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TWO NEW CYANIDE-BRIDGED COMPLEXES, $\{[Cu(men)_2][Ni(CN)_4]\}_n$ AND $[Mn(bpy)_2]_4[Mo(CN)_8]_2\cdot 0.5MeOH\cdot 0.75H_2O$: SYNTHESES AND CRYSTAL STRUCTURES

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Two novel cyano-bridged complexes, $\{[Cu(men)_2][Ni(CN)_4]\}_n$ (**1**) (men = N,N′-dimethyl-ethylenediamine) and $[Mn(bpy)_2]_4[Mo(CN)_8]_2\cdot 0.5MeOH\cdot 0.75H_2O$ (**2**) (bpy = 2,2′-bipyridine) have been synthesized and structurally characterized by IR spectroscopy and X-ray crystallography. The complex **1** has one-dimensional zigzag chain structure in which the Ni atom is coordinated by four cyanide groups, and the Cu atom is surrounded by four nitrogen atoms of the two men ligands in equatorial plane and two nitrogen atoms of the bridging cyanide in axial positions; the Cu centre is in a distorted octahedral environment. Owing to weak interactions, complex **1** is self-assembled into two-dimensional network via N—H…N hydrogen bonds. In **2**, the basic structural unit is centrosymmetric and contains four Mn centers connected by two octacyanomolybdates via eight cyanide bridges. Each Mo atom is linked via four cyanide groups to four Mn, and the other four cyanide groups are terminal. From X-ray single crystal analysis (room temperature), **1** crystallizes in monoclinic space group $P2_1/n$ with $a = 6.7332(7)$, $b = 13.9248(15)$, $c = 9.0869(10)$ Å, $\beta = 98.4030(10)°$, $V = 843.05(16)$ Å^3, $Z = 2$; **2** crystallizes in monoclinic space group $P2_1/n$ with $a = 13.886(6)$, $b = 24.116(11)$, $c = 15.263(7)$ Å, $\beta = 90.175(6)°$, $V = 5111(4)$ Å^3, $Z = 2$.

Keywords: Cyanide, bimetallic complex, coordination polymer, hydrogen bond, 1D chain, 2D network.

Cyanometallate molecular building blocks are widely employed to design various cyano-bridged complexes with predetermined structures and potential for technologically useful molecule-based materials with electronic, magnetic and photomagnetic applications [1—5]. Compared with most metal cyanides, the tetracyanonickelate anion $[Ni(CN)_4]^{2-}$ is an ideal building block because of its ability to link various central atoms and thus to form molecules with one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) structures [6—9]. The $[M(CN)_8]^{3-,4-}$ (M = Mo, W, Nb) units exhibit various geometrical structures such as square antiprism, dodecahedron, bicapped trigonal prism, while cyanide groups are powerful for bridging transition metals. These characteristics make them potential flexible building blocks to construct various architectures [10—14]. Nevertheless, structurally characterized polymers based on $[Mo(CN)_8]^{3-,4-}$ as a building block are still relatively rare [15]. As a part of our continuing study in this field, two new cyanide-bridged complexes, $\{[Cu(men)_2][Ni(CN)_4]\}_n$ (men = N,N′-dimethyl-ethylenediamine) and $[Mn(bpy)_2]_4[Mo(CN)_8]_2\cdot 0.5MeOH\cdot 0.75H_2O$ (bpy = 2,2-bipyridine), are reported here: their synthesis and crystal structures.

EXPERIMENTAL

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Materials and measurements. $K_4[Mo(CN)_8] \cdot 2H_2O$ was synthesized according to the literature method [16, 17]. All other chemicals were of reagent grade and used without further purification. Elemental analyses for C, H and N were carried out on a Perkin-Elmer elemental analyzer (model 240). The infrared spectra were obtained on a Perkin-Elmer 983G infrared spectrometer in the 4000—200 cm^{-1} range using KBr pellets.

Preparation of $\{[Cu(men)_2][Ni(CN)_4]\}_n$ (1). Single crystals of **1** were grown in a methanol/water solution by slow diffusion method using an H-shape tube. $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 37.5 mg) and men (0.2 mmol, 17.6 mg) were dissolved in MeOH/water (5 ml), and added in one arm; $K_2[Ni(CN)_4] \cdot H_2O$ (0.1 mmol, 25.9 mg) was dissolved in water (5 ml) and added in the other one. Then the tube was filled with methanol. Well-shaped blue crystals suitable for X-ray determination formed after several weeks. Found (%): C 35.80, H 6.01, N 27.83. Calcd for $C_{12}H_{24}N_8CuNi$ (%): C 35.77, H 5.95, N 27.47. IR (KBr, cm^{-1}): ν(C≡N), 2129 cm^{-1}.

Preparation of $[Mn(bpy)_2]_4[Mo(CN)_8]_2 \cdot 0.5MeOH \cdot 0.75H_2O$ (2). To a solution of $MnCl_2 \cdot 4H_2O$ (0.8 mmol, 158.4 mg) and $K_4[Mo(CN)_8] \cdot 2H_2O$ (0.4 mmol, 198.6 mg) in water (10 ml), was added a solution of bpy (1.6 mmol, 250.0 mg) in MeOH (10 ml) with stirring to give a yellow green precipitate immediately. The precipitate was filtered off, and the filtrate was allowed to stand at room temperature in the dark. Yellow crystals were obtained upon slow evaporation at room temperature. Found (%): C 54.48, H 3.39, N 21.28. Calcd for $C_{97}H_{69}N_{32}Mn_4Mo_2O_{2.5}$ (%): C 54.53, H 3.35, N 20.98. IR (KBr, cm^{-1}): ν(C≡N), 2119 cm^{-1}.

X-Ray diffraction studies. All measurements were conducted at 293 K on a Bruker Smart 1000 or Rigaku Saturn CCD diffractometers with graphite monochromated MoK_α radiation (λ = 0.71073 Å) for complexes **1** and **2**, respectively. The empirical absorption correction from equivalents was carried out. The structure was solved by direct methods using SHELXS-97 program and refined with SHELXL-97 [18] by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. Crystallographic data and collection parameters for both complexes are listed in Table 1. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 669935 and 670673 for **1** and **2**, respectively.

Table 1

Crystallographic Data and Structure Refinement for the Title Complexes

Formula	$C_{12}H_{24}N_8CuNi$	$C_{97}H_{69}N_{32}Mn_4Mo_2O_{2.5}$
Temperature, K	293(2)	293(2)
M	402.64	2134.48
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, b, c, Å	6.7332(7), 13.9248(15), 9.0869(10)	13.886(6), 24.116(11), 15.263(7)
β, deg.	98.4030(10)	90.175(6)
V, Å^3	843.05(16)	5111(4)
Z	2	2
D_{calc}, g/cm^3	1.586	1.387
Reflections collections	4455	47966
Independent reflections (R_{int})	1483 (0.0169)	11958 (0.1532)
Max. and min. transmission	1.0000 and 0.6602	0.9846 and 0.9402
Data / restraints / parameters	1483 / 0 / 105	11958 / 44 / 670
GOOF on F^2	1.062	1.190
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0213$, $wR2 = 0.0563$	$R1 = 0.0975$, $wR2 = 0.2580$
R indices (for all data)	$R1 = 0.0270$, $wR2 = 0.0592$	$R1 = 0.1424$, $wR2 = 0.2791$
Residual max and min, e/Å^3	0.22 and –0.43	1.75 and –0.77
CCDC deposition N	669935	670673

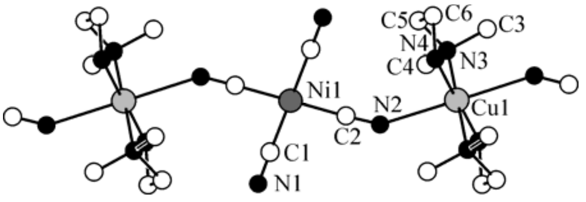

Fig. 1. 1D zigzag chain in **1** with the atomic labeling scheme. H atoms are omitted for clarity

RESULTS AND DISCUSSION

Description of the structure of 1. Complex **1** is built up of $[Cu(men)_2]^{2+}$ cations and $[Ni(CN)_4]^{2-}$ anions forming an one-dimensional zigzag chain as shown in Fig. 1. The selected bond lengths and angles are listed in Table 2. The coordination geometry of Cu centre is a distorted octahedron, with four nitrogen atoms [Cu(1)—N(4) = Cu(1)—N(4)#1 = 1.9875(13) Å and Cu(1)—N(3) = Cu(1)—N(3)#1 = 2.1169(13) Å (symmetry code: #1 $-x$, $-y+1$, $-z$)] of the diamines in the equatorial plane and two nitrogen atoms [Cu(1)—N(2) = Cu(1)—N(2)#1 = 2.6002(18) Å] of two bridging cyanide ligands situated at the axial sites. Therefore, the axial Cu—N bonds are much weaker than those in the equatorial plane. The C—N—Cu bond angles are far from 180°: 138.81(15)° [C(2)—N(2)—Cu(1) = = C(2)#1—N(2)#1—Cu(1)]. In **1**, each $[Ni(CN)_4]^{2-}$ unit uses two *trans* C≡N groups to connect to two $[Cu(men)_2]^{2+}$ fragments giving rise to 1D chain structure with alternate Ni—CN—Cu linkages, and all cyanide groups also interact with neighboring chains by hydrogen bonds. As shown in Fig. 2, every two neighboring chains are parallel and interconnected by the hydrogen-bonds [N(2)…N(4) = 3.634, N(1)…N(4) = 3.348 Å]. Finally, complex **1** reveals self-assembly into two-dimensional network via hydrogen bonds of N—H…N type, in which N(4) acts as μ_2-bridge connecting nitrogen atoms [N(1) and N(2)] of cyanide groups from different chains. The main shortest distances between metallic sites are 5.244(4) Å [Cu(1)…Ni(1)].

Description of the structure of 2. The molecular structure of **2** is shown in Fig. 3, and selected bond lengths and angles are listed in Table 3. The molecule is centrosymmetric and contains four Mn centers connected by two octacyanomolybdate units *via* eight cyanide bridges. Each Mo atom connects four Mn atoms by cyanide bridges in a square antiprismatic arrangement, the four other cyano groups being terminal. The Mo(1) atom is coordinated by eight CN groups with Mo—C and C—N mean distances of 2.154 Å and 1.151 Å, respectively. The Mo—C and Mo—N bond distances are in the range typical for other octacyanomolybdates with different cations. The Mn atoms are hexacoordinate, having an octahedral geometry with two bpy and two *cis* positioned cyanide bridges. The shortest distance between metallic sites is 5.596 Å for Mn(1)…Mn(2), which is comparable with that in Mn_4Mo_2 cluster (5.611 Å) [19]. For the complex, with the help of MeOH of crystallization, the clusters are connected into a supramolecular hydrogen bonding structure.

CONCLUSION

In this work, we have prepared and studied two new Cu^{II}—Ni^{II} and Mo^{IV}—Mn^{II} bimetallic cyanide-bridged complexes $\{[Cu(men)_2][Ni(CN)_4]\}_n$ (**1**) and $[Mn(bpy)_2]_4[Mo(CN)_8]_2 \cdot 0.5MeOH \cdot 0.75H_2O$ (**2**).

Table 2

Selected Bond Lengths (Å) *and Angles* (deg.) *for* **1**

Cu(1)—N(4)#1	1.9875(13)	N(4)#1—Cu(1)—N(4)	180.0	C(2)#2—Ni(1)—C(2)	180.00(11)
Cu(1)—N(3)#1	2.1169(13)	N(4)—Cu(1)—N(3)#1	94.71(6)	C(1)—Ni(1)—C(1)#2	180.00(15)
Cu(1)—N(2)#1	2.6000(13)	N(4)—Cu(1)—N(3)	85.29(6)	C(3)—N(3)—Cu(1)	112.23(10)
Ni(1)—C(2)#2	1.8647(19)	N(3)#1—Cu(1)—N(3)	180.0	C(5)—N(3)—Cu(1)	103.26(10)
Ni(1)—C(1)	1.8735(19)	C(2)—Ni(1)—C(1)	90.06(7)	C(2)—N(2)—Cu(1)	138.81(15)

Cu(1)—N(4)	1.9875(13)	C(2)—Ni(1)—C(1)#2	89.94(7)	C(4)—N(3)—Cu(1)	114.91(11)
Cu(1)—N(3)	2.1169(13)	C(2)#2—Ni(1)—C(1)	89.94(7)	C(6)—N(4)—Cu(1)	109.85(11)
Cu(1)—N(2)	2.6000(13)				
Ni(1)—C(2)	1.8647(19)				
Ni(1)—C(1)#2	1.8735(19)				

Symmetry codes: #1 $-x, -y+1, -z$; #2 $-x, -y, -z$.

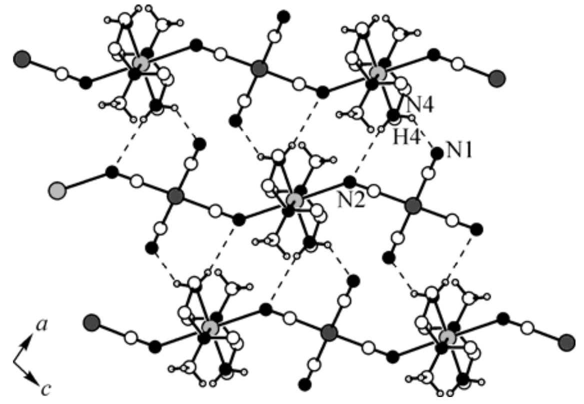

Fig. 2. Coordination polymeric chains interacting by hydrogen bonds in **1**

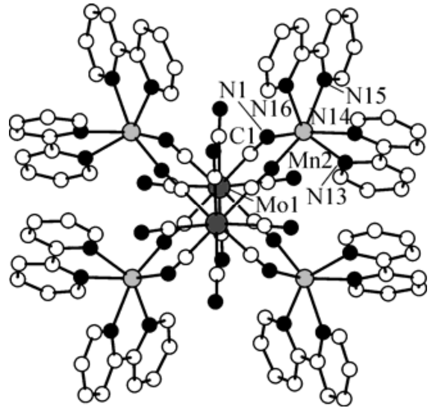

Fig. 3. The molecular structure of **2.** Water molecules, lattice MeOH molecules and H atoms are omitted for clarity

Table 3

Selected Bond Lengths (Å) *and Angles* (deg.) *for* **2**

Mo(1)—C(1)	2.171(8)	Mo(1)—C(5)	2.145(8)	C(6)—Mo(1)—C(1)	69.8(3)	C(5)—Mo(1)—C(4)	77.0(3)
Mo(1)—C(2)	2.152(7)	Mo(1)—C(6)	2.134(7)	C(6)—Mo(1)—C(4)	72.3(3)	C(2)—Mo(1)—C(1)	73.0(3)
Mo(1)—C(3)	2.179(8)	Mo(1)—C(7)	2.145(8)	C(7)—Mo(1)—C(5)	73.0(4)	C(5)—Mo(1)—C(3)	74.5(3)
Mo(1)—C(4)	2.158(8)	Mo(1)—C(8)	2.149(9)	C(8)—Mo(1)—C(3)	74.3(3)	C(7)—Mo(1)—C(8)	70.8(3)
Mn(1)—N(2)	2.180(6)	Mn(2)—N(1)	2.166(7)	N(6)#1—Mn(1)—N(2)	90.5(2)	N(4)#1—Mn(2)—N(1)	90.2(3)
Mn(1)—N(6)#1	2.163(6)	Mn(2)—N(4)#1	2.155(7)	C(6)—N(6)—Mn(1)#1	154.5(6)	C(4)—N(4)—Mn(2)#1	171.6(7)
				C(2)—N(2)—Mn(1)	171.0(6)	C(1)—N(1)—Mn(2)	151.9(6)

Symmetry code: #1 $-x+2, -y, -z+1$.

The complex **1** is a 1D zigzag chain extended into two-dimensional network via hydrogen bonds. The complex **2** is centrosymmetric and contains four Mn^{II} centers connected by two octacyanomolybdate(IV) units via eight cyanide bridges to form a hexanuclear molecular cluster.

REFERENCES

1. *Kania R., Lewinski K., Sieklucka B.* // Dalton Trans. – 2003. – P. 1033.
2. *Dunbar K.R., Heintz R.A.* // Prog. Inorg. Chem. – 1997. – **45**. – P. 283.
3. *Mallah T., Thiébaut S., Verdaguer M., Veillet P.* // Science. – 1993. – **262**. – P. 1554.
4. *Verdaguer M., Bleuzen A., Marvaud V. et al.* // Coord. Chem. Rev. – 1999. – **192**. – P. 1023.
5. *Ohba M., Okawa K.* // Ibid. – 2000. – **198**. – P. 313.
6. *Kou H.Z., Liao D.Z., Jiang Z.H. et al.* // Inorg. Chem. Commun. – 2000. – **3**. – P. 151.
7. *Kou H.Z., Si S.F., Gao S. et al.* // Eur. J. Inorg. Chem. – 2002. – P. 699.
8. *Miyoshi T., Iwamoto T., Sasaki Y.* // Inorg. Chim. Acta. – 1973. – **7**. – P. 97.
9. *Janiak C., Wu H.P., Klufers P., Mayer P.* // Acta Crystallogr. – 1999. – **C55**. – P. 1966.
10. *Larionova J., Gross M., Pilkington M. et al.* // Angew. Chem., Int. Ed. – 2000. – **39**. – P. 1605.
11. *Zhong Z.J., Seino H., Mizobe Y. et al.* // J. Amer. Chem. Soc. – 2000. – **122**. – P. 2952.
12. *Sieklucka B., Szklarzewicz J., Kemp T.J., Errington W.* // Inorg. Chem. – 2000. – **39**. – P. 5156.
13. *Withers J.R., Li D.F., Triplet J. et al.* // Ibid. – 2006. – **45**. – P. 4307.
14. *Li D.F., Gao S., Zheng L.M., Tang W.X.* // J. Chem. Soc., Dalton Trans. – 2002. – P. 2805.

15. *Willemin S., Larionova J., Clérac R. et al.* // Eur. J. Inorg. Chem. – 2003. – P. 1866.
16. *Furman N.H., Miller C.O., Arvan P.G., Audrieth L.F.* // Inorg. Synth. – 1950. – **3**. – P. 160.
17. *Leipoldt J.G., Bok L.D.C., Cilliers P.J.* // Z. Anorg. Allg. Chem. – 1974. – **409**. – P. 343.
18. (a) *Sheldrick G.M.* SHELXS-97. Program for the Solution of Crystal Structures. – University of Göttingen, Germany, 1997. (b) *Sheldrick G.M.* SHELXL-97. Program for the Refinement of Crystal Structures. – University of Göttingen, Germany, 1997.
19. *Sieklucka B., Szklarzewicz J., Kemp T.J., Errington W.* // Inorg. Chem. – 2000. – **39**. – P. 5156.