One- and three-dimensional octacyanometalate(IV) networks constructed via a building block approach:

\[
\{[trans-Ni^{II}(tn)_2(OH_2)][trans-Ni^{II}(\mu-NC)_2(tn)_2]\cdot[\mu-NC]_3M^{IV}(CN)_5 \cdot 6H_2O}\ (M^{IV} = Mo, W)
\]

and \(Cs_4[Cu^{II}(OH_2)_4]_2[Cu^{II}(NH_3)]_4[Mo^{IV}(CN)_8]_4 \cdot 2H_2O\)

Jeffrey R. Withers, Chad Ruschman, Sean Parkin, Stephen M. Holmes *

Department of Chemistry, University of Kentucky, 15 Chemistry-Physics Building, Lexington, KY 40506-0055, United States

Received 17 February 2005; accepted 30 June 2005
Available online 15 August 2005

Abstract

Treatment of \([Ni^{II}(tn)_3]OTs_2\), or aqueous solutions containing nickel(II) \(p\)-toluenesulfonate and 1,3-propanediamine \((tn)\) with aqueous \(K_4M^{IV}(CN)_8\cdot2H_2O\) \((M^{IV} = Mo, W)\) affords one-dimensional chains of \([trans-Ni^{II}(tn)_2(OH_2)][trans-Ni^{II}(\mu-NC)_2(tn)_2]\cdot[\mu-NC]_3M^{IV}(CN)_5 \cdot 6H_2O\) stoichiometry \((M^{IV} = Mo, 2; W, 3)\). An additional three-dimensional network, \(Cs_4[Cu^{II}(OH_2)_4]_2[Cu^{II}(NH_3)]_4[Mo^{IV}(CN)_8]_4 \cdot 2H_2O\) \((4)\), is obtained by treating aqueous solutions of \(Cs_3Mo^{V}(CN)_8\) with \(CuCl_2 \cdot 2H_2O\) in concentrated ammonia. Each network has been characterized via structural and magnetic methods. The distorted square antiprismatic \(M^{IV}(CN)_8\) centers are diamagnetic and the paramagnetism of each network originates from the \(Ni^{II}\) and \(Cu^{II}\) centers present.

Keywords: Cyanide networks; Octacyanometalates

1. Introduction

The rational design of cyanometalate networks and clusters has seen a dramatic resurgence of activity in recent years. [1–8] Through the judicious choice of cyanometalate and transition metal building blocks, a variety of compounds exhibiting room temperature magnetism [2–7], single molecule magnetism [8–11], high spin ground states [5,12], and magnetism [13] have been reported. Of all the classes of molecule-based magnets, Prussian blue analogues constructed from early transition metal hexacyanometalate building blocks such as \(V(CN)_6\) and \(Cr(CN)_6\) exhibit some of the highest magnetic ordering temperatures [2,3,6,7]; the current record is held by \(KV^{III}[Cr^{III}(CN)_6] \cdot 2H_2O\), which remains magnetic up to 376 K [6].

As part of an ongoing effort to investigate and develop new classes of cyanometalate-based magnets we turned our attention towards a fundamentally different building block: octacyanometalate ions \(M(CN)_8^{4+}\). Octacyanometalates are an interesting class of building blocks as they can form up to eight cyanide bridges per \(M(CN)_8^{4+}\) center and can be used to rapidly construct a rich and diverse array of networks and clusters [4,15]. The \(M(CN)_8^{4+}\) centers generally adopt square antiprismatic, dodecahedral, or bicapped trigonal prismatic structures and several magnetic and photomagnetic clusters and network derivatives have been described [13a,13b,13m,13n,15]. Surprisingly, few octacyanometalate networks have been crystallographically characterized and only recently have the spectroscopic
and structural characterization of several $M^{II}_{n}$·$M^{IV}_{n}$ (CN)$_{n}$·$n$H$_2$O [13h–13n] ($2 \leq n \leq 9$) and amine-functionalized networks have been described [13b,14]; analogues containing Cu$^{II}$/Mo(CN)$_{n}$ and Co$^{III}$/W(CN)$_{n}$ units are reported to exhibit reversible photo-induced magnetization changes and we anticipate that incorporation of such bistable materials into electronic circuitry may ultimately afford molecule-based nanoscale switchable devices [13a,13b,13l–13n,15].

While we experienced limited success in crystallizing octacyanometalate networks via hydrothermal and slow diffusion methods, 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), find extensive use in the preparation of so-called “expanded Prussian blue solid solutions” [16], but surprisingly few octacyanometalate clusters containing these amines are also relatively rare [18].

In the present contribution, we describe the synthesis, structural, spectroscopic, and magnetic characterization of three unusual amine-expanded octacyanometalate(IV) networks that crystallize from aqueous mixtures of amines, octacyanometalate, and divalent transition metal salts.

2. Experimental

2.1. General considerations

All operations were conducted in the dark. Solvents were distilled under dinitrogen from CaH$_2$ (acetonitrile), Mg turnings (methanol), or sodium-benzophenone (diethyl ether). Deionized water, ammonium hydroxide (Malinkrodt), and CuCl$_2$·2H$_2$O (Baker) were used as received. The preparation of K$_4[Mo_4(CN)_{10}]$·2H$_2$O [19,20], K$_4[W(CN)_8]$·2H$_2$O [21], and Ni(OTs)$_2$·2H$_2$O were described elsewhere. C$_3$H$_4$Ni$_2$S$_2$O$_6$·H$_2$O [19] and [Ni(tn)$_3$][OTs]$_2$·2H$_2$O (Baker) [22] were prepared via modifications to previously described procedures. The IR spectra were recorded as Nujol mulls of amines, octacyanometalate, and divalent transition metal salts.

2.2. Preparation of complexes and networks

2.2.1. $[\text{Ni}^{II}(\text{tn})_3][\text{OTs}]_2$ (1)

An aqueous (20 mL) solution of Ni(OTs)$_2$ (3.57 g, 7.02 mmol) was prepared by heating (100 °C) and 1,3-propanediamine (3.0 mL, 35.9 mmol) was added affording a purple suspension. The mixture was filtered and the filtrate was concentrated (10 mL) by heating to boiling. The concentrated mixture was allowed to stand at ~20 °C for 2 h and then warm to room temperature. The purple crystals were isolated by suction filtration and were washed with EtOH (2 × 10 mL), Et$_2$O (10 mL), and dried under vacuum at room temperature for 2 h. Yield: 2.99 g (71.7%).

2.2.2. $[\text{trans-Ni}^{II}(\text{tn})_2(\text{OH})_2][\text{trans-Ni}^{II}(\text{tn})_2]$·$[\mu$-$\text{NC}]_3\text{Mo}^{IV}(\text{CN})_6\cdot6\text{H}_2\text{O}$ (2)

A hot methanol (40 mL) solution of Ni(OTs)$_2$ (1.54 g, 1.57 mmol) was treated with 1,3-propanediamine (2.64 mL, 35.6 mmol) and was allowed to cool to room temperature. Additional MeOH (85 mL) was added and addition of K$_4[Mo(CN)_6]$·2H$_2$O (0.95 g, 1.91 mmol) in water (7 mL) afforded brown crystals within 2 h; the slow deposition of crystals ceased after four weeks at room temperature. The brown needles were isolated by suction filtration and were washed with water (10 mL), EtOH (10 mL), and dried under vacuum at room temperature overnight. Yield: 0.305 g (49.1%).

2.2.2. $[\text{trans-ni}^{II}(\text{tn})_2(\text{OH})_2][\text{trans-ni}^{II}(\text{tn})_2]$·$[\mu$-$\text{NC}]_3\text{Mo}^{IV}(\text{CN})_6\cdot6\text{H}_2\text{O}$ (2)
2.2.3. \([\text{trans-Ni}^{II}_2(\text{tn})_2(\text{OH}_2)]\) and \([\text{trans-Ni}^{II}_2(\text{tn})]^{1-}\) \((\mu-\text{NC})_3W^{IV}(\text{CN})_5·6\text{H}_2\text{O}}\) (3)

An aqueous (25 mL) solution of I (0.72 g, 1.14 mmol) was treated with aqueous (10 mL) \(\text{K}_4[\text{W(CN)}_8]\cdot2\text{H}_2\text{O}\) (0.70 g, 1.19 mmol) and the resulting brown solution was allowed to stand; brown needles began to deposit within 1 h and ceased after 24 h. The brown needles were isolated by suction filtration and washed with water (2 × 10 mL), \(\text{MeOH (2} × 10 \text{ mL), Et}_2\text{O (2} × 10 \text{ mL), and dried under vacuum at room temperature overnight. Yield: 0.24 g (47.9%). Anal. Calc. for C_{18}H_{46}N_{18}Ni_{2}O_{7}W: C, 24.30; H, 5.51; N, 28.34. Found: C, 27.29; H, 5.31; N, 25.01%. IR (nujol, cm\(^{-1}\)): 3350 (vs, br), 2952 (vs), 2922 (vs), 2856 (vs), 2172 (vs, sh), 2158 (vs), 2145 (vs, sh), 2125 (vs), 2109 (vs, sh), 2084 (vs, sh), 1683 (m, sh), 1660 (s, sh), 1613 (vs), 1462 (vs), 1455 (vs), 1377 (vs), 1262 (vs), 1250 (vs), 1241 (vs), 1169 (w), 1155 (w), 1079 (m), 1073 (m), 919 (w), 887 (w), 843 (m), 810 (m), 719 (vs), 705 (vs), 664 (m), 649 (m), 614 (m), 476 (m). \(\mu_{\text{eff (\mu B)}}\) Calc.: 4.0. \(\mu_{\text{eff (\mu B)}}\) Found: 4.41.

2.2.4. \(\text{Cs}_4\text{Cu}^{II}(\text{OH}_2)_4\cdot2\text{Cu}^{II}(\text{NH}_3)_4\cdot\text{Mo}^{IV}(\text{CN})_8\cdot4\cdot2\text{H}_2\text{O}}\) (4)

Treatment of a concentrated ammonia (30 mL) solution of CuCl\(_2\cdot2\text{H}_2\text{O}\) (0.53 g, 1.94 mmol) with \(\text{Cs}_4[\text{Mo(CN)}_8]\) (0.89 g, 1.16 mmol) in ammonia (30 mL) afforded a brown solution that was allowed to stand for 2 weeks. The iridescent copper plates that deposited were isolated by suction filtration and washed with water (3 × 10 mL), \(\text{EtOH (3} × 5 \text{ mL), and Et}_2\text{O (2} × 10 \text{ mL). The crystals were dried under vacuum at room temperature overnight. Yield: 0.72 g (96.0%). Anal. Calc. for C_{19}H_{48}N_{18}O_{7}Cu_{6}Mo_{4}: C, 15.33; H, 1.29; N, 20.12. Found: C, 15.74; H, 1.22; N, 20.91%. IR (nujol, cm\(^{-1}\)): 3350 (vs, br), 2952 (vs), 2922 (vs), 2856 (vs), 2172 (vs, sh), 2158 (vs), 2145 (vs, sh), 2125 (vs), 2109 (vs, sh), 2084 (vs, sh), 1683 (m, sh), 1660 (s, sh), 1613 (vs), 1462 (vs), 1455 (vs), 1377 (vs), 1262 (vs), 1250 (vs), 1241 (vs), 1169 (w), 1155 (w), 1079 (m), 1073 (m), 919 (w), 887 (w), 843 (m), 810 (m), 719 (vs), 705 (vs), 664 (m), 649 (m), 614 (m), 476 (m). \(\mu_{\text{eff (\mu B)}}\) Calc.: 4.24. \(\mu_{\text{eff (\mu B)}}\) Found: 4.34.

2.3. Structure determinations and refinements

Crystals of 2 and 3 were grown from aqueous [Ni(tn)_3]OTs_2 or Ni(OTs)_2/1,3-propanediamine mixtures treated with either \(\text{K}_4\text{Mo(CN)}_8\cdot2\text{H}_2\text{O}}\) (2) or \(\text{K}_4\text{W(CN)}_8\cdot2\text{H}_2\text{O}}\) (3) Crystals of 4 were grown from aqueous ammonium solutions of CuCl\(_2\cdot4\text{H}_2\text{O}\) and \(\text{Cs}_4\text{Mo(CN)}_8\). X-ray diffraction data were collected at 90.0(2) K on a Nonius kappaCCD diffractometer from irregular shaped crystals mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained (DENZO) [25] from ten 1° frames and were refined via a least-squares scheme using all data-collection frames (SCALEPACK) [26]. Lorentz/polarization corrections were applied during data reduction. The structures were solved by direct methods (SHELXS97) [26] and completed.
by difference Fourier methods (SHELXL97) [26]. Refinement was performed against $F^2$ by weighted full-matrix least-squares (SHELXL97) [26] and empirical absorption corrections (either SCALEPACK [25] or SADABS [26]) 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 [27]. Crystal data, relevant details of the structure determinations, and selected geometrical parameters are provided in Tables 1–3.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

We have previously described that a series of bi- and trimetallic clusters and salts, rather than networks, are obtained when aqueous [MIII(en)$_3$]OTs$_2$ (OTs$^-$ = p-toluenesulfonate) is treated with M(CN)$_6^{3-}$ (M = MoIV,V, WIV,V). We rationalized that substitution of ethylenediamine (en) for 1,3-propanediamine (tn), would afford kinetically labile NiII(tn)$_3$ ions that undergo dissociative tn loss, forming reactive cis-NiII(tn)$_2$(OH)$_2$$_{2+}$ intermediates, and a series of amine-expanded octacyanometalate networks of [NiII(tn)$_2$]MIV(CN)$_6$·nH$_2$O and [NiII(tn)$_2$]MIV(CN)$_6$·2nH$_2$O stoichiometry. Indeed, treatment of either aqueous mixtures of nickel(II) tosylate and 1,3-propanediamine or [NiII(tn)$_3$]OTs$_2$ with M(CN)$_6^{3-}$ (M = MoIV,V, WIV,V) affords isostuctural one-dimensional networks of [(trans-NiII(tn)$_3$)(OH)$_2$] [trans-NiII(tn)$_3$][(μ-CN)$_3$MIV(CN)$_5$]·6H$_2$O (M$^{IV}$ = Mo, 2; W, 3) stoichiometry.

Rationalizing that bidentate amines may hinder the formation of two- and three-dimensional networks, we reasoned that unidentate donors such as ammonia may facilitate greater network dimensionality. However, attempts to prepare two-dimensional copper(II) substituted analogues described by Meske and co-workers consistently met with failure [14f]. Treatment of copper(II) chloride dihydrate with cesium octacyanomolybdate(V) in aqueous ammonia unexpectedly affords a three-dimensional network of Cs$_4$[CuII(OH)$_2$]$_2$[CuII(NH$_3$)$_4$][MoIV(CN)$_8$]$_2$·2H$_2$O stoichiometry, via Mo$^{IV}$-CN$_6$ reduction; such behavior has been previously reported [28,29].

The infrared spectra of 2–4 suggest that bridging and terminal cyano ligands are present and the cyano stretching absorptions ($\nu_{CN}$) range from 2061 to 2172 cm$^{-1}$. The highest energy $\nu_{CN}$ absorptions are found for the Cu$^\text{II}$ derivative, consistent with the formation of M$^{III}$-NC-M$^{IV}$ units and depopulation of the cyanide $\sigma$ orbital; increasing $\pi$-backbonding progressing from Cu$^\text{II}$ to Ni$^\text{II}$ compensates this effect and progressively lowers the $\nu_{CN}$ absorption energies from 2172 to 2153 cm$^{-1}$ for 4 and 2, respectively [30]. These $\nu_{CN}$ absorptions are shifted to higher energies relative to those found for K$_4$Mo(CN)$_8$·2H$_2$O (2126, 2012, 2009 cm$^{-1}$ for 2; 2061, 2012, 1985 cm$^{-1}$ for 3; 2061, 2126, 2012, 2009 cm$^{-1}$ for 4).

Table 2: Selected bond distances (Å) for [MIII(tn)$_3$]OTs$_2$[MIII(tn)$_2$][μ-CN]MIV(CN)$_6$·6H$_2$O (2), [MIII(tn)$_3$]OTs$_2$[trans-NiII(tn)$_3$]·2H$_2$O (3), and Cs$_4$[CuII(OH)$_2$]$_2$[CuII(NH$_3$)$_4$][MoIV(CN)$_8$]$_2$·2H$_2$O (4).

<table>
<thead>
<tr>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(1)–C(1)</td>
<td>2.149(3)</td>
<td>W(1)–C(1)</td>
</tr>
<tr>
<td>Mo(1)–C(2)</td>
<td>2.156(3)</td>
<td>W(1)–C(2)</td>
</tr>
<tr>
<td>Mo(1)–C(3)</td>
<td>2.158(3)</td>
<td>W(1)–C(3)</td>
</tr>
<tr>
<td>Mo(1)–C(4)</td>
<td>2.159(3)</td>
<td>W(1)–C(4)</td>
</tr>
<tr>
<td>Mo(1)–C(5)</td>
<td>2.163(3)</td>
<td>W(1)–C(5)</td>
</tr>
<tr>
<td>Mo(1)–C(6)</td>
<td>2.173(3)</td>
<td>W(1)–C(6)</td>
</tr>
<tr>
<td>Mo(1)–C(7)</td>
<td>2.162(3)</td>
<td>W(1)–C(7)</td>
</tr>
<tr>
<td>Mo(1)–C(8)</td>
<td>2.158(3)</td>
<td>W(1)–C(8)</td>
</tr>
<tr>
<td>C(1)–N(1)</td>
<td>1.150(4)</td>
<td>C(1)–N(1)</td>
</tr>
<tr>
<td>C(2)–N(2)</td>
<td>1.150(4)</td>
<td>C(2)–N(2)</td>
</tr>
<tr>
<td>Ni(1)–N(1)</td>
<td>2.040(2)</td>
<td>Ni(2)–N(2)</td>
</tr>
<tr>
<td>Ni(1)–N(9)</td>
<td>2.102(2)</td>
<td>Ni(2)–N(13)</td>
</tr>
<tr>
<td>Ni(1)–N(10)</td>
<td>2.137(2)</td>
<td>Ni(2)–N(14)</td>
</tr>
<tr>
<td>Ni(1)–N(11)</td>
<td>2.088(2)</td>
<td>Ni(2)–N(15)</td>
</tr>
<tr>
<td>Ni(1)–N(12)</td>
<td>2.115(2)</td>
<td>Ni(2)–N(16)</td>
</tr>
<tr>
<td>Ni(1)–O(1)</td>
<td>2.192(2)</td>
<td>Ni(2)–O(1)</td>
</tr>
<tr>
<td>Ni(2)–N(2)</td>
<td>2.069(2)</td>
<td>Ni(1)–N(5A)</td>
</tr>
<tr>
<td>Ni(2)–N(3A)</td>
<td>2.091(3)</td>
<td>Ni(1)–N(1)</td>
</tr>
<tr>
<td>Ni(2)–N(13)</td>
<td>2.135(2)</td>
<td>Ni(1)–N(9)</td>
</tr>
<tr>
<td>Ni(2)–N(14)</td>
<td>2.104(3)</td>
<td>Ni(1)–N(10)</td>
</tr>
<tr>
<td>Ni(2)–N(15)</td>
<td>2.129(2)</td>
<td>Ni(1)–N(11)</td>
</tr>
<tr>
<td>Ni(2)–N(16)</td>
<td>2.133(2)</td>
<td>Ni(1)–N(12)</td>
</tr>
</tbody>
</table>
2060 cm$^{-1}$ and $K_4W(CN)_8 \cdot 2H_2O$ (2125, 2095, 2056 cm$^{-1}$) [31], and are comparable to those exhibited by a variety of networks containing copper(II) and nickel(II) centers [14]. Unfortunately, the infrared characterization of $[M^{IV}(NH_3)_{6}]_2[M^{IV}(CN)_8] \cdot 2H_2O$ ($M^{IV} = Mo, Ni$) lattices have not been reported [13f].

Generally, $M^{IV}(CN)_{8}^{4-}$ compounds exhibit cyanide stretching absorptions that range from 2060 to 2160 (ionic) and 2085 to 2141 cm$^{-1}$ (cyaneid-bridged) [17,18,31–33]. The $\nu_{CN}$ absorptions 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 $\nu_{CN}$ absorptions are expected to move to higher energies [30,34]. If however, increased $\pi$-backbonding compensates the kinematic effect by decreasing the C–N bond order, then red-shifted $\nu_{CN}$ absorptions that scale as a function of the donor–acceptor charge-transfer absorption oscillator strength, will be observed [30,34]. Assuming that $\pi$-backbonding effects are minor, we tentatively assign the bridging and terminal cyano stretching absorptions as those near 2140 and 2080 cm$^{-1}$, respectively.

### 3.2. Crystallographic studies

Crystals of 2 and 3 are in the $P\bar{1}$ space group and crystallize as one-dimensional chains of $[[trans-Ni^{II}(tn)_2(OH_2)](trans-Ni^{II}(tn)_2)][(\mu-NC) Mo^{IV}(CN)_8] \cdot 6H_2O$ stoichiometry (Table 1). The winding 1-D chains are composed of $[\mu-\mu-CN]Ni^{II}(tn)_2(\mu-\mu-CN)M^{IV}(CN)_8] \cdot 6H_2O$ units that propagate parallel to the crystallographic $a$ direction (Figs. 1 and 2). These “T-shaped” chains pack via inversion centers around a channel of lattice water molecules that are hydrogen bonded to adjacent cyanide, ammine, and aquo ligands along the crystallographic $c$ direction. Coordination networks containing similar chain-like species have recently been reported by Kahn et al. we postulate that 2 and 3 are the efflorescent crystals described by Gao et al. [14e,15e].

Extensive interchain hydrogen bonding interactions are present between lattice water, aquo ligands, and terminal cyanides in 2 and 3. The nearest neighbor contacts for 2 range from 2.685(5) (O(2WA)···O(3WA)) to 2.689(5) Å (N(6DD)···O(1WA)) while those for 3 range from 2.792(4) (O(1A)···O(1WB)) to 3.060(4) Å (O(5WC)···O(6WA)). Additional hydrogen bonding interactions (ca. 3.0–3.1 Å) are also present between lattice waters and coordinated $tn$ and aquo ligands.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{CN}$ (sym)</th>
<th>$\nu_{CN}$ (asym)</th>
<th>$\nu_{CN}$ (trans)</th>
<th>$\nu_{CN}$ (Raman)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2060 cm$^{-1}$</td>
<td>2125, 2095</td>
<td>2056 cm$^{-1}$</td>
<td>2085, 2141 cm$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>2060 cm$^{-1}$</td>
<td>2125, 2095</td>
<td>2056 cm$^{-1}$</td>
<td>2085, 2141 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Table 3

Selected bond angles (°) for [(trans-Ni$^{II}$(tn)$_2$(OH)$_2$][trans-Ni$^{II}$(tn)$_2$][(\mu-NC) Mo$^{IV}$(CN)$_8$] \cdot 6H$_2$O, (2), [(trans-Ni$^{II}$(tn)$_2$(OH)$_2$][trans-Ni$^{II}$(tn)$_2$][\mu-NC) W$^{IV}$(CN)$_8$] \cdot 6H$_2$O, (3), and Cs$_4[\text{Cu}$I$(\text{OH}_2)$_2]$[\text{Cu}$II$(\text{NH}_3))$_4$[Mo$^{IV}$(CN)$_8$] \cdot 2H$_2$O (4)
Each three-connected M IV(CN)₈⁴⁻ center adopts a distorted square antiprismatic geometry and forms cyanide linkages to adjacent trans-Ni III(tn)₂(μ-NC)₂ and trans-(μ-CN) Ni III(tn)₂(OH₂) units. The average M IV–C bond distances are 2.160(3) and 2.162(2) Å, while the C–M IV–C bond angles range from 69.42(10)° to 143.58(10)° and 71.30(7)° to 144.96(8)°, for 2 and 3, respectively (Tables 2 and 3). Cyanide nitrogen atoms N₁, N₂, and N₃ form μ-CN linkages to adjacent Ni III(tn)₂ and Ni III(tn)₂(OH₂) fragments, whose M IV–C bond distances range from 2.149(3) to 2.173(3) and 2.157(2) to 2.177(2) Å, for 2 and 3, respectively. These M IV–C and M II–N bond distances are comparable to previously reported values.

The one-dimensional chain backbones are comprised of trans-Ni III(tn)₂(μ-NC)₂ units connected via cyanide linkages to each octacyanometalate(IV) center. The Ni–N₄ bond distances within each fragment range from 2.088(2) to 2.137(2) and 2.040(2) to 2.0384(18) Å while the Ni–N cyanide bond distances are nearly identical, ranging from 2.069(2) to 2.091(3) and 2.072(4) to 2.093(5) Å for 2 and 3, respectively. For 2 and 3, the nickel(II)–nitrile N–Ni(1)–N bond angles are nearly linear, 176.5(3)° and 176.5(3)° while the N₄–Ni–N cyanide bond angles are nearly 90° (Tables 2 and 3).

Appended to each chain via a single bridging cyanide are trans-(μ-CN)Ni III(tn)₂(OH₂) units. These fragments exhibit slightly longer Ni–N cyanide and Ni–N₄ bond distances in comparison to the trans-Ni III(tn)₂(μ-NC)₂ fragments, with Ni–N cyanide bond distances of 2.040(2) and 2.0384(18) Å, and Ni–N₄ bond distances ranging from 2.088(2) to 2.137(2) and 2.0875(18) to 2.1384(18) Å, for 2 and 3, respectively (Table 2). The Ni(1)–N(1)–C(1) and O(1)–Ni(1)–N(1) bond angles are described in Table 3.

Crystals of 4 are in the monoclinic C2/m space group (Table 1) and consist of anionic two-dimensional sheets containing an infinite array of distorted Cs₂[(H₃N)Cu III(μ-NC)₂Mo IV(CN)₃]₄⁻ box-like units (Fig. 3). The copper(II) and molybdenum(IV) centers reside in alternate corners of each box and are connected via μ-CN linkages, forming anionic...
\{Cs[(H_3N)Cu^{II}(\mu-NC)_3Mo^{IV}(CN)_4]_4\}_{\delta}^{4e-} \text{ slabs (Fig. 4)}. The parallel slabs are connected via disordered cyanides to trans-Cu^{III}(OH_2)_4(\mu-NC)_2 units that also exhibit canting along the Jahn–Teller N–Cu–N bond axis (Fig. 5).

Overall, 4 adopts an unusual and complicated three-dimensional structure of Cs_4[Cu^{II}(OH_2)_4Cu^{I}(NH_3)_4][Mo^{IV}(CN)_8]_4 \cdot 2H_2O stoichiometry (Fig. 6).

For 4, the average Mo–C bond lengths of the Mo^{IV}(\mu-CN)_6(CN)_2^{4+} centers range from 2.152(12) to 2.184(16) Å (Table 2). The cyanides linked to adjacent Cu^{II} centers range from 2.152(12) (Mo–C(1)) to 2.170(12) (Mo–C(2)) while those connected to Cu^{III} centers external to the sheet range from 2.147(12) (Mo–C(4)) to 2.184(16) (Mo–C(5)). The longest Mo–C bonds are found for terminal cyanides (2.184(16) Å) while cyanides trans- to the ammine in (H_3N)Cu(\mu-NC)_5 are comparatively shorter (2.170(12) Å); the cis-cyanides range from 2.152(12) to 2.161(11) Å (Table 2). Overall, the Mo^{IV}(CN)_4^{4+} centers exhibit Mo–C–N bond angles ranging from 72.6(5)° to 146.2(5)° and adopt a distorted square antiprismatic coordination geometry (Table 3).

The Cu–N bond distances for the highly distorted (H_3N)Cu(\mu-NC)_5^{3+} units range from 1.985(8) to 2.575(9) Å for 4. Tetragonal elongation along N(1)–Cu(1)–N(3A) bond vector in each (H_3N)Cu(\mu-NC)_5 fragment affords comparatively longer Cu–N bond distances, 2.257(9) (N_1–Cu_1) and 2.575(9) Å (N_{3A}–Cu_{1}), relative to either the Cu_1–NH_3 (1.985(8) Å, Cu_1–N_7), or remaining cyanide linkages (ca. 2.020(10) Å; Table 2). The N–Cu_1–N bond angles range from 90.61(17)° to 94.6(3)° (Table 3) and we conclude that the Jahn–Teller axis lies along the N(1)–Cu(1)–N(3A) bond vector.

In comparison, the trans-Cu(OH_2)_4(\mu-NC)_2 fragments connecting each sheet clearly show that the Jahn–Teller axis lies along the N(4)–Cu(2)–N(4A) vector. Rather long Cu–N bond distances (2.477(11) Å) are found between the copper and disordered cyanides with average Cu–O values of 2.04(3) Å. The copper atoms occupy crystallographically equivalent positions where the cyano and aquo ligands are disordered via canting (26.5°) along the Jahn–Teller axis (Fig. 5). Overall, incorporation of Jahn–Teller distorted copper(II) ions into 4 affords a rather complicated, unusual, and highly distorted three-dimensional structure (Fig. 6).
3.3. Magnetic studies

Given that each lattice contains diamagnetic centers, we did not initiate extensive magnetic studies. The room temperature effective magnetic moments ($\mu_{\text{eff}}$) of 2–4 using crushed crystals indicate that the $\text{M}^{\text{IV}}(\text{CN})_8^{4-}$ ($\text{M}^{\text{IV}} = \text{Mo, W}$) centers are diamagnetic and that the paramagnetism of each network is due to the divalent transition metal centers (Ni, Cu) present. The calculated $\mu_{\text{eff}}$ values expected, assuming that $g = 2$, for a 2:1 ratio of paramagnetic (M II) and diamagnetic (M IV) centers is 4.0 $\mu_B$ for 2 and 3; a 6:4 ratio of Cu II to Mo IV centers would afford a value of 4.24 $\mu_B$ for 4. The experimental values are close to those expected and are 4.53, 4.41, and 4.34 $\mu_B$ for 2–4, respectively. Assuming that spin-orbit coupling effects are operative, then the calculated $g$ values are 2.27, 2.21, and 2.05 for the Ni II and Cu II centers in 2–4, respectively [24,35,36].

4. Conclusions

In summary, a series of one- and three-dimensional octacyanometalate(IV) networks containing 1,3-propanediamine and ammine ligands have been synthesized and characterized via structural and magnetic methods. The distorted square antiprismatic $\text{M}^{\text{IV}}(\text{CN})_8^{4-}$ centers are diamagnetic and the paramagnetism of each network originates from the Ni II and Cu II centers present. The photomagnetic properties of each network will be reported in a subsequent manuscript.

5. Supplementary material

CCDC numbers 263402–263404 contain the supplementary crystallographic data for this paper. These data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund (PRF-38388-G3), the National Science Foundation Foundation Research Experience for Undergraduates (CHE-0097668), and the University of Kentucky Summer Faculty Research Fellowship programs for partial financial support. S.M.H. is also grateful for access to the Frederick Seitz Materials Research Laboratory magnetometer facility at the University of Illinois at Urbana-Champaign.

References

[29] (a) W.L. Waltz, A.W. Adamson, P.D. Fleischauer, J. Am. Chem. Soc. 89 (1967) 3923;
(c) S. Zofia, B. Hanna, Roczn. Chem. 48 (1974) 389;
(d) S.I. Zofia, Roczn. Chem. 47 (1973) 1993;
(b) K.O. Hartman, F.A. Miller, Acta 24A (1968) 669;
(c) K.F. Purcell, S.M. Yeh, J.S. Eck, Inorg. Chem. 16 (1977) 1708;
(d) M.Y. Darenbourg, H.L.C. Barros, Inorg. Chem. 18 (1979) 3286;
(e) M.J. Scott, R.H. Holm, J. Am. Chem. Soc. 116 (1994) 11357;
(g) B.S. Lim, R.H. Holm, Inorg. Chem. 37 (1998) 4898;
(m) K.F. Purcell, J. Am. Chem. Soc. 89 (1967) 247;
[34] (a) W.K. Robinson, S.A. Friedberg, Phys. Rev. 117 (1960) 402;
(c) M. Murmoo, C.M. Kepert, New J. Chem. 22 (1998) 1515;