

One- and three-dimensional octacyanometalate(IV) networks constructed via a building block approach: $$\{[trans-Ni^{II}(tn)_2(OH_2)][trans-Ni^{II}(\mu-NC)_2(tn)_2]-[(\mu-NC)_3M^{IV}(CN)_5] \cdot 6H_2O\} (M^{IV} = Mo, W)$$ and $Cs_4[Cu^{II}(OH_2)_4]_2[Cu^{II}(NH_3)_4][Mo^{IV}(CN)_8]_4 \cdot 2H_2O$

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Abstract

Treatment of $[Ni^{II}(tn)_3][OTs]_2$ or aqueous solutions containing nickel(II) *p*-toluenesulfonate and 1,3-propanediamine (tn) with aqueous $K_4M^{IV}(CN)_8 \cdot 2H_2O$ ($M^{IV} = Mo, W$) affords one-dimensional chains of $\{[trans-Ni^{II}(tn)_2(OH_2)][trans-Ni^{II}(tn)_2]-[(\mu-NC)_3M^{IV}(CN)_5] \cdot 6H_2O\}$ 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 $M^{IV}(CN)_8^{4-}$ centers are diamagnetic and the paramagnetism of each network originates from the Ni^{II} and Cu^{II} centers present.
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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 photomagnetism [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 $V(CN)_6^{4-}$ and $Cr(CN)_6^{3-}$ exhibit some of the highest magnetic ordering temperatures [2,3,6,7]; the

current record is held by $KV^{II}[Cr^{III}(CN)_6] \cdot 2H_2O$, 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 $M(CN)_8^{n-}$. Octacyanometalates are an interesting class of building blocks as they can form up to eight cyanide bridges per $M(CN)_8^{n-}$ center and can be used to rapidly construct a rich and diverse array of networks and clusters [4,15]. The $M(CN)_8^{n-}$ 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

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and structural characterization of several $M^{II}_2 \cdot [M^{IV}(\text{CN})_8] \cdot n\text{H}_2\text{O}$ [$13\text{h}–13\text{n}$] ($2 \leq n \leq 9$) and amine-functionalized networks been described [$13\text{b}, 14$]; analogues containing $\text{Cu}^{II}/\text{Mo}(\text{CN})_8^{n-}$ and $\text{Co}^{II/III}/\text{W}(\text{CN})_8^{n-}$ 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 [$13\text{a}, 13\text{b}, 13\text{l}–13\text{n}, 15$].

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 solids” [16], but surprisingly few octacyanometalate derivatives are known [$14\text{a}–14\text{g}, 15, 17$]; 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 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Baker) were used as received. The preparation of $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ [19,20], $\text{K}_4[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ [21], and $\text{Ni}(\text{OTs})_2$ [22] are described elsewhere while $\text{Cs}_3[\text{Mo}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ [13o,21,23] and $[\text{Ni}(\text{tn})_3][\text{OTs}]_2$ [22] were prepared via modifications to previously described procedures. The IR spectra were recorded as Nujol mulls between KBr plates on a Mattson Galaxy 5200 FTIR instrument. Room-temperature magnetic susceptibility measurements were conducted on a Johnson–Matthey Magnetic Susceptibility Balance. Variable temperature magnetic measurements were conducted on Quantum Design MPMS or MPMS2 SQUID magnetometers located at the Frederick Seitz Materials Characterization Laboratory at the University of Illinois at Urbana-Champaign. Photomagnetic studies were conducted using a Quantum Design Fiber Optic Sample Holder (FOSH) using infrared filtered white, red (Meade #23A), or blue (Meade #80A) light from a Dolan Jen-

ner Fiber-Lite source. Diamagnetic corrections were estimated using Pascal's constants [24]: $\chi_{\text{dia}} = -200.32 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **1**, $-458.32 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **2**, $-464.32 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **3**, and $-848.92 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **4**. Microanalyses were performed by the University of Illinois Microanalytical Laboratory.

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 $\text{Ni}(\text{OTs})_2$ (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), Et₂O (10 mL), and dried under vacuum at room temperature for 2 h. Yield: 2.99 g (71.7%). *Anal.* Calc. for $\text{C}_{23}\text{H}_{45}\text{N}_6\text{NiS}_2\text{O}_{6.5}$: C, 43.48; H, 7.64; N, 13.21. Found: C, 43.52; H, 7.08; N, 12.94%. IR (nujol, cm^{-1}): 3477 (s, br), 3306 (vs), 3269 (vs), 3182 (vs), 2227 (w), 2133 (w), 1912 (w), 1611 (vs), 1494 (m), 1402 (m), 1261 (s), 1197 (vs), 1182 (vs), 1123 (vs), 1107 (vs, sh), 1075 (s, sh), 1064 (s, sh), 1033 (vs), 1011 (vs), 946 (vs), 904 (m), 856 (w), 840 (w), 815 (s), 803 (w, sh), 773 (w), 710 (m), 685 (vs), 662 (s, sh), 614 (m), 567 (vs), 521 (w), 479 (w), 451 (w). μ_{eff} (μ_{B}) Calc.: 2.83. μ_{eff} (μ_{B}) Found: 2.93.

2.2.2. $\{[\text{trans-Ni}^{II}(\text{tn})_2(\text{OH}_2)][\text{trans-Ni}^{II}(\text{tn})_2]/[(\mu\text{-NC})_3\text{Mo}^{IV}(\text{CN})_5] \cdot 6\text{H}_2\text{O}\}$ (**2**)

A hot methanol (40 mL) solution of $\text{Ni}(\text{OTs})_2$ (1.54 g, 1.57 mmol) was treated with 1,3-propanediamine (2.64 mL, 3.56 mmol) and was allowed to cool to room temperature. Additional MeOH (85 mL) was added and addition of $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ (0.95 g, 1.91 mmol) in water (7 mL) afforded brown crystals within 1 h; the slow deposition of crystals ceased after four weeks at room temperature. The brown needles were isolated by suction filtration and washed with water (10 mL), EtOH (10 mL), Et₂O (3×10 mL), and dried under vacuum at room temperature overnight. Yield: 0.305 g (49.1%). *Anal.* Calc. for $\text{C}_{18}\text{H}_{46}\text{N}_{18}\text{Ni}_2\text{O}_7\text{Mo}$: C, 30.07; H, 7.09; N, 28.07. Found: C, 30.51; H, 6.01; N, 27.66%. IR (nujol, cm^{-1}): 3633 (vs), 3547 (s), 3326 (vs), 3292 (vs), 3271 (vs), 3257 (vs), 3168 (s), 2154 (s), 2142 (s), 2129 (vs), 2120 (vs), 2109 (vs), 2077 (m), 1673 (m), 1609 (s), 1592 (s), 1402 (m), 1330 (w), 1310 (w), 1279 (m), 1196 (s), 1158 (m), 1131 (vs), 1086 (m), 1067 (m), 1050 (m), 1019 (s), 1003 (vs), 905 (s), 879 (w), 647 (s), 615 (s), 469 (m). μ_{eff} (μ_{B}) Calc.: 4.0. μ_{eff} (μ_{B}) Found: 4.53.

2.2.3. $\{[trans-Ni^{II}(tn)_2(OH_2)][trans-Ni^{II}(tn)_2]-[(\mu-NC)_3W^{IV}(CN)_5] \cdot 6H_2O\} (3)$

An aqueous (25 mL) solution of **1** (0.72 g, 1.14 mmol) was treated with aqueous (10 mL) $K_4[W(CN)_8] \cdot 2H_2O$ (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), MeOH (2×10 mL), Et_2O (2×10 mL), and dried under vacuum at room temperature overnight. Yield: 0.24 g (47.9%). *Anal.* Calc. for $C_{18}H_{46}N_{18}Ni_2O_7W$: C, 24.30; H, 5.51; N, 28.34. Found: C, 27.29; H, 5.31; N, 25.01%. IR (nujol, cm^{-1}): 3625 (vs), 3540 (vs), 3340 (vs), 3290 (vs), 3255 (vs), 3167 (vs), 2153 (s), 2140 (s, sh), 2128 (vs, sh), 2115 (vs), 2103 (vs), 2076 (s, sh), 2061 (vs), 1677 (m), 1659 (m), 1612 (s), 1591 (vs), 1401 (m), 1332 (m), 1280 (s), 1259 (m), 1196 (m), 1160 (s), 1128 (vs), 1084 (s), 1067 (s), 1050 (m), 1017 (s), 1001 (s), 903 (s), 879 (m), 674 (m), 649 (m), 614 (m), 476 (m). $\mu_{eff}(\mu_B)$ Calc.: 4.0. $\mu_{eff}(\mu_B)$ Found: 4.41.

2.2.4. $Cs_4[Cu^{II}(OH_2)_4]_2[Cu^{II}(NH_3)]_4[Mo^{IV}(CN)_8]_4 \cdot 2H_2O (4)$

Treatment of a concentrated ammonia (30 mL) solution of $CuCl_2 \cdot 2H_2O$ (0.33 g, 1.94 mmol) with $Cs_3[Mo(CN)_8]$ (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), EtOH (3×5 mL), and Et_2O

(3×10 mL). The crystals were dried under vacuum at room temperature overnight. Yield: 0.72 g (96.0%). *Anal.* Calc. for $C_{32}H_{40}N_{44}O_2Cs_4Cu_6Mo_4$: C, 15.33; H, 1.29; N, 20.12. Found: C, 15.74; H, 1.22; N, 21.75%. 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), 1097 (m), 1073 (m), 1038 (m), 919 (w), 887 (w), 843 (m), 810 (m), 719 (vs), 705 (vs), 664 (s), 605 (w), 590 (w), 566 (w), 548 (m), 532 (m), 520 (s), 467 (vs), 462 (vs), 426 (vs), 414 (vs), 403 (vs). $\mu_{eff}(\mu_B)$ Calc.: 4.24. $\mu_{eff}(\mu_B)$ 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 $K_4Mo(CN)_8 \cdot 2H_2O$ (**2**) or $K_4W(CN)_8 \cdot 2H_2O$ (**3**). Crystals of **4** were grown from aqueous ammonia solutions of $CuCl_2 \cdot 4H_2O$ and $Cs_3Mo(CN)_8$. 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

Table 1

Crystallographic data for $\{[trans-Ni^{II}(tn)_2(OH_2)][trans-Ni^{II}(tn)_2][(\mu-NC)_2Mo^{IV}(CN)_6] \cdot 6H_2O\}_\infty$ (**2**), $\{[trans-Ni^{II}(tn)_2(OH_2)][trans-Ni^{II}(tn)_2][(\mu-NC)_2W^{IV}(CN)_6] \cdot 6H_2O\}$ (**3**), and $Cs_4[Cu^{II}(OH_2)_4]_2[Cu^{II}(NH_3)]_4[Mo^{IV}(CN)_8]_4 \cdot 2H_2O$ (**4**)

Compound	(2)	(3)	(4)
Chemical formula	$C_{20}H_{53}MoN_{16}Ni_2O_{6.5}$	$C_{20}H_{53}N_{16}Ni_2O_{6.5}W$	$C_{32}H_{32}Cs_4Cu_6Mo_4N_{36}O_{18}$
Formula weight	835.14	923.05	2505.49
Temperature (K)	90.0(2)	90.0(2)	90.0(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal size (mm)	$0.22 \times 0.22 \times 0.10$	$0.30 \times 0.20 \times 0.05$	$0.60 \times 0.15 \times 0.01$
Space group	triclinic	triclinic	monoclinic
Crystal system	$P\bar{1}$	$P\bar{1}$	$C2/m$
a (Å)	10.05000(10)	10.05000(10)	11.0247(9)
b (Å)	11.2870(2)	11.27600(10)	10.3382(8)
c (Å)	16.8840(3)	16.8740(2)	15.6133(13)
α (°)	105.6820(7)	105.7020(4)	90
β (°)	101.0440(7)	101.0610(4)	90.543
γ (°)	92.3270(7)	92.3430(5)	90
V (Å ³)	1801.12(5)	1797.93(3)	1779.5(2)
ρ (g cm ⁻³)	1.540	1.705	2.252
Z	2	2	2
μ (mm ⁻¹)	1.436	4.286	4.523
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0303$ $wR_2 = 0.0681$	$R_1 = 0.0185$ $wR_2 = 0.0421$	$R_1 = 0.0332$ $wR_2 = 0.0645$
R indices (for all data)	$R_1 = 0.0407$ $wR_2 = 0.0743$	$R_1 = 0.0212$ $wR_2 = 0.0427$	$R_1 = 0.0495$ $wR_2 = 0.0702$

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

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 $[M^{II}(\text{en})_3][\text{OTs}]_2(\text{OTs}^- = p\text{-toluenesulfonate})$ is treated with $M(\text{CN})_8^{n-}$ ($M = \text{Mo}^{\text{IV,V}}, \text{W}^{\text{IV,V}}$). We rationalized that substitution of ethylenediamine (en) for 1,3-propanediamine (tn), would afford kinetically labile $\text{Ni}^{\text{II}}(\text{tn})_3^{2+}$ ions that undergo dissociative tn loss, forming reactive $\text{cis-Ni}^{\text{II}}(\text{tn})_2(\text{OH}_2)_2^{2+}$ intermediates, and a series of amine-expanded octacyanometalate networks of $[\text{Ni}^{\text{II}}(\text{tn})_2]_2[\text{M}^{\text{IV}}(\text{CN})_8] \cdot n\text{H}_2\text{O}$ and $[\text{Ni}^{\text{II}}(\text{tn})_2]_3[\text{M}^{\text{V}}(\text{CN})_8]_2 \cdot n\text{H}_2\text{O}$ stoichiometry. In-

deed, treatment of either aqueous mixtures of nickel(II) tosylate and 1,3-propanediamine or $[\text{Ni}^{\text{II}}(\text{tn})_3][\text{OTs}]_2$ with $M(\text{CN})_8^{n-}$ ($M = \text{Mo}^{\text{IV,V}}, \text{W}^{\text{IV,V}}$) affords isostructural one-dimensional networks of $\{[\text{trans-Ni}^{\text{II}}(\text{tn})_2(\text{OH}_2)] [\text{trans-Ni}^{\text{II}}(\text{tn})_2][(\mu\text{-NC})_3\text{M}^{\text{IV}}(\text{CN})_5] \cdot 6\text{H}_2\text{O}\}$ ($\text{M}^{\text{IV}} = \text{Mo}$, **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 $\text{Cs}_4[\text{Cu}^{\text{II}}(\text{OH}_2)_4]_2[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Mo}^{\text{IV}}(\text{CN})_8]_4 \cdot 2\text{H}_2\text{O}$ stoichiometry, via $\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$ 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 (ν_{CN}) range from 2061 to 2172 cm^{-1} . The highest energy ν_{CN} absorptions are found for the Cu^{II} derivative, consistent with the formation of $\text{M}^{\text{II}}\text{--NC--M}^{\text{IV}}$ units and depopulation of the cyanide 5σ orbital; increasing π -backbonding progressing from Cu^{II} to Ni^{II} compensates this effect and progressively lowers the ν_{CN} absorption energies from 2172 to 2153 cm^{-1} for **4** and **2**, respectively [30]. These ν_{CN} absorptions are shifted to higher energies relative to those found for $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ (2126, 2012,

Table 2

Selected bond distances (Å) for $\{[\text{trans-Ni}^{\text{II}}(\text{tn})_2(\text{OH}_2)][\text{trans-Ni}^{\text{II}}(\text{tn})_2][(\mu\text{-NC})_2\text{Mo}^{\text{IV}}(\text{CN})_6] \cdot 6\text{H}_2\text{O}\}_\infty$ (**2**), $\{[\text{trans-Ni}^{\text{II}}(\text{tn})_2(\text{OH}_2)][\text{trans-Ni}^{\text{II}}(\text{tn})_2][(\mu\text{-NC})_2\text{W}^{\text{IV}}(\text{CN})_6] \cdot 6\text{H}_2\text{O}\}_\infty$ (**3**), and $\text{Cs}_4[\text{Cu}^{\text{II}}(\text{OH}_2)_4]_2[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Mo}^{\text{IV}}(\text{CN})_8]_4 \cdot 2\text{H}_2\text{O}$ (**4**)

(2)		(3)		(4)	
Mo(1)–C(1)	2.149(3)	W(1)–C(1)	2.160(2)	Mo–C(1)	2.152(12)
Mo(1)–C(2)	2.156(3)	W(1)–C(2)	2.157(2)	Mo–C(2)	2.170(12)
Mo(1)–C(3)	2.158(3)	W(1)–C(3)	2.165(2)	Mo–C(3)	2.161(11)
Mo(1)–C(4)	2.159(3)	W(1)–C(4)	2.156(2)	Mo–C(4)	2.147(14)
Mo(1)–C(5)	2.168(3)	W(1)–C(5)	2.165(2)	Mo–C(5)	2.184(16)
Mo(1)–C(6)	2.173(3)	W(1)–C(6)	2.157(2)	Mo–C(5B)	2.148(16)
Mo(1)–C(7)	2.162(3)	W(1)–C(7)	2.162(2)	Mo–C(6)	2.153(8)
Mo(1)–C(8)	2.158(3)	W(1)–C(8)	2.177(2)	Mo–C(6A)	2.153(8)
C(1)–N(1)	1.150(4)	C(1)–N(1)	1.148(3)	C(1)–N(1)	1.165(13)
C(2)–N(2)	1.150(4)	C(2)–N(2)	1.145(3)	Cu(1)–N(1)	2.257(10)
Ni(1)–N(1)	2.040(2)	Ni(2)–N(2)	2.0384(18)	Cu(1)–N(2A)	2.005(9)
Ni(1)–N(9)	2.102(2)	Ni(2)–N(13)	2.0998(18)	Cu(1)–N(3A)	2.575(10)
Ni(1)–N(10)	2.137(2)	Ni(2)–N(14)	2.1384(18)	Cu(1)–N(6A)	2.028(6)
Ni(1)–N(11)	2.088(2)	Ni(2)–N(15)	2.0875(18)	Cu(1)–N(6B)	2.028(6)
Ni(1)–N(12)	2.115(2)	Ni(2)–N(16)	2.1158(18)	Cu(1)–N(7)	1.985(8)
Ni(1)–O(1)	2.191(2)	Ni(2)–O(1)	2.1904(15)	Cu(2)–N(4)	2.477(11)
Ni(2)–N(2)	2.069(2)	Ni(1)–N(5A)	2.093(3)	Cu(2)–O(8)	2.03(3)
Ni(2)–N(3A)	2.091(3)	Ni(1)–N(1)	2.0715(18)	Cu(2)–O(9)	2.043(11)
Ni(2)–N(13)	2.135(2)	Ni(1)–N(9)	2.1401(18)		
Ni(2)–N(14)	2.104(3)	Ni(1)–N(10)	2.1041(19)		
Ni(2)–N(15)	2.120(2)	Ni(1)–N(11)	2.1155(18)		
Ni(2)–N(16)	2.133(2)	Ni(1)–N(12)	2.1394(18)		

Table 3

Selected bond angles (°) for $\{[trans-Ni^{II}(tn)_2(OH_2)] [trans-Ni^{II}(tn)_2][(\mu-NC)_2Mo^{IV}(CN)_6] \cdot 6H_2O\}_\infty$ (**2**), $\{[trans-Ni^{II}(tn)_2(OH_2)] [trans-Ni^{II}(tn)_2][(\mu-NC)_2W^{IV}(CN)_6] \cdot 6H_2O\}_\infty$ (**3**), and $Cs_4[Cu^{II}(OH_2)_4]_2[Cu^{II}(NH_3)_4][Mo^{IV}(CN)_8]_4 \cdot 2H_2O$ (**4**)

(2)		(3)		(4)	
C(1)–Mo(1)–C(2)	123.58(10)	C(1)–W(1)–C(2)	123.41(8)	C(1)–Mo–C(2)	72.6(4)
C(1)–Mo(1)–C(3)	73.46(10)	C(1)–W(1)–C(3)	71.30(7)	C(1)–Mo–C(3)	145.0(4)
C(1)–Mo(1)–C(4)	77.31(10)	C(1)–W(1)–C(4)	71.45(8)	C(1)–Mo–C(4)	146.2(4)
C(1)–Mo(1)–C(5)	143.58(10)	C(1)–W(1)–C(5)	135.99(8)	C(1)–Mo–C(5)	87.9(5)
C(1)–Mo(1)–C(6)	131.50(10)	C(1)–W(1)–C(6)	144.96(8)	C(1)–Mo–C(5B)	73.8(5)
C(1)–Mo(1)–C(7)	69.42(10)	C(1)–W(1)–C(7)	80.96(7)	C(1)–Mo–C(6)	88.8(2)
C(1)–Mo(1)–C(8)	77.13(10)	C(1)–W(1)–C(8)	74.63(8)	C(1)–Mo–C(6A)	88.8(2)
Mo(1)–C(1)–N(1)	177.7(2)	W(1)–C(1)–N(1)	171.26(18)	C(2)–Mo–C(3)	72.3(4)
Mo(1)–C(2)–N(2)	171.0(2)	W(1)–C(2)–N(2)	177.28(18)	C(2)–Mo–C(6)	73.43(19)
Ni(1)–N(1)–C(1)	174.0(2)	Ni(2)–N(2)–C(2)	174.36(18)	C(3)–Mo–C(6)	81.4(2)
Ni(2)–N(2)–C(2)	149.5(2)	Ni(1)–N(1)–C(1)	148.91(16)	Mo–C(1)–N(1)	174.7(9)
N(1)–Ni(1)–O(1)	177.41(9)	N(2)–Ni(2)–O(1)	177.25(7)	Mo–C(2)–N(2)	178.3(9)
N(1)–Ni(1)–N(9)	91.61(9)	N(1)–Ni(1)–N(9)	92.42(7)	Mo–C(6)–N(6)	174.6(7)
N(1)–Ni(1)–N(10)	90.62(9)	N(1)–Ni(1)–N(10)	91.35(7)	N(1)–Cu(1)–N(2B)	91.9(3)
N(1)–Ni(1)–N(11)	91.49(9)	N(1)–Ni(1)–N(11)	93.33(7)	N(1)–Cu(1)–N(6B)	90.61(17)
N(1)–Ni(1)–N(12)	93.30(10)	N(1)–Ni(1)–N(12)	88.86(7)	N(1)–Cu(1)–N(7)	94.6(3)
N(9)–Ni(1)–N(10)	89.34(9)	N(9)–Ni(1)–N(10)	89.07(7)	N2B–Cu(1)–N(7)	173.3(3)
N(9)–Ni(1)–N(11)	176.89(10)	N(9)–Ni(1)–N(11)	174.18(7)	C(1)–N(1)–Cu(1)	170.2(8)
N(9)–Ni(1)–N(12)	91.15(10)	N(9)–Ni(1)–N(12)	88.86(7)	C(6)–N(6)–Cu(1)	161.4(6)
N(10)–Ni(1)–N(12)	176.03(9)	N(10)–Ni(1)–N(12)	177.92(8)	C(2B)–N(2B)–Cu(1)	170.7(8)
N(2)–Ni(2)–N(3A)	176.49(9)	N(2)–Ni(2)–N(5A)	176.54(7)	O(8)–Cu(2)–O(9)	90.4(5)
N(2)–Ni(2)–N(13)	92.06(9)	N(2)–Ni(2)–N(13)	91.65(7)	C(4)–N(4)–Cu(2)	138.8(10)
N(2)–Ni(2)–N(14)	91.41(10)	N(2)–Ni(2)–N(14)	90.54(7)	N(4)–Cu(2)–O(8)	86.0(2)
N(2)–Ni(2)–N(15)	93.57(10)	N(2)–Ni(2)–N(15)	91.41(7)	N(4)–Cu(2)–O(8A)	94.0(2)
N(2)–Ni(2)–N(16)	88.85(9)	N(2)–Ni(2)–N(16)	93.28(7)	N(4)–Cu(2)–O(9)	61.7(2)
N(13)–Ni(2)–N(14)	91.41(10)	N(13)–Ni(2)–N(14)	89.44(7)	N(4)–Cu(2)–O(9A)	118.3(2)
N(13)–Ni(2)–N(16)	88.74(10)	N(13)–Ni(2)–N(16)	91.02(7)	N(4)–Cu(2)–N(4B)	180.0
N(14)–Ni(2)–N(15)	91.28(10)	N(14)–Ni(2)–N(15)	90.66(7)		

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 $[M^{II}(NH_3)_4]_2[Mo^{IV}(CN)_8] \cdot 2H_2O$ ($M^{II} = Co, Ni$) lattices have not been reported [13f].

Generally, $M^{IV}(CN)_8^{4-}$ compounds exhibit cyano stretching absorptions that range from 2060 to 2160 (ionic) and 2085 to 2141 cm^{-1} (cyanide-bridged) [17,18,31–33]. The ν_{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 ν_{CN} absorptions are expected to move to higher energies [30,34]. If however, increased π -backbonding 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 [30,34]. Assuming that π -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 $\{[trans-Ni^{II}(tn)_2(OH_2)] [trans-Ni^{II}(tn)_2][(\mu-NC)_3M^{IV}(CN)_5] \cdot 6H_2O\}$. stoichiometry (Table 1). The winding 1-D chains are composed of $[trans-(\mu-CN)Ni^{II}(tn)_2(\mu-NC)M^{IV}(CN)_6]$. ($M^{IV} = Mo, 2; W, 3$) linkages with appended $trans-Ni(tn)_2(OH_2)$ 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 2.869(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.

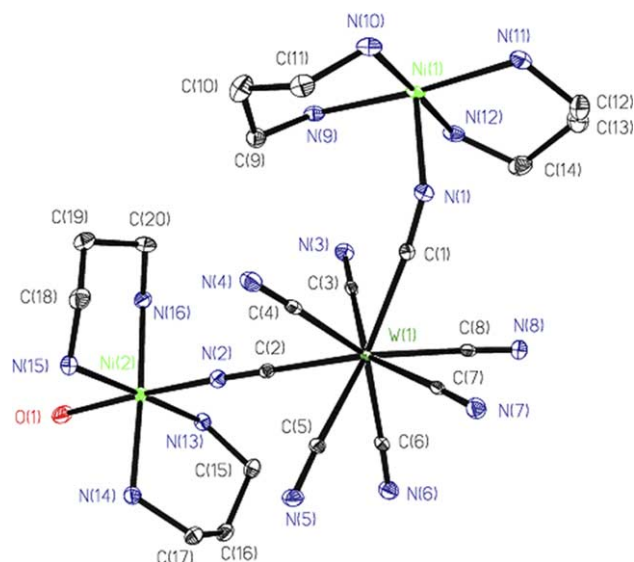


Fig. 1. X-ray structure of asymmetric unit of **3**. Hydrogen atoms are omitted for clarity and ellipsoids are at the 50% probability level.

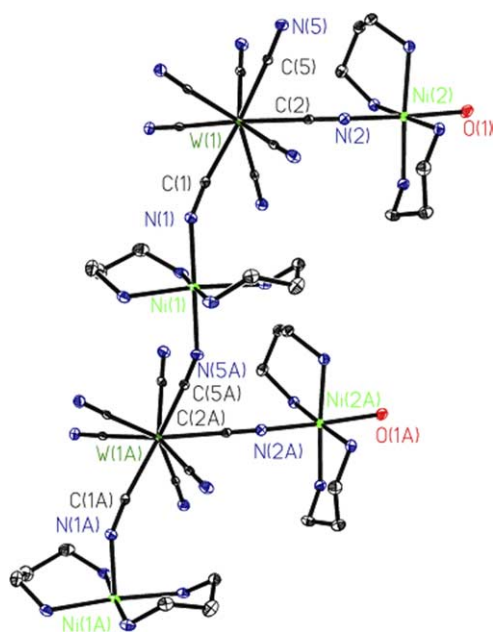


Fig. 2. X-ray structure of **3**. Hydrogen atoms and lattice water are omitted for clarity and all ellipsoids are at the 50% level.

Each three-connected $M^{IV}(CN)_8^{4-}$ center adopts a distorted square antiprismatic geometry and forms cyanide linkages to adjacent $trans-Ni^{II}(tn)_2(\mu-NC)_2$ and $trans-(\mu-CN)Ni^{II}(tn)_2(OH_2)$ 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 N_1 , N_2 , and N_3 form $\mu-CN$ linkages to adjacent $Ni^{II}(tn)_2$ and $Ni^{II}(tn)_2(OH_2)$ 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 $trans-Ni^{II}(tn)_2(\mu-NC)_2$ units connected via cyanide linkages to each octacyanometalate(IV) center. The $Ni-N_{tn}$ 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 $N_{tn}-Ni-N_{cyanide}$ bond angles are nearly 90° (Tables 2 and 3).

Appended to each chain via a single bridging cyanide are $trans-(\mu-CN)Ni^{II}(tn)_2(OH_2)$ units. These fragments exhibit slightly longer $Ni-N_{cyanide}$ and $Ni-N_{tn}$ bond distances in comparison to the $trans-Ni^{II}(tn)_2(\mu-NC)_2$ fragments, with $Ni-N_{cyanide}$ bond distances of 2.040(2) and 2.0384(18) Å, and $Ni-N_{tn}$ 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 $\{Cs[(H_3N)Cu^{II}(\mu-NC)_5Mo^{IV}(CN)_3]_4\}_n^{3n-}$ box-like units (Fig. 3). The copper(II) and molybdenum(IV) centers reside in alternate corners of each box and are connected via $\mu-CN$ linkages, forming anionic

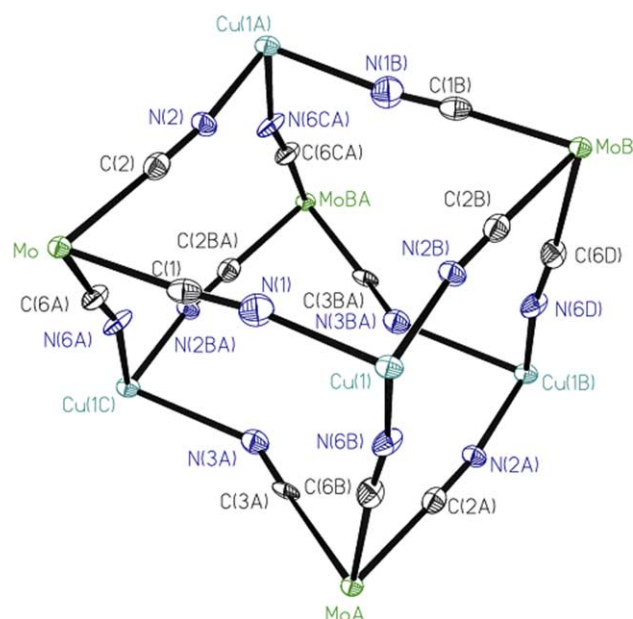


Fig. 3. X-ray structure of **4** showing distorted square portion of anionic 2-D sheet. Ellipsoids are at the 50% probability level and ammonia ligands, hydrogen atoms, cesium cations, and selected cyanides are eliminated for clarity.

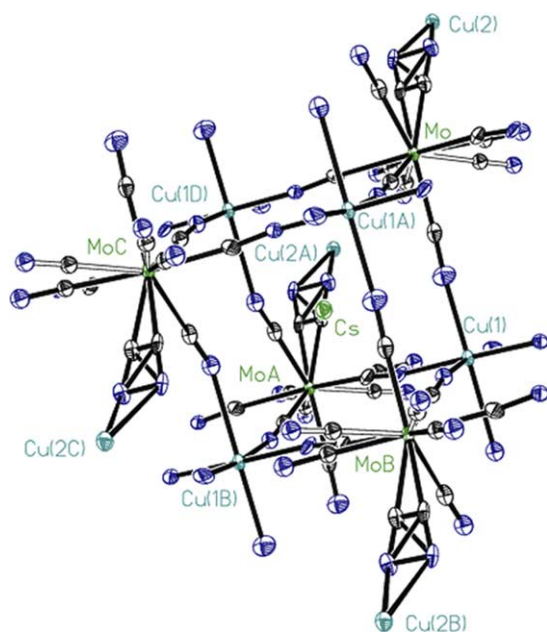


Fig. 4. X-ray structure of **4** showing distorted square portion of anionic 2-D sheet. Ellipsoids are at the 50% probability level and selected cyanide carbon and all aqua and hydrogen atoms are eliminated for clarity. Only nitrogen atoms (dark blue), carbon (black), copper (pale blue), and molybdenum (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\{\text{Cs}[(\text{H}_3\text{N})\text{Cu}^{\text{II}}(\mu\text{-NC})_5\text{Mo}^{\text{IV}}(\text{CN})_3]_4\}_n^{4n-}$ slabs (Fig. 4). The parallel slabs are connected via disordered cyanides to *trans*- $\text{Cu}^{\text{II}}(\text{OH}_2)_4(\mu\text{-NC})_2$ 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 $\text{Cs}_4[\text{Cu}^{\text{II}}(\text{OH}_2)_4]_2[\text{Cu}^{\text{II}}(\text{NH}_3)]_4[\text{Mo}^{\text{IV}}(\text{CN})_8]_4 \cdot 2\text{H}_2\text{O}$ stoichiometry (Fig. 6).

For **4**, the average Mo–C bond lengths of the $\text{Mo}^{\text{IV}}(\mu\text{-CN})_6(\text{CN})_2^{4-}$ 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^{II} 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 $(\text{H}_3\text{N})\text{Cu}(\mu\text{-NC})_5$ are comparatively shorter (2.170(12) Å); the *cis*-cyanides range from 2.152(12) to 2.161(11) Å (Table 2). Overall, the $\text{Mo}^{\text{IV}}(\text{CN})_8^{4-}$ 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 $(\text{H}_3\text{N})\text{Cu}(\mu\text{-NC})_5^{3-}$ 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 $(\text{H}_3\text{N})\text{Cu}(\mu\text{-NC})_5$ fragment affords comparatively longer Cu–N bond distances, 2.257(9) (N₁–Cu₁) and 2.575(9) Å (N_{3A}–Cu₁), relative to either the Cu₁–NH₃ (1.985(8) Å, Cu₁–N₇),

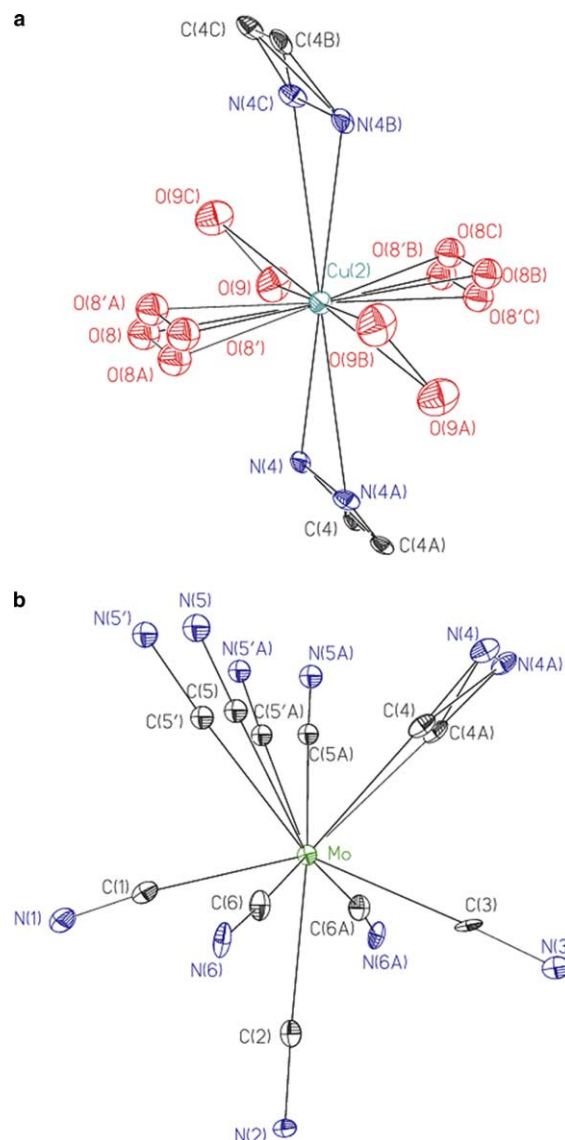


Fig. 5. X-ray structure of interlayer-bridged copper (a) and intralayer molybdenum centers (b) in **4**. Ellipsoids are at the 20% level.

or remaining cyanide linkages (ca. 2.020(10) Å; Table 2). The N–Cu₁–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*- $\text{Cu}(\text{OH}_2)_4(\mu\text{-NC})_2$ 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).

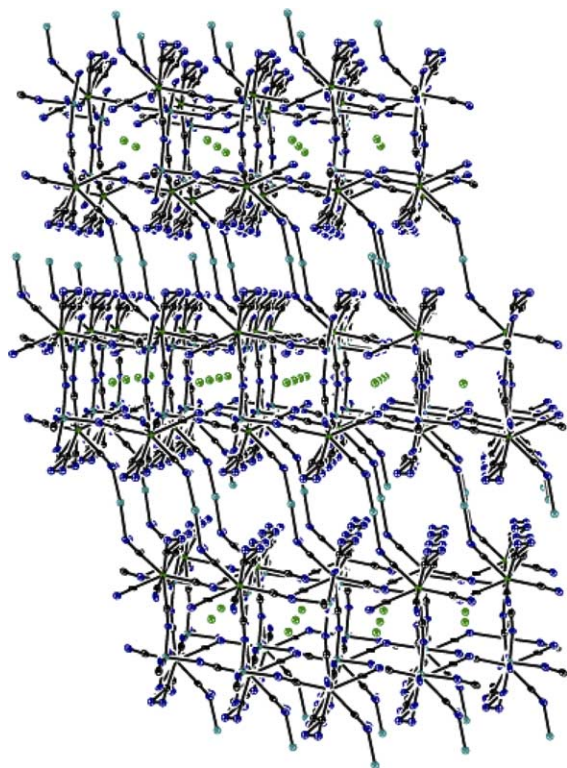


Fig. 6. X-ray structure of **4** showing connectivity of anionic 2-D sheets (center) via *trans*-(μ -CN)Cu(OH₂)₄(μ -NC) linkages down the *b* axis. Ellipsoids are at the 50% level and only carbon (black), cesium (green), copper (pale blue), nitrogen (blue), and molybdenum (dark green) are shown for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Magnetic studies

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

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