m), 1029 (vs, sh), 1012 (vs), 975 (vs), 872 (m), 855 (m), 664 (s), 621 (s), 505 (s), 486 (v), 472 (m), 464 (m), 430 (m), 418 (w), 404 (w). μ_{eff} Calcd (μ_B): 5.48. μ_{eff} Found (μ_B): 6.66.

Synthesis of [*cis*-Co^{II}(en)$_2$(OH$_2$)]$_2$[(*μ*-NC)$_2$$W^{IV}(CN)_6$] (4). Solid $Co(OTs)_2$ (0.75 g, 1.87 mmol) was dissolved into MeOH (15 mL) and ethylenediamine (0.70 mL, 10.4 mmol) was added over 15 s. The peach suspension was evacuated to dryness under vacuum at room temperature, and the residue was suspended in water (15 mL). Aqueous (10 mL) $K_4Mo(CN)_8{\cdot}2H_2O$ (1.02 g, 1.75 mmol) was quickly added, and the amber solution was allowed to stand 18 days. The yellow crystals were isolated by filtration, washed with EtOH (2 × 10 mL) and Et_2O (2 × 10 mL), and dried under vacuum for 2 h at room temperature. Yield: 0.395 g (48.0%). Anal. Calcd for $C_{16}H_{36}N_{16}O_2Co_2W$: C, 24.42; H, 4.62; N, 28.49. Found: C, 24.96; H, 4.32; N, 28.60. IR (Nujol, cm^{-1}): 3501 (vs, br), 3343 (vs, br), 3292 (vs, br), 2139 (vs), 2124 (s), 2112 (vs), 2097 (s), 1778 (w), 1755 (w), 1752 (w), 1664 (vs), 1620 (s), 1593 (vs), 1464 (vs), 1392 (s), 1377 (s), 1277 (s), 1126 (s), 1112 (s), 1065 (s), 1012 (vs), 977 (vs), 872 (m), 855 (m), 800 (m), 664 (vs), 621 (vs), 510 (vs), 486 (vs), 464 (vs), 438 (m), 404 (m). μ_{eff} Calcd (μ_B): 5.48. μ_{eff} Found (μ_B): 7.05.

Synthesis of [Δ-Ni^{II}(en)$_3$][*cis*-Ni^{II}(en)$_2$(OH$_2$)(*μ*-NC)Mo^{IV}(CN)$_7$]·5H$_2$O (5).[48] An aqueous (40 mL) solution of [Ni(en)$_3$][OTs]$_2$ (2.04 g, 3.46 mmol) was treated with aqueous (20 mL) $K_4[Mo(CN)_8]{\cdot}2H_2O$ (1.62 g, 3.26 mmol), and the resulting brown solution was allowed to stand for 3 days at room temperature. The brown blocks that deposited were isolated by suction filtration and were washed with water (2 × 10 mL), EtOH (2 × 10 mL), and Et_2O (2 × 20 mL). The crystals were dried under vacuum at room temperature overnight. Yield: 1.12 g (83.5%). Anal. Calcd for $C_{18}H_{46}N_{18}O_3MoNi_2$: C, 27.83; H, 5.99; N, 32.47. Found: C, 27.97; H, 5.74; N, 32.80. IR (Nujol, cm^{-1}): 3565 (vs, br), 2150 (s), 2145 (s), 2125 (s), 2112 (vs), 2102 (s), 2074 (w), 1658 (m), 1642 (m), 1597 (s), 1327 (m), 1279 (m) 1143 (s), 1107 (m), 1037 (m), 1021 (s), 978 (m), 869 (w), 845 (w), 680 (m), 642 (m), 522 (m), 512 (w), 460 (w), 412 (w). μ_{eff} Calcd (μ_B): 4.00. μ_{eff} Found (μ_B): 4.38.

Synthesis of [Δ-Ni^{II}(en)$_3$][*cis*-Ni^{II}(en)$_2$(OH$_2$)(*μ*-NC)W^{IV}(CN)$_7$]·2H$_2$O (6). An aqueous (40 mL) solution of [Ni(en)$_3$][OTs]$_2$ (1.99 g, 3.37 mmol) was treated with aqueous (20 mL) $K_4[W(CN)_8]{\cdot}2H_2O$ (2.25 g, 3.85 mmol), and the resulting brown solution was allowed to stand at room temperature for 3 days. The brown blocks that deposited were isolated by suction filtration and were washed with water (2 × 10 mL), EtOH (2 × 10 mL), and Et_2O (2 × 10 mL). The crystals were dried under vacuum at room temperature overnight. Yield: 1.26 g (86.5%). Anal. Calcd for $C_{18}H_{44}N_{18}Ni_2O_2W$: C, 25.53; H, 5.01; N, 29.79. Found: C, 25.52; H, 5.25; N, 29.79. IR (Nujol, cm^{-1}): 3571 (m), 3469 (vs), 3346 (vs), 3346 (vs), 3315 (vs), 3289 (vs), 3269 (vs), 3173 (vs), 2151 (s), 2143 (s), 2124 (s), 2110 (vs), 2072 (w), 1658 (w), 1642 (m), 1630 (m), 1592 (s), 1411 (w), 1327 (m), 1279 (m), 1143 (m), 1109 (m), 1100 (m), 1030 (vs), 1021 (vs), 979 (m), 868 (w), 842 (m), 720 (m), 673 (m), 664 (m), 645 (m, sh), 507 (m), 474 (m). μ_{eff} Calcd (μ_B): 4.00. μ_{eff} Found (μ_B): 4.41.

Synthesis of [*cis*-Ni^{II}(en)$_2$(OH$_2$)]$_2$[(*μ*-NC)$_2$$Mo^{IV}(CN)_6$] (7). An aqueous (20 mL) solution of [Ni(en)$_3$][OTs]$_2$ (3.00 g, 5.16 mmol) was treated with aqueous (14 mL) $Cs_3[Mo(CN)_8]$ (1.86 g, 2.65 mmol), and the resulting brown gel was allowed to stand at room temperature for two weeks; within 1 h bubbles were observed in addition to brown blocks. The brown crystals were isolated by suction filtration and were washed with water (2 × 10 mL), EtOH (2 × 10 mL), and Et_2O (20 mL). The crystals were dried under vacuum at room temperature overnight. Yield: 1.28 g (69.3%, Mo-based). Anal. Calcd for $C_{16}H_{36}N_{16}MoNi_2O_2$: C, 27.51; H, 5.21; N, 32.10. Found: C, 27.74; H, 5.41; N, 32.49. IR (Nujol, cm^{-1}): 3590 (s), 3572 (s), 3469 (vs), 3347 (vs), 3316 (vs), 3290 (vs), 3268 (vs), 3173 (vs), 2144 (s), 2111 (vs), 2102 (vs), 2074 (m), 1642 (m), 1630 (m), 1592 (s), 1327 (m), 1278 (m), 1143 (m), 1109 (m), 1100 (m), 1031 (vs), 1020 (vs), 980 (m), 869 (w), 845 (w), 807 (w, sh), 673 (m), 666 (m), 647 (m), 521 (m), 505 (m), 458 (m). μ_{eff} Calcd (μ_B): 4.00. μ_{eff} Found (μ_B): 4.27.

Structure Determinations and Refinements. Crystals of **1**−**4** were grown from concentrated aqueous ethylenediamine solutions of either $Mn(OTs)_2$ (**1**, **2**) or $Co(OTs)_2$ (**3**, **4**) and aqueous $K_4Mo(CN)_8{\cdot}2H_2O$ (**1**, **3**) or $K_4W(CN)_8{\cdot}2H_2O$ (**2**, **4**). Crystals of **5**−**7** were grown from aqueous solutions of [Ni(en)$_3$][OTs]$_2$ with either $K_4Mo(CN)_8{\cdot}2H_2O$ (**5**), $K_4W(CN)_8{\cdot}2H_2O$ (**6**), or $Cs_3W(CN)_8$ (**7**), respectively. X-ray diffraction data were collected at 90.0(2) K on a Nonius Kappa CCD diffractometer from irregular shaped crystals

Table 1. Crystallographic Data for [Λ-Mn^{II}(en)$_3$][*cis*-Mn^{II}(en)$_2$(OH_2)(μ-NC)W^{IV}(CN)$_8$]·2H_2O (**2**), [*cis*-Co^{II}(en)$_2$(OH_2)]$_2$[(μ-NC)$_2W^{IV}$(CN)$_6$]·4H_2O (**4**), [Δ-Ni^{II}(en)$_3$][*cis*-Ni^{II}(en)$_2$(OH_2)(μ-NC)Mo^{IV}(CN)$_7$]·2H_2O (**5**), [Δ-Ni^{II}(en)$_3$][*cis*-Ni^{II}(en)$_2$(OH_2)(μ-NC)W^{IV}(CN)$_7$]·2H_2O (**6**), and [*cis*-Ni^{II}(en)$_2$(OH_2)]$_2$[(μ-NC)$_2Mo^{IV}$(CN)$_6$]·4H_2O (**7**)

	2	**4**	**5**	**6**	**7**
chemical formula	$C_{18}H_{46}Mn_2N_{18}O_3W$	$C_{16}H_{44}Co_2N_{16}O_6W$	$C_{18}H_{46}MoN_{18}Ni_2O_3$	$C_{18}H_{46}N_{18}Ni_2O_3W$	$C_{16}H_{44}MoN_{16}Ni_2O_6$
fw	856.46	858.38	776.09	864.00	770.03
temp, K	90.0 (2)	90.0 (2)	90.0 (2)	90.0 (2)	90.0 (2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.071073
cryst size (mm^3)	0.20 × 0.20 × 0.18	0.12 × 0.12 × 0.10	0.25 × 0.20 × 0.10	0.30 × 0.30 × 0.25	0.25 × 0.23 × 0.22
space group	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic
cryst syst	$P2_12_12_1$	$C2/c$	$P2_12_12_1$	$P2_12_12_1$	$C2/c$
a, Å	11.5650(2)	17.1162(3)	11.5497(4)	11.5576(4)	17.0725(4)
b, Å	15.0820(2)	11.0546(2)	14.9007(7)	14.9065(6)	11.0054(3)
c, Å	18.8610(3)	17.6671(3)	18.7582(7)	18.7669(8)	17.5905(5)
β, deg		108.783(6)			108.6950(10)
V, Å^3	3289.80(9)	3164.82(10)	3228.3(2)	3233.2	3130.69(14)
ρ, g cm^{-3}	1.729	1.802	1.594	1.775	1.634
Z	4	8	4	4	4
μ, mm^{-1}	4.295	4.719	1.587	4.754	1.643
final R indices	R_1 = 0.0245	R_1 = 0.0200	R_1 = 0.0402	R_1 = 0.0388	R_1 = 0.0262
[$I > 2\sigma(I)$]^a	wR_2 = 0.0426	wR_2 = 0.0423	wR_2 = 0.0564	wR_2 = 0.0696	wR_2 = 0.0567
R indices	R_1 = 0.0299	R_1 = 0.0236	R_1 = 0.0673	R_1 = 0.0553	R_1 = 0.0386
(for all data)	wR_2 = 0.0439	wR_2 = 0.0430	wR_2 = 0.0620	wR_2 = 0.0748	wR_2 = 0.0603

^{a} $R = \sum||F_o| - |F_o||\sum|F_o|$. $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

Table 2. Selected Bond Distances (Å) for Crystallographic Data for [Λ-Mn^{II}(en)$_3$][*cis*-Mn^{II}(en)$_2$(OH_2)(μ-NC)W^{IV}(CN)$_8$]·2H_2O (**2**), [*cis*-Co^{II}(en)$_2$(OH_2)]$_2$[(μ-NC)$_2W^{IV}$(CN)$_6$]·4H_2O (**4**), [Δ-Ni^{II}(en)$_3$][*cis*-Ni^{II}(en)$_2$(OH_2)(μ-NC)Mo^{IV}(CN)$_7$]·2H_2O (**5**), [Δ-Ni^{II}(en)$_3$][*cis*-Ni^{II}(en)$_2$(OH_2)(μ-NC)W^{IV}(CN)$_7$]·2H_2O (**6**), and [*cis*-Ni^{II}(en)$_2$(OH_2)]$_2$[(μ-NC)$_2Mo^{IV}$(CN)$_6$]·4H_2O (**7**)

2		**4**		**5**		**6**		**7**	
W_1-C_1	2.152(3)	$W-C_5$	2.161(2)	Mo_1-C_1	2.156(4)	W_1-C_1	2.142(6)	$Mo-C_1$	2.168(3)
W_1-C_2	2.164(4)	$W-C_6$	2.166(2)	Mo_1-C_2	2.176(3)	W_1-C_2	2.182(5)	$Mo-C_2$	2.164(3)
W_1-C_3	2.177(3)	$W-C_7$	2.167(2)	Mo_1-C_3	2.158(4)	W_1-C_3	2.142(6)	$Mo-C_3$	2.164(3)
W_1-C_4	2.159(3)	$W-C_8$	2.169(2)	Mo_1-C_4	2.160(4)	W_1-C_4	2.152(6)	$Mo-C_4$	2.164(3)
W_1-C_5	2.172(4)	C_5-N_5	1.155(3)	Mo_1-C_5	2.174(4)	W_1-C_5	2.188(6)	C_4-N_4	1.150(3)
W_1-C_6	2.165(4)	$Co-N_1$	2.1305(19)	Mo_1-C_6	2.180(4)	W_1-C_6	2.168(6)	$Ni-N_4$	2.090(2)
W_1-C_7	2.171(3)	$Co-N_2$	2.1670(18)	Mo_1-C_7	2.178(4)	W_1-C_7	2.173(6)	$Ni-N_5$	2.106(2)
W_1-C_8	2.170(3)	$Co-N_3$	2.1411(19)	Mo_1-C_8	2.172(4)	W_1-C_8	2.163(6)	$Ni-N_6$	2.091(2)
C_1-N_1	1.150(4)	$Co-N_4$	2.1535(19)	C_1-N_1	1.143(4)	C_1-N_1	1.146(7)	$Ni-N_7$	2.115(2)
Mn_1-N_1	2.210(3)	$Co-N_5$	2.1197(19)	Ni_1-N_1	2.077(3)	Ni_1-N_1	2.090(5)	$Ni-N_8$	2.087(2)
Mn_1-N_9	2.274(3)	$Co-O_1$	2.1983(15)	Ni_1-N_9	2.102(3)	Ni_1-N_9	2.114(5)	$Ni-O_{3W}$	2.1616(19)
Mn_1-N_{10}	2.272(3)	Ni_1-N_{10}	2.105(3)	Ni_1-N_{10}	2.115(5)				
Mn_1-N_{11}	2.259(3)	Ni_1-N_{11}	2.108(3)	Ni_1-N_{11}	2.125(5)				
Mn_1-N_{12}	2.272(3)	Ni_1-N_{12}	2.105(3)	Ni_1-N_{12}	2.111(5)				
Mn_1-O_1	2.2044(19)	Ni_1-O_1	2.121(2)	Ni_1-O_1	2.126(3)				
Mn_2-N_{13}	2.287(3)	Ni_2-N_{13}	2.123(3)	Ni_2-N_{13}	2.133(5)				
Mn_2-N_{14}	2.277(3)	Ni_2-N_{14}	2.140(3)	Ni_2-N_{14}	2.121(5)				
Mn_2-N_{15}	2.282(3)	Ni_2-N_{15}	2.107(3)	Ni_2-N_{15}	2.098(4)				
Mn_2-N_{16}	2.265(3)	Ni_2-N_{16}	2.133(3)	Ni_2-N_{16}	2.136(5)				
Mn_2-N_{17}	2.244(3)	Ni_2-N_{17}	2.120(3)	Ni_2-N_{17}	2.118(5)				
Mn_2-N_{18}	2.296(3)	Ni_2-N_{18}	2.131(3)	Ni_2-N_{18}	2.140(4)				

mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained (DENZO)[58] from ten 1° frames and were refined via a least-squares scheme using all data-collection frames (SCALEPACK).[58] Lorentz/polarization corrections were applied during data reduction. The structures were solved by direct methods (SHELXS97)[59] and completed by difference Fourier methods (SHELXL97).[59] Refinement was performed against F^2 by weighted full-matrix least-squares (SHELXL97),[59] and empirical absorption corrections (either SCALEPACK[58] or SADABS[59]) were applied. Hydrogen atoms were found in difference maps and subsequently placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography vol. C.[60] Crystal data, relevant details of the structure determinations, and selected geometrical parameters are provided in Tables 1−3.

Results and Discussion

Synthesis and Spectroscopic Characterization. We had initially anticipated that a series of crystalline, amine-expanded analogues of [M^{II}(L)$_2$]$_2$[M^{IV}(CN)$_8$]·$n$$H_2O$ and [M^{II}(L)$_2$]$_3$[M^{V}(CN)$_8$]$_2$·$n$$H_2O$ stoichiometry would be obtained when aqueous [M^{II}(en)$_3$][OTs]$_2$ (OTs^- = p-toluenesulfonate) was treated with M(CN)$_8{}^{n-}$ (M = $Mo^{IV,V}$, $W^{IV,V}$). Instead, bi-and trimetallic octacyanometalate(IV) salts and clusters are obtained regardless of addition order or reagent stoichiometry. Treatment of either methanolic ethylenediamine and M^{II}(OTs)$_2$ (M^{II} = Mn, **1**, **2**; Co, **3**, **4**) mixtures or [Ni^{II}(en)$_3$][OTs]$_2$ (**5**, **6**) with M^{IV}(CN)$_8{}^{4-}$ affords bi- and trimetallic

(58) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326.
(59) (a) Sheldrick, G. M. *SADABS*−*An empirical absorption correction program*; Bruker Analytical X-ray Systems: Madison, WI, 1996. (b) Sheldrick, G. M. *SHELX-97. Programs for Crystal Structure Solution and Refinement*; University of Gottingen: Gottingen, Germany, 1997.
(60) *International Tables for Crystallography vol. C*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992.

Table 3. Selected Bond Angles (deg) for $[\Lambda\text{-}Mn^{II}(en)_3][cis\text{-}Mn^{II}(en)_2(OH_2)(\mu\text{-}NC)W^{IV}(CN)_8]\cdot 2H_2O$ (**2**), $[cis\text{-}Co^{II}(en)_2(OH_2)]_2[(\mu\text{-}NC)_2W^{IV}(CN)_6]\cdot 4H_2O$ (**4**), $[\Delta\text{-}Ni^{II}(en)_3][cis\text{-}Ni^{II}(en)_2(OH_2)(\mu\text{-}NC)Mo^{IV}(CN)_7]\cdot 2H_2O$ (**5**), $[\Delta\text{-}Ni^{II}(en)_3][cis\text{-}Ni^{II}(en)_2(OH_2)(\mu\text{-}NC)W^{IV}(CN)_7]\cdot 2H_2O$ (**6**), and $[cis\text{-}Ni^{II}(en)_2(OH_2)]_2[(\mu\text{-}NC)_2Mo^{IV}(CN)_6]\cdot 4H_2O$ (**7**)

2		**4**		**5**		**6**		**7**	
$C_1-W_1-C_2$	74.41(12)	C_5-W-C_{5A}	80.48(11)	$C_1-Mo_1-C_2$	75.65(12)	$C_1-W_1-C_2$	75.76(19)	C_4-Mo-C_1	142.99(9)
$C_1-W_1-C_3$	74.45(12)	C_5-W-C_6	71.92(8)	$C_1-Mo_1-C_3$	85.23(13)	$C_1-W_1-C_3$	84.7(2)	C_4-Mo-C_{1A}	112.43(9)
$C_1-W_1-C_4$	144.45(12)	C_5-W-C_{6A}	142.54(8)	$C_1-Mo_1-C_4$	143.28(13)	$C_1-W_1-C_4$	142.5(2)	C_4-Mo-C_2	142.89(9)
$C_1-W_1-C_5$	141.19(12)	C_5-W-C_7	76.96(8)	$C_1-Mo_1-C_5$	142.31(13)	$C_1-W_1-C_5$	142.3(2)	C_4-Mo-C_{2A}	71.96(9)
$C_1-W_1-C_6$	83.92(12)	C_5-W-C_{7A}	73.67(8)	$C_1-Mo_1-C_6$	108.78(13)	$C_1-W_1-C_6$	109.7(2)	C_4-Mo-C_3	73.89(9)
$C_1-W_1-C_7$	109.66(12)	C_5-W-C_8	143.10(8)	$C_1-Mo_1-C_7$	71.88(13)	$C_1-W_1-C_7$	71.8(2)	C_4-Mo-C_{3A}	77.35(9)
$C_1-W_1-C_8$	71.17(12)	C_5-W-C_{8A}	112.02(8)	$C_1-Mo_1-C_8$	73.30(13)	$C_1-W_1-C_8$	73.4(2)	C_4-Mo-C_{4A}	80.30(13)
$W_1-C_1-N_1$	177.1(3)	$W-C_5-N_5$	176.34(19)	$Mo_1-C_1-N_1$	175.0(3)	$W_1-C_1-N_1$	176.6(5)	$Mo-C_4-N_4$	176.0(2)
$C_1-N_1-Mn_1$	152.4(3)	$Co-N_5-C_5$	169.57(18)	$C_1-N_1-Ni_1$	158.2(3)	$C_1-N_1-Ni_1$	158.1(5)	$Ni-N_4-C_4$	169.9(2)
$N_1-Mn_1-O_1$	92.77(9)	N_5-Co-N_1	92.00(7)	$N_1-Ni_1-O_1$	92.30(10)	$N_1-Ni_1-O_1$	91.79(16)	N_4-Ni-N_5	170.64(8)
$N_1-Mn_1-N_9$	168.60(10)	N_5-Co-N_2	89.21(7)	N_1-Ni_1-N	987.76(11)	$N_1-Ni_1-N_9$	88.32(18)	N_4-Ni-N_6	88.96(8)
$N_1-Mn_1-N_{10}$	91.78(10)	N_5-Co-N_3	89.11(7)	$N_1-Ni_1-N_{10}$	91.40(11)	$N_1-Ni_1-N_{10}$	91.33(18)	N_4-Ni-N_7	89.43(8)
$N_1-Mn_1-N_{11}$	88.69(10)	N_5-Co-N_4	169.53(8)	$N_1-Ni_1-N_{11}$	173.06(11)	$N_1-Ni_1-N_{11}$	173.36(18)	N_4-Ni-N_8	91.86(8)
$N_1-Mn_1-N_{12}$	93.34(10)	O_1-Co-N_1	92.49(6)	$N_1-Ni_1-N_{12}$	91.23(11)	$N_1-Ni_1-N_{12}$	91.14(18)	O_{3W}-Ni-N_4	87.28(18)
$O_1-Mn_1-N_9$	89.23(8)	O_1-Co-N_2	172.92(7)	$O_1-Ni_1-N_9$	168.92(10)	$O_1-Ni_1-N_9$	169.10(16)	O_{3W}-Ni-N_5	88.48(8)
$O_1-Mn_1-N_{10}$	96.55(10)	O_1-Co-N_3	92.50(7)	$O_1-Ni_1-N_{10}$	86.32(10)	$O_1-Ni_1-N_{10}$	86.41(16)	O_{3W}-Ni-N_6	92.59(8)
$O_1-Mn_1-N_{11}$	163.58(10)	O_1-Co-N_4	88.28(7)	$O_1-Ni_1-N_{11}$	87.22(10)	$O_1-Ni_1-N_{11}$	87.47(16)	O_{3W}-Ni-N_7	173.24(7)
$O_1-Mn_1-N_{12}$	85.95(9)	O_1-Co-N_5	87.68(6)	$O_1-Ni_1-N_{12}$	94.35(10)	$O_1-Ni_1-N_{12}$	93.99(17)	O_{3W}-Ni-N_8	91.35(8)
$N_{13}-Mn_2-N_{14}$	77.49(10)					$N_{13}-Ni_2-N_{14}$	81.69(11)	$N_{13}-Ni_2-N_{14}$	81.49(18)
$N_{13}-Mn_2-N_{15}$	100.56(11)					$N_{13}-Ni_2-N_{15}$	169.93(11)	$N_{13}-Ni_2-N_{15}$	169.70(19)
$N_{13}-Mn_2-N_{16}$	173.62(10)					$N_{13}-Ni_2-N_{16}$	94.15(11)	$N_{13}-Ni_2-N_{16}$	93.89(19)
$N_{13}-Mn_2-N_{17}$	87.51(10)					$N_{13}-Ni_2-N_{17}$	94.30(11)	$N_{13}-Ni_2-N_{17}$	94.35(19)
$N_{13}-Mn_2-N_{18}$	93.52(10)					$N_{13}-Ni_2-N_{18}$	91.03(11)	$N_{13}-Ni_2-N_{18}$	91.01(19)

complexes of $[M^{II}(en)_3][cis\text{-}M^{II}(en)_2(OH_2)(\mu\text{-}NC)M^{IV}(CN)_7]$ (**1**, **2**, **5**, **6**) and $[cis\text{-}M^{II}(en)_2(OH_2)]_2[(\mu\text{-}NC)_2M^{IV}(CN)_6]$ (**3**, **4**) stoichiometry. Treatment of aqueous $[Ni^{II}(en)_3][OTs]_2$ with $Cs_3[Mo^V(CN)_8]$ affords an additional trimetallic cluster (**7**) via $M^V(CN)_8{}^{3-}$ reduction, and such behavior has been previously reported.[61−62]

The infrared spectra of **1**−**7** clearly show bridging and terminal cyano ligands are present and range from 2142 to 2062 cm^{-1}.[63,64] The cyano stretching absorptions for the Ni^{II} (**5**−**7**) derivatives are highest in energy while the Mn^{II} (**1**, **2**) derivatives exhibit the lowest and are consistent with the formation of $M^{II}-NC-M^{IV}$ bridging units and the depopulation of the cyanide 5σ orbital;[65] increasing π-back-bonding progressing from Ni^{II} to Mn^{II} compensates this effect and progressively lowers the energy of the ν_{CN} absorptions from 2142 to 2134 cm^{-1} for **5** and **2**, respectively. Similar trends are observed for **3**, **5**, and **7**.[65]

Generally, $M^{IV}(CN)_8{}^{4-}$ compounds exhibit cyano stretching absorptions (ν_{CN}) that range from 2060 to 2160 (ionic) and 2085 to 2141 cm^{-1} (cyanide-bridged).[42,63−64,66−68] The ν_{CN} of bridging cyanides are often found at higher energies than terminal ones, but this assumption is only applicable to compounds derived from bridged metal centers that do not function as donor−acceptor pairs. If kinematic effects, or the mechanical restraint of cyanide motion in M−CN−M′ units, are operative between the cyanide-bridged donor and acceptor centers, the ν_{CN} absorptions are expected to move to higher energies.[65,69] If, however, increased π-back-bonding compensates the kinematic effect by decreasing the C−N bond order, then red-shifted ν_{CN} absorptions that scale as a function of the donor−acceptor charge-transfer absorption oscillator strength will be observed.[65,69] Assuming that π-back-bonding effects are minor, we tentatively assign the bridging and terminal cyano stretching absorptions as those near 2140 and 2080 cm^{-1}, respectively.

Crystallographic Studies. Crystals of **2**, **5**, and **6** are in the orthorhombic ($P2_12_12_1$) space group and crystallize as bimetallic $[M^{II}(en)_3][(OH_2)(en)_2M^{II}(\mu\text{-}NC)M^{IV}(CN)_7]\cdot 2H_2O$ salts (Table 1).[48] The salts consist of D_3-symmetric $M^{II}(en)_3{}^{2+}$

(61) (a) Bogdanov, M.; Grybos, R.; Samotus, A.; Bogolitsyn, K. *Transition Met. Chem. (Dordrecht, Neth.)* **1993**, *18*, 599−603. (b) Dennis, C. R.; Basson, S. S.; Leipoldt, J. G. *Polyhedron* **1983**, *2*, 1357−1362. (c) Li, D.; Gao, S.; Zheng, L.; Yu, K.; Tang, W. *New. J. Chem.* **2002**, *26*, 1190−1195. (d) Marchaj, A.; Plesinski, A.; Stasicka, Z. *Rocz. Chem.* **1976**, *50*, 1239−1250.

(62) (a) Waltz, W. L.; Adamson, A. W.; Fleischauer, P. D. *J. Am. Chem. Soc.* **1967**, *89*, 3923−2924. (b) Butter, K. R.; Kemp, T. J.; Sieklucka, B.; Samotus, A. *J. Chem. Soc., Dalton Trans.* **1986**, 1217−1223. (c) Zofia, S.; Hanna, B. *Rocz. Chem.* **1974**, *48*, 389−398. (d) Zofia, S. I. *Rocz. Chem.* **1973**, *47*, 1993−2002. (e) Gray, G. W.; Spence, J. T. *Inorg. Chem.* **1971**, *10*, 2751−2755.

(63) (a) Arimoto, Y.; Ohkoshi, S.; Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hashimoto, K. *Chem. Lett.* **2002**, 832−833. (b) Song, Y.; Ohkoshi, S.; Arimoto, Y.; Seino, H.; Mizobe, Y.; Hashimoto, K. *Inorg. Chem.* **2003**, *42*, 1848−1856. (c) Arimoto, Y.; Ohkoshi, S.-I.; Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hashimoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 9240−9241. (d) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Verdaguer, M.; Ohkoshi, S.-I.; Hashimoto, K. *Inorg. Chem.* **2000**, *39*, 5095−5101. (e) Korzeniak, T.; Podgajny, R.; Alcock, N. W.; Lewinski, K.; Balanda, M.; Wasiutynski, T.; Sieklucka, B. *Polyhedron* **2003**, *22*, 2183−2190. (f) Li, D.; Gao, S.; Zheng, L.; Tang, W. *J. Chem. Soc., Dalton Trans.* **2002**, 2805−2806. (g) Herrera, J. M.; Bleuzen, A.; Dromzee, Y.; Julve, M.; Lloret, F.; Verdaguer, M. *Inorg. Chem.* **2003**, *42*, 7052−7059. (h) Li, D.; Zheng, L.; Zhang, Y.; Gao, S.; Tang, W. *Inorg. Chem.* **2003**, *42*, 8203−8213. (i) Li, D.; Zheng, L.; Wang, X.; Huang, J.; Gao, S.; Tang, W. *Chem. Mater.* **2003**, *15*, 2094−2098. (j) Li, D.; Gao, S.; Zheng, L.; Sun, W.; Okamura, T.; Ueyama, N.; Tang, W. *New J. Chem.* **2002**, *26*, 485−486.

(64) (a) Sieklucka, B.; Szklarzewicz, J.; Kenp, T. J.; Errington, W. *Inorg. Chem.* **2000**, *39*, 5156−5158. (b) Kashiwagi, T.; Ohkoshi, S.-I.; Seino, H.; Mizobe, Y.; Hashimoto, K. *J. Am. Chem. Soc.* **2004**, *126*, 5024−5025.

(65) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed, Part B; Wiley: New York, 1997; pp 54−58 and 105−116.

(66) (a) Long, T. V.; Vernon, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 1919−1924. (b) Kiernan, P. M.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 2489−2494.

(67) Hartman, K. O.; Miller, F. A. *Spectrochim. Acta* **1955**, *24*, 669−672.

(68) Brame, E. G.; Johnson, F. A.; Larsen, E. M.; Meloche, V. W. *J. Inorg. Nucl. Chem.* **1958**, *2*, 99−103.

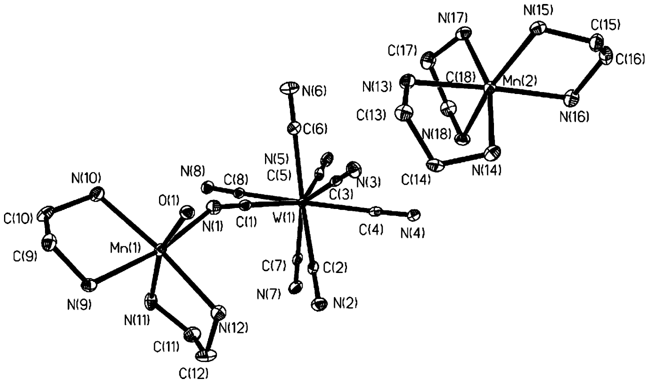

Figure 1. X-ray structure of [Λ-$Mn^{II}(en)_3$][*cis*-$Mn^{II}(en)_2(OH_2)(\mu$-NC)-$W^{IV}(CN)_7$]$\cdot 2H_2O$ (**2**). Ellipsoids are at the 50% probability level, and hydrogen atoms are eliminated for clarity.

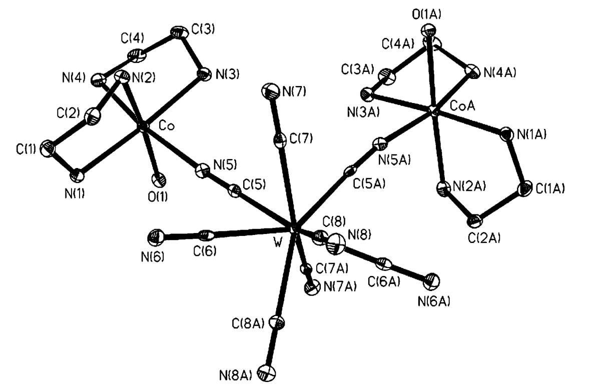

Figure 2. X-ray structure of [*cis*-$Co^{II}(en)_2(OH_2)]_2[(\mu$-NC$)_2W^{IV}(CN)_6]\cdot$ $2H_2O$ (**4**). Ellipsoids are at the 50% probability level, and hydrogen atoms are eliminated for clarity.

cations that cocrystallize with *cis*-$M^{II}(en)_2(OH_2)^{2+}$ and distorted square-antiprismatic $M^{IV}(CN)_8{}^{4-}$ centers linked by a single μ-CN bridge (Figure 1). Both D_3-symmetric Λ- (**2**) and Δ-$M^{II}(en)_3{}^{2+}$ (**5**, **6**) enantiomers can be crystallized from racemic $[M^{II}(en)_3][OTs]_2$ and $K_4M^{IV}(CN)_8\cdot 2H_2O$ mixtures, and neither prior resolution of the $M(en)_3{}^{2+}$ salts nor isolation of both enantiomers of **1**, **2**, **5**, or **6** was pursued.

The average $M^{II}-N$ bond distances for the $M^{II}(en)_3{}^{2+}$ centers are 2.275(3), 2.126(3), and 2.124(5) Å while the $N-M^{II}{}_2-N$ bond angles range from 77.49(10)° to 173.62(10)°, 81.69(11)° to 169.93(11)°, and 81.49(18)° to 169.70(19)° for **2**, **5**, and **6**, respectively (Tables 2 and 3). The distorted square antiprismatic $M^{IV}(CN)_8{}^{4-}$ (M^{IV} = Mo, W) centers are linked via μ-CN bridges to a *cis*-$M^{II}(en)_2$-$(OH_2)^{2+}$ (M^{II} = Mn, Ni) fragment *cis* to the coordinated aqua ligand. The $M^{II}{}_1-N_1$ bond distances are 2.210(3), 2.077(3), and 2.090(5) Å, while the $M_1-N_1-C_1$ bond angles are 152.4(3)°, 158.2(3)°, and 158.1(5)° for **2**, **5**, and **6**, respectively. The $M^{IV}-C_1-N_1$ bond angles are 177.1(3)°, 175.0(3)°, and 176.6(5)°, and the $M^{II}-O$ and $O-M^{II}-N_1$ bond distances and angles are 2.2044(19), 2.121(2), and 2.126(3) Å and 92.77(9)°, 92.30(10)°, and 91.79 (16)°, for **2**, **5**, and **6**, respectively.

Compounds **4** and **7** are trimetallic clusters of [*cis*-M^{II}-$(en)_2(OH_2)]_2[(\mu$-NC$)_2M^{IV}(CN)_6]\cdot 4H_2O$ stoichiometry that crystallize in the monoclinic (*C*2/*c*) space group (Table 1). The [*cis*-$M^{II}(en)_2(OH_2)]^{2+}$ centers are related by a crystallographic 2-fold and are linked by μ-CN linkages to the $[M^{IV}(CN)_8]^{4-}$ center; the bridging cyanides are *cis* to the aqua ligand present in each [*cis*-$M^{II}(en)_2(OH_2)]^{2+}$ unit (Figure 2). The average $W^{IV}-C$ and $Mo^{IV}-C$ bond distances for the distorted square antiprismatic $M^{IV}(CN)_8{}^{4-}$ centers are 2.166(2) and 2.165(3) Å and the C_5-W-C_{5A} and C_4-Mo-C_{4A} bond angles are 80.48(11)° and 80.30(13)°; the $Co-N_5-C_5$, $W-C_5-N_5$, $Ni-N_4-C_4$, and $Mo-C_4-N_4$ bond angles are 169.57(18)° and 176.34(19)° for **4** and 169.9(2)°, and 176.0(2)° for **7**, respectively (Tables 2 and 3).

Magnetic Studies. Previous reports show that the temperature dependence of the magnetic susceptibility of **5** exhibits weak antiferromagnetic coupling or zero-field splitting of the Ni^{II} centers below ca. 20 K (Figure 1).[48] Given that **1**–**7** each contain diamagnetic centers, we did not initiate extensive magnetic studies of **1**–**7**. The room temperature effective magnetic moments (μ_{eff}) of **1**–**7** suggest that the $M^{IV}(CN)_8{}^{4-}$ centers are diamagnetic and the paramagnetism of each cluster is entirely due to the Mn^{II} ($S = {}^5/_2$), Co^{II} ($S = {}^3/_2$), and Ni^{II} ($S = 1$) centers present. The calculated μ_{eff} values expected for a 2:1 ratio of paramagnetic (M^{II}) and diamagnetic (M^{IV}) centers assuming $g = 2$ are 8.37 (**1**, **2**), 5.48 (**3**, **4**), and 4.0 μ_B (**5**–**7**); the experimental values are 8.47, 8.21, 6.66, 7.05, 4.38, 4.41, and 4.23 μ_B for **1**–**7**, respectively. Assuming spin–orbit effects are operative, the calculated *g* values are 2.49, 2.57, 2.19, 2.21, and 2.13 for **3**–**7**, respectively.[56–57,70–72]

While we were unable to isolate any crystals suitable for crystallographic studies of networks containing bidentate ethylenediamine, octacyanometalate, and divalent transition metal centers,[43–48] a series of cyanide-bridged trimetallic clusters were obtained, presumably via rate-limiting dissociative loss of ethylenediamine and substitution by water. Subsequent water loss from the putative *cis*-$M^{II}(en)_2(OH_2)_2{}^{2+}$

(69) (a) Bignozzi, C. A.; Argazzi, R.; Schoonover, J. R.; Gordon, K. C.; Dyer, R. B.; Scandola, F. *Inorg. Chem.* **1992**, *31*, 5260–5267. (b) Watzky, M. A.; Endicott, J. F.; Song, X.; Lei, Y.; Mccatangay, A. *Inorg. Chem.* **1996**, *35*, 3463–3473. (c) Purcell, K. F.; Yeh, S. M.; Eck, J. S. *Inorg. Chem.* **1977**, *16*, 1708–1715. (d) Darensbourg, M. Y.; Barros, H. L. C. *Inorg. Chem.* **1979**, *18*, 3286–3288. (e) Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11357–11367. (f) Vahrenkamp, H.; Geiss, A.; Richardson, G. N. *J. Chem. Soc., Dalton Trans.* **1997**, 3643–3651. (g) Lim, B. S.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 4898–4908. (h) Richardson, G. N.; Brand, U.; Vahrenkamp, H. *Inorg. Chem.* **1999**, *38*, 3070–3079. (i) Geiss, A.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **1999**, 1793–1803. (j) Geiss, A.; Vahrenkamp, H. *Inorg. Chem.* **2000**, *39*, 4029–4036. (k) Podgajny, R.; Desplanches, C.; Sieklucka, B.; Sessoli, R.; Villar, V.; Paulsen, C.; Wernsdorfer, W.; Dromzée, Y.; Verdaguer, M. *Inorg. Chem.* **2002**, *41*, 1323–1327. (l) Bignozzi, C. A.; Scandola, F. *Inorg. Chem.* **1984**, *23*, 1540–1545. (m) Purcell, K. F. *J. Am. Chem. Soc.* **1967**, *89*, 247–250. (n) Purcell, K. F. *Inorg. Chem.* **1967**, *6*, 6139–6143.

(70) (a) Robinson, W. K.; Friedberg, S. A. *Phys. Rev.* **1960**, *117*, 402–408. (b) Manson, J. L.; Kmety, C. R.; Huang, Q.-Z.; Lynn, J. W.; Bendele, G. M.; Pagola, S.; Stephens, P. W.; Liable-Sands, L. M.; Rheingold, A. L.; Epstein, A. J.; Miller, J. S. *Chem. Mater.* **1998**, *10*, 2252–2560. (c) Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 12096–12097.

(71) Haque, M.-U.; Caughlan, C. N.; Emerson, K. *Inorg. Chem.* **1970**, *9*, 2421–2424.

(72) (a) Enemark, J. E.; Quinby, M. S.; Reed, L. L.; Steuck, M. J.; Walthers, K. K. *Inorg. Chem.* **1970**, *9*, 2397–2403. (b) Kurmoo, M.; Kepert, C. J. *New J. Chem.* **1998**, *22*, 1515–1524. (c) Manson, J. L.; Arif, A. M.; Miller, J. S. *J. Mater. Chem.* **1999**, *9*, 979–983.

intermediate and coordination of $M^{IV}(CN)_8{}^{4-}$ affords a single *μ*-cyano linkage per $M^{II}(en)_2(OH_2)^{2+}$ center, suggesting that the *cis*-$[M^{II}(en)_2(OH_2)(\mu\text{-NC})M^{IV}(CN)_7]^{2-}$ units present in each cluster are kinetic reaction products; we presume that networks are the thermodynamically favored products. Similar intermediates have been proposed by Sieklucka in the formation of octacyanometalate clusters derived from *cis*-$[Mn(bpy)_2(OH_2)_2]^{2+}$ units.[48,53]

Conclusions

We have described the synthesis, spectroscopic, and magnetic characterization of eight unusual bi- and trimetallic clusters containing divalent and square antiprismatic octacyanometalate(IV) centers that are linked by cyanides. Coordinated ethylenediamine limits the number of cyano linkages formed, and a series of clusters rather than networks are obtained. We postulate that slow formation of *cis*-$M^{II}(en)_2(OH_2)_2{}^{2+}$ from $M^{II}(en)_3{}^{2+}$ and subsequent substitution of an single aquo ligand by a terminal cyanide from $M^{IV}(CN)_8{}^{4-}$ affords *cis*-$M^{II}(en)_2(OH_2)(\mu\text{-NC})M^{IV}(CN)_7{}^{2-}$ species rather than octacyanometalate networks. In a subsequent manuscript, we will report that several 1-D and 3-D lattices can be prepared via substitution of ethylenediamine for other amine donors.

Acknowledgment. We wish to acknowledge Alisha Marie O'Connell for valuable assistance early in the project. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund (PRF-38388-G3) and the National Science Foundation Research Experience for Undergraduates (CHE-0097668) for partial support of this research. S.M.H. is also grateful to the University of Kentucky and the University of Kentucky Summer Faculty Research Fellowship program for additional financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for **2** and **4**−**7** and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048936M