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Jun Xia [a] [b], Tian-Tian Li [a], Xiao-Qinq Zhao [b] & Jun-Fu Wei [a]
[a] School of Environment and Chemical Engineering, Tianjin Polytechnic University, Tianjin, P.R. China
[b] Department of Chemistry, Nankai University, Tianjin, P.R. China

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# Cyano-bridged heterometallic complexes directed by binuclear copper units

JUN XIA*†‡, TIAN-TIAN LI†, XIAO-QINQ ZHAO‡ and JUN-FU WEI†

†School of Environment and Chemical Engineering, Tianjin Polytechnic University, Tianjin, P.R. China
‡Department of Chemistry, Nankai University, Tianjin, P.R. China

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A tridentate N,O-donor, 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (HL), has been employed to synthesize cyano-bridged complexes and six heterometallic complexes with $[Cu_2L_2]$ or $[Cu_2L_2(H_2O)]$ have been generated by using slow diffusion. With slightly different synthetic conditions, subtle variations in the crystal structures of the complexes occur. $[Cu_2L_2][Fe(CN)_5NO]\cdot 2CH_3CN$ (**1**) and $[Cu_2L_2][Fe(CN)_5NO]\cdot H_2O$ (**2**), synthesized in different solvents with the same precursor, exhibit a very similar 1-D zig-zag chain motif in different space groups, $P2_1$ and $P$-1, respectively. Similarly, $[Cu_2L_2(H_2O)][Ni(CN)_4]\cdot H_2O$ (**3**) and $[Cu_2L_2][Ni(CN)_4]\cdot H_2O$ (**4**), synthesized with different diffusion methods, feature trinuclear and 1-D zig-zag chain structures, which indicates a solvent effect of water. $[Cu_2L_2(H_2O)]_2[Cu_2L_2][W(CN)_8]_2\cdot 8H_2O$ (**5**) is composed of two $[W(CN)_8]^{3-}$ and three $[Cu_2L_2]^{2+}$ units. In the octanuclear structure, $[W(CN)_8]^{3-}$ and one $[Cu_2L_2]^{2+}$ bridge and the other two $[Cu_2L_2]^{2+}$ are terminal to stop extending the 1-D structure. $[CuL][Ag_{2.24}Cu_{0.76}(CN)_4]$ (**6**) exhibits a discrete structure, in which the complex anion forms a unique 2-D $6^3$ network and the complex cations are inserted in the space between two adjacent networks. Magnetic properties of **1** and **4** are discussed.

*Keywords*: Cyano-bridged complexes; Heterometallic complexes; Crystal structures; Solvent effect

## 1. Introduction

Cyano-bridged coordination polymers have received attention for diverse structures (0-D, 1-D chains, 2-D grids and 3-D frameworks) [1] and for potential applications in zeolite materials, luminescent materials, catalysts, *etc.* [2]. The unique magnetism of the cyano-bridged complexes is the most fascinating aspect. Cyanide is an efficient pathway to tune magnetic interactions between paramagnetic metal centers. Transition-metal cyanides have been documented as magnetic materials, including high Tc magnets [3], single-molecule magnets [4], single-chain magnets [5], and spin crossover materials [6].

It is a challenge to get suitable single crystals of cyano-bridged complexes for X-ray diffraction because of poor solubility. To solve this problem, the hybrid approach [7] is employed. First, paramagnetic metals and organic ligands form unsaturated complex cations $[ML_x]^{m+}$, which further react with anionic cyanides $[M'(CN)_y]^{n-}$ to build

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*Corresponding author. Email: xiajun@tjpu.edu.cn

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cyano-bridged complexes. In this strategy, the hybrid ligand should exhibit good reactivity with metal ions and suitable competition with cyanide groups. Some diamine [8], bipyridine [9], Schiff base [10] and macrocycle compounds [11] are judicious choices, and recent research reveals that some pyrazole derivatives are favorable [12]. Our research has produced some new heterometallic cyano-bridged complexes [13]. The complex cation of cyano-bridged complexes has one metal center and significant variety may be induced by using multi-nuclear complex units as building blocks. HL, 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol, has drawn our attention because it is a tridentate $N_2O$-donor and can react with $Cu^{2+}$ to form $[Cu_2L_2]^{2+}$. The structure of the block is nearly planar like some macrocycle complexes, which should coordinate to $[M'(CN)_y]^{n-}$ for the low steric hindrance [14]. In this article, six cyano-bridged heterometallic complexes, $[Cu_2L_2][Fe(CN)_5NO]\cdot 2CH_3CN$ (**1**), $[Cu_2L_2][Fe(CN)_5NO]\cdot H_2O$ (**2**), $[Cu_2L_2(H_2O)][Ni(CN)_4]\cdot H_2O$ (**3**), $[Cu_2L_2][Ni(CN)_4]\cdot H_2O$ (**4**), $[Cu_2L_2(H_2O)]_2[Cu_2L_2][W(CN)_8]_2\cdot 8H_2O$ (**5**), and $[CuL][Ag_{2.24}Cu_{0.76}(CN)_4]$ (**6**), were obtained by this strategy. Some subtle changes are observed on structures of the complexes which were synthesized under similar conditions, indicating solvent and coordination water effects are important in the synthesis.

## 2. Experimental

### 2.1. *Materials and equipment*

All reagents were commercially available and used as received. Solvents and chemicals were analytical grade and used without purification. $Na_2[Fe(CN)_5NO]$, $K_2[Ni(CN)_4]$, and $K[Ag(CN)_2]$,were purchased from Aldrich Chemical Co. Inc. $K_3[W(CN)_8]$ was prepared according to the literature [15]. HL was synthesized according to the literature procedure [16]. Infrared spectra were obtained in KBr disks on a Bruker Tensor 27 Spectrometer from 4000 to 400 $cm^{-1}$. Elemental analyzes of C, H, and N were determined with a Perkin-Elmer 240 CHN elemental analyzer.

### 2.2. *Syntheses of 1–6*

**2.2.1. Synthesis of $[Cu_2L_2][Fe(CN)_5NO]\cdot 2CH_3CN$ (1).** An acetonitrile solution of HL (0.025 g, 0.1 mmol) was mixed with $CuCl_2\cdot 6H_2O$ (0.017 g, 0.1 mmol) in water to afford a blue solution. The resulting solution was carefully put on top of an aqueous solution of $Na_2[Fe(CN)_5NO]$ (0.015 g, 0.05 mmol) in a 15 mL test tube. The tube was left undisturbed in the dark and well-formed blue crystals obtained in 33% yield based on Cu after several weeks were washed with ether. Elemental analysis (%) Calcd for $C_{35}H_{44}N_{16}O_3Cu_2Fe$: H, 4.78; C, 45.66; N, 24.35%. Found: H, 5.01; C, 45.26; N, 24.31%; IR (KBr, $cm^{-1}$): 2954 (w), 2885(w), 2147(s), 1921(s), 1636(m), 1556(m), 1421(m), 1396(m), 1350(m), 1300(w), 1238(w), 1056(w), 912(w), 776(w), 642(w).

**2.2.2. Synthesis of $[Cu_2L_2][Fe(CN)_5NO]\cdot H_2O$ (2).** A methanolic solution of HL (0.025 g, 0.1 mmol) was mixed with $CuCl_2\cdot 6H_2O$ (0.017 g, 0.1 mmol) in water to afford a blue solution. The resulting solution was put into one side of a U-shaped tube containing silica gel, as well as an aqueous solution of $Na_2[Fe(CN)_5NO]$ (0.015 g, 0.05 mmol). The tube was left undisturbed in the dark and blue plate crystals were obtained in 17% yield based on Cu after several weeks and washed with ether. Elemental analysis (%) Calcd for $C_{31}H_{40}N_{14}O_4Cu_2Fe$: H, 4.67; C, 43.47; N, 22.91%. Found: H, 4.97; C, 43.01; N, 23.43%; IR (KBr, $cm^{-1}$): 2974(w), 2929(w), 2138(s), 1888(s), 1646(m), 1567(m), 1461(m), 1418 (m), 1393(m), 1309(m), 1259(m), 1040(w), 906(w), 860(m), 701(w), 662(w).

**2.2.3. Synthesis of $[Cu_2L_2(H_2O)][Ni(CN)_4]\cdot H_2O$ (3).** The preparation was carried out with a method similar to that of **1**, except for use of $K_2[Ni(CN)_4]$. Blue block crystals were obtained and washed with ether in 20% yield based on Cu. Elemental analysis (%) Calcd for $C_{30}H_{42}N_{12}O_4Cu_2Ni$: H, 5.12; C, 43.87; N, 20.47%. Found: H, 5.69; C, 43.53; N, 20.31%; IR (KBr, $cm^{-1}$): 3145(w), 3018(w), 2924(w), 2835(w), 2140(w), 2123(s), 1651(m), 1555(s), 1466(m), 1385(m), 1349(m), 1303(m), 1260(m), 1143(w), 1096(w), 1052(w), 913(w), 810(w), 636(w).

**2.2.4. Synthesis of $[Cu_2L_2][Ni(CN)_4]\cdot H_2O$ (4).** An acetonitrile solution of HL (0.124 g, 0.5 mmol) was mixed with $CuCl_2\cdot 6H_2O$ (0.085 g, 0.5 mmol) in DMF to afford a blue solution. To this solution, $K_2[Ni(CN)_4]$ (0.061 g, 0.25 mmol) in water was added. The reaction mixture was stirred for 30 min and filtered. Diffusion of ether vapor into the clear mother liquor produced blue needle crystals in 23% yield based on Cu. Elemental analysis (%) Calcd for $C_{30}H_{40}N_{12}O_3Cu_2Ni$: H, 4.98; C, 44.86; N, 20.93%. Found: H, 5.32; C, 44.47; N, 21.31%; IR (KBr, $cm^{-1}$): 2990(w), 2919(w), 2173(s), 2100(w), 1619(m), 1552(m), 1394(w), 1058(w), 911(w), 796(w).

**2.2.5. Synthesis of $[Cu_2L_2(H_2O)]_2[Cu_2L_2][W(CN)_8]_2\cdot 8H_2O$ (5).** The preparation was carried out with a method similar to that of **4**, except for use of $K_3[W(CN)_8]$. Blue needle crystals were obtained in 23% yield based on Cu and washed with ether. Elemental analysis (%) Calcd for $C_{47}H_{67}N_{20}O_8Cu_3W$: H, 4.74; C, 39.87; N, 19.79%. Found: H, 5.11; C, 39.82; N, 19.71%; IR (KBr, $cm^{-1}$): 2992(w), 2925(w), 2890(w), 2145(s), 2107(m), 1633 (m), 1552(s), 1468(m), 1396(m), 1350(m), 1303(m), 1257(m), 1144(w), 1092(w), 1057(w), 911(w), 797(w), 646(w).

**2.2.6. Synthesis of $[CuL][Ag_{2.24}Cu_{0.76}(CN)_4]$ (6).** The preparation was carried out with a method similar to that of **1**, except for use of $K[Ag(CN)_2]$. Blue block crystals were obtained and washed with ether in 15% yield based on Cu. Elemental analysis (%) Calcd for $C_{17}H_{19}N_8OCu_{1.76}Ag_{2.24}$: H, 2.70; C, 28.95; N, 15.89%. Found: H, 2.43; C, 28.72; N, 16.10%; IR (KBr, $cm^{-1}$): 2995(w), 2922(w), 2894(w), 2159(s), 2131(m), 1552(s), 1469 (m), 1422(m), 1393(m), 1348(m), 1301(m), 1259(m), 1144(w), 1088(w), 1057(w), 907(w), 801(w), 646(w).

### 2.3. *X-ray crystallography*

Single-crystal X-ray diffraction data collection for **1**–**6** was performed on Bruker SMART 1000 (**2** and **3**) and Rigaku Saturn (**1**,**4**–**6**) CCD diffractometers (Mo Kα radiation,

Table 1. Summary of crystal data, data collection, structure and refinement details for **1**–**6**.

| Parameters | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{35}H_{44}N_{16}O_3Cu_2Fe$ | $C_{31}H_{40}N_{14}O_4Cu_2Fe$ | $C_{30}H_{42}N_{12}O_4Cu_2Ni$ | $C_{30}H_{40}N_{12}O_3Cu_2Ni$ | $C_{47}H_{67}N_{20}O_8Cu_3W$ | $C_{17}H_{19}N_8OAg_{2.24}Cu_{1.76}$ |
| *M*r | 919.79 | 855.70 | 820.55 | 802.53 | 1414.68 | 704.64 |
| Temp/K | 293(2) | 293(2) | 294(2) | 293(2) | 113(2) | 113(2) |
| Cryst. system | Monoclinic | Triclinic | Triclinic | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1$ | *P*-1 | *P*-1 | C2/c | *P*-1 | *P*-1 |
| $a$/Å | 9.763(2) | 8.419(5) | 8.7880(16) | 20.837(4) | 10.7685(2) | 8.9505(12) |
| $b$/Å | 19.956(4) | 10.670(7) | 9.8643(15) | 8.4407(15) | 12.7947(2) | 11.3724(16) |
| $c$/Å | 10.942(2) | 11.840(8) | 11.9325(18) | 21.141(4) | 21.3968(7) | 12.2713(19) |
| $\alpha$/° | 90 | 69.326(9) | 69.363(2) | 90 | 89.569(5) | 62.876(8) |
| $\beta$/° | 99.94(3) | 81.107(10) | 68.608(2) | 103.349(3) | 80.621(5) | 74.225(10) |
| $\gamma$/° | 90 | 84.242(11) | 77.430(2) | 90 | 79.313(4) | 73.689(10) |
| $V$/Å$^3$ | 2099.8(7) | 981.9(11) | 896.6(3) | 3617.8(12) | 2857.4(14) | 1050.6(3) |
| $Z$ | 2 | 1 | 1 | 4 | 2 | 2 |
| $D_{\text{calcd}}$/g cm$^{-3}$ | 1.455 | 1.447 | 1.520 | 1.473 | 1.644 | 2.228 |
| $\mu$/mm$^{-1}$ | 1.399 | 1.491 | 1.747 | 1.728 | 3.176 | 3.841 |
| Reflcns. collected | 26,362 | 3897 | 5024 | 18,819 | 29,997 | 12,416 |
| Indep. reflcns. | 9787 | 2943 | 4156 | 4302 | 13,429 | 4584 |
| $R_{\text{int}}$ | 0.0737 | 0.0662 | 0.0182 | 0.0462 | 0.0414 | 0.0391 |
| $R_1$ [$I > 2\sigma(I)$]$^{\text{a}}$ | 0.0547 | 0.1028 | 0.0522 | 0.0359 | 0.0331 | 0.0477 |
| $wR_2$ [$I > 2\sigma(I)$] | 0.1099 | 0.1834 | 0.1291 | 0.0857 | 0.0740 | 0.0973 |
| Goodness of fit | 0.982 | 1.218 | 1.032 | 1.051 | 1.062 | 1.022 |

a$R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$; $wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$.

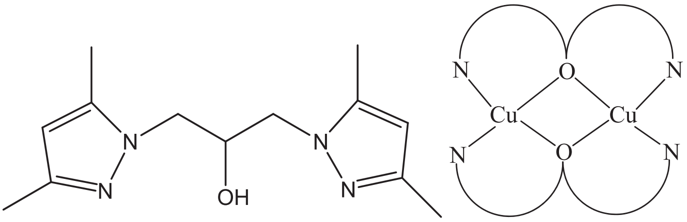
$\lambda = 0.71073$ Å). The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on $F^2$ using SHELXTL [17]. The hydrogens were located and allowed for as riding atoms with isotropic temperature factors. The diffraction data of **2** were not high quality as the crystal was extremely thin. It led to a low parameter of diffrn_measured_fraction_theta_full during the structure solution by omitting bad diffraction points. An unusual alert of single-bonded metal also is seen in **6** caused by the disordered Cu(I) and Ag(I) ions occupying the same lattice positions. The crystallographic data for **1**–**6** are listed in table 1.

## 3. Results and discussion

### 3.1. *Syntheses and characterization*

Conventional solution evaporation is not efficient to obtain single crystals of cyano-bridged complexes. Thus, three different diffusion techniques were employed, including gas diffusion and solution diffusion in test tube or U-shape tube, which generate single crystals. Some tridentate ligands, such as bis(2-pyridylcarbonyl)amidate, tris(pyrazolyl)hydroborate, 1,4,7-triazacyclononane and tris(2-pyridylmethyl)amine, have been used in the synthesis of cyano-bridged complexes. HL is longer and more flexible, which drives formation of $[M_2L_2]$ cation by bridging two metal centers (scheme 1). The two metal ions are so close to each other that each is coordinated to one ligand further to reduce steric hindrance, forming five-coordinate geometry. Cu exhibits higher reactivity to HL than other transition metals, such as Ni, Mn, Co, and Fe, which do not show any complex formation.

FT-IR spectra have been recorded for **1**–**6,** and the $CN^-$ is evidenced by strong bands at 2100–2200 $cm^{-1}$. Generally, *v*(CN) decreases when the coordination increases [18], and different bands should occur for bridging and terminal cyanides with bridging cyanide at higher frequency. For **1** and **2**, FT-IR spectra only have one sharp peak at 2147 and 2138 $cm^{-1}$, respectively, although single-crystal X-ray diffraction reveals both bridging and terminal cyanides are present. The peak at 1921 or 1888 $cm^{-1}$ in the spectra is assigned to NO stretch. For **3**–**5**, two types of cyanides occur by single-crystal X-ray diffraction, and the spectra agree; cyanide stretch is split (**3**: 2140, 2123; **4**: 2173, 2100; **5**: 2145, 2107 $cm^{-1}$). The peaks at 2140, 2173, and 2145 $cm^{-1}$ belong to bridging $CN^-$. For **6**, single-crystal X-ray diffraction reveals the cyanides only are bridging and the splitting (2159 and 2131 $cm^{-1}$) suggests their different bridging modes: bidentate (–C≡N–) and tridentate (>C≡N–).



Scheme 1. Schematic illustration of HL and $[Cu_2L_2]^{2+}$.

### 3.2. *Description of crystal structures*

Cu in **1**–**5** exhibit similar coordination geometries; **1** is taken as an example to depict in detail. Compound **1** crystallizes in the monoclinic space group $P2_1$ and the asymmetric unit of **1** contains two crystallographically independent coppers, Cu1 and Cu2, as shown in figure 1(a). Both coppers are five-coordinate in a distorted square-pyramidal $N_3O_2$ environment; two pairs of N and O from two L form the square, in which the Addison τ factor is 0.14 (0 for the perfectly tetragonal geometry) [19], and one N from cyanide occupies the apical site with axial distance of 2.306 Å for Cu1 and 2.371 Å for Cu2. Cu is almost located into the $N_2O_2$ squares and mean deviations are 0.1085 (Cu1) and 0.1152 (Cu2) Å, respectively. The corresponding bond lengths of Cu–N and Cu–O are reasonable (see table 2). Through two $\mu_2$–O bridges of L, Cu1 and Cu2 are connected to form a binuclear $[Cu_2L_2]$. The Cu···Cu distance is 3.064(8) Å, close to the sum of van der Waals radii for copper (2.8 Å), implying weak Cu···Cu interaction. The Cu–O–Cu angles are 103.7° and 104.8°. To reduce steric hindrance, pyrazol rings of L are located at *trans* positions of the $Cu_2O_2$ plane, in which the dihedral angles between pyrazol rings are 68.6° and 69.6°, respectively. The binuclear units are linked through linear –NC–Fe–CN– bridges of $[Fe(CN)_5NO]^{2-}$ (Fe–C–N angles: 173.4° and 175.4°) to form a 1-D zig-zag chain structure, as shown in figure 1(b).

Complex **2** is crystallized as thin sheet-like crystals, resulting in low-quality diffraction data, while the solution structure is reasonable according to IR and EA data. The structure of **2** is almost the same as that of **1**: the $[Cu_2L_2]$ units are connected by linear –NC–Fe–CN– bridges (Fe–C–N angles: 176.3°) to form a zig-zag chain, and the difference

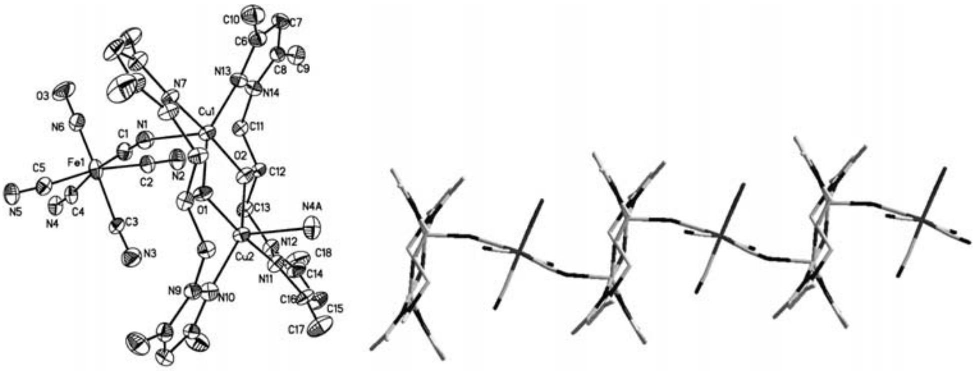


Figure 1. The structure of **1**: asymmetric unit (a) and 1-D zig-zag chain (b).

Table 2. Selected Cu–O and Cu–N bond lengths (Å) in **1**–**6**.

| | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| $Cu–N_{pyrazole}$ | 1.998–2.022 | 1.980 | 1.995–2.030 | 1.999 | 1.976–1.997 | 1.959 |
| $Cu–N_{cyanide}$ | 2.307–2.374 | 2.328 | 2.309 | 2.183 | 2.293–2.317 | |
| $Cu–O_{alcohol}$ | 1.922–1.962 | 1.960 | 1.926–1.962 | 1.935 | 1.934–1.948 | 1.914 |
| $Cu–O_{water}$ | | | 2.409 | | 2.382 | |

is the lattice molecules replaced by water molecules. The corresponding bond lengths of Cu–N and Cu–O are listed in table 2.

In **3**, two crystallographically independent coppers have five-coordinate square-pyramidal geometry. The difference is that one copper shows the $N_2O_3$ environment. Compared with $N_3O_2$ environment in **1** and **2**, the cyanide N at the apical position of the square pyramid is replaced by water; the corresponding bond length is listed in table 2. $[Ni(CN)_4]^{2-}$ is terminal, connected to one $[Cu_2L_2]^{2+}$ with cyanide bridge. Thus, terminal water and $[Ni(CN)_4]^{2-}$ prevent **3** extending to a 1-D chain structure and a trinuclear $Cu_2Ni$ is formed, as shown in figure 2(a). For **4**, single-crystal X-ray diffraction reveals that only one crystallographically independent copper is observed, as a $N_3O_2$ square pyramid (see table 2). In this case, $[Ni(CN)_4]^{2-}$ bridges to connect two $[Cu_2L_2]$ units, extending to a 1-D zig-zag chain structure (figure 2(b)).

In **5**, three crystallographically independent coppers are observed, as shown in figure 3 (a). The coordination environments of Cu1 and Cu3 are similar to **1**–**4**, with $N_3O_2$ square pyramids (see table 2); Cu2 forms a $N_2O_3$ square pyramid similar to that of **3**, in which

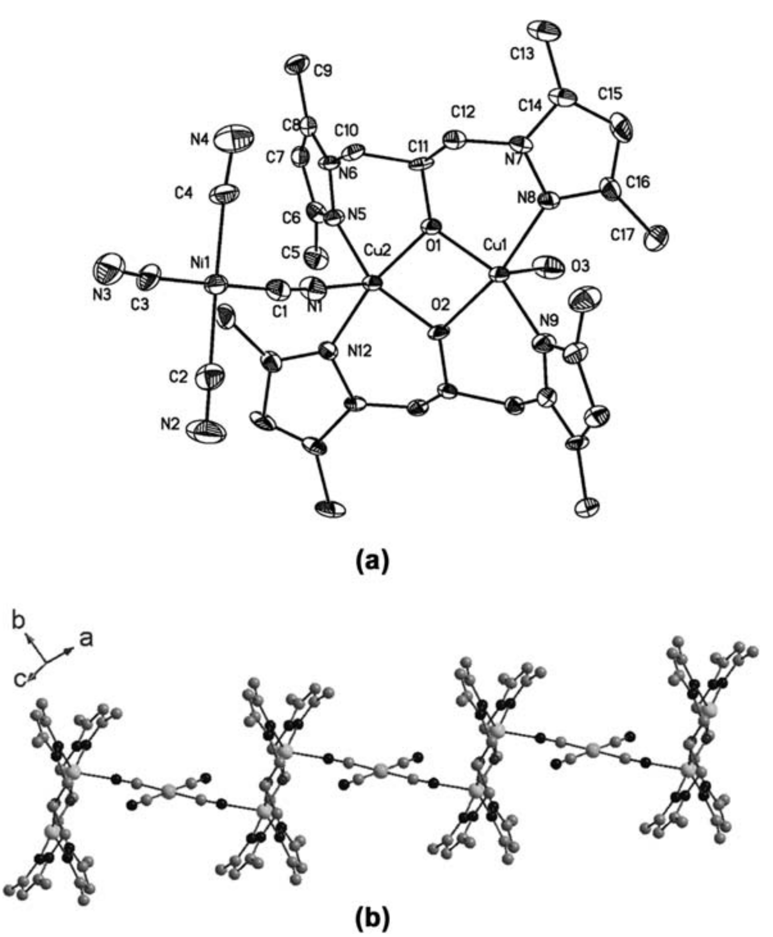


Figure 2. (a) The trinuclear structure of **3** and (b) the 1-D zig-zag chain structure of **4**.

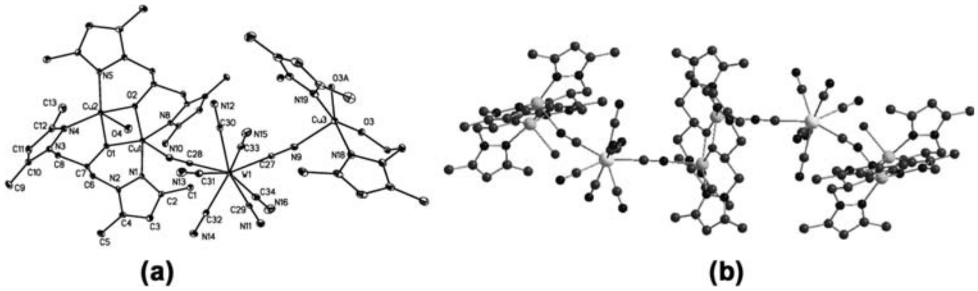


Figure 3. (a) Asymmetric unit of **5** and (b) octanuclear structure of **5**.

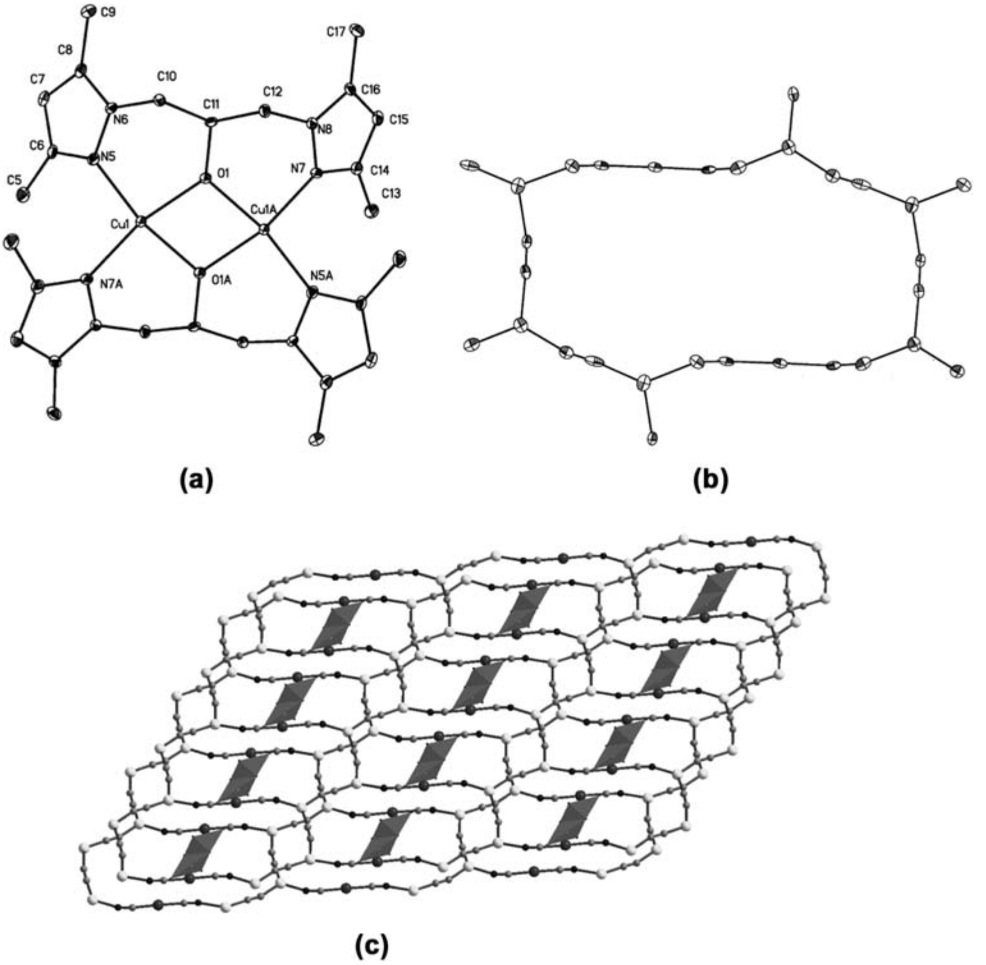


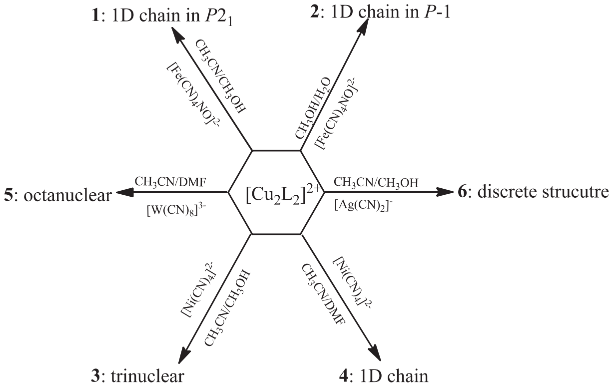
Figure 4. (a) The four-coordinate Cu in **6**; (b) the octanuclear ring consisting of monovalent metal; and (c) the double-deck structure in **6**, polyhedron: $[Cu_2L_2]^{2+}$.

water occupies the apical site. The coordinated water of Cu2 has been arranged towards $[W(CN)_8]^{3-}$, although *trans*-arrangement could reduce steric hindrance. Furthermore, there are two types of $[Cu_2L_2]^{2+}$ units, one constructed from Cu3 is a bridge to link two $[W(CN)_8]^{3-}$ units, while another consisting of Cu1 and Cu2 is terminal connecting one $[W(CN)_8]^{3-}$ to break up the possible extension of **5**. As a result, a unique $Cu_6W_2$ octanuclear structure is formed, as shown in figure 3(b).

Single-crystal X-ray diffraction reveals that there is only one crystallographically independent $Cu^{2+}$ in **6**, as shown in figure 4(a). The Cu is four-coordinate by two pyrazol N and two alcohol O in an irregular $N_2O_2$ square with the apical site unoccupied (see table 2), resulting in $[Cu_2L_2]^{2+}$ with a discrete structure. The counterion consists of $Cu^+$ and $Ag^+$ with the ratio of 19:56 based on the result of X-ray diffraction, indicating that $Cu^{2+}$ is reduced to $Cu^+$. The monovalent metal ions are linked through cyanide bridges to form an octanuclear ring, as shown in figure 4(b), in which a two two-coordinated line and three-coordinated triangle are observed. The two-coordinate site is occupied by $Ag^+$, while the ions in the triangle are disordered, resulting from mixture of $Cu^+$ and $Ag^+$ with ratio of 19:31. Through cyanide bridges, the rings form a 2-D $6^3$-network. This is the first example to provide a 2-D network in silver cyanides. The shortest distance between two silvers in adjacent networks is 3.454 Å, implying Ag···Ag interaction. Through the Ag···Ag interaction, a double-deck motif is formed with enough space to allow $[Cu_2L_2]^{2+}$ units to be vertically inserted into the space, with coppers nearly located in the 2-D layer planes, as shown in figure 4(c).

### 3.3. *Solvent effect on the structures*

Solvents affect the structures of these heterometallic complexes subtly (scheme 2). For **1** and **2**, both complexes have a 1-D chain-like structure with similar molecular formulas of $[Cu_2L_2][Fe(CN)_5NO]$ solvent. As the crystallization solvents are different, acetonitrile for **1** and water for **2**, the complexes crystallize in space groups of $P2_1$ and $P$-1, respectively. For **3** and **4**, solvent effect is focused on water, which plays different roles in the complexes. One water molecule is coordinated to Cu of $[Cu_2L_2]$ and makes it a terminal unit, resulting in 0-D and 1-D structures of **3** and **4**, respectively. Compared with **3**, similar effect of water molecules could be also observed in **5**, which induces the same terminal



Scheme 2. Structure varieties for **1**–**6**.

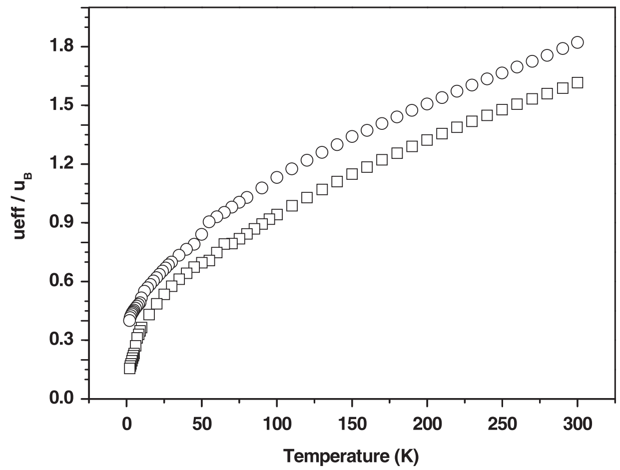


Figure 5. Plots of $\mu_{eff}$ (○ for **1** and □ for **4**) *vs.* T from 2 to 300 K for **1** and **4**.

$[Cu_2L_2]$ units in the structure due to water coordination. Meanwhile, for polynuclear **3** and **5**, $[W(CN)_8]$ is a bridge, while the $[Ni(CN)_4]^{2-}$ is terminal, resulting in octanuclear **5** and trinuclear **3**. A similar phenomenon can also be found in pentanuclear $[\{Cu_2L'\}_2(\mu\text{-}NC)_2Mo(CN)_6(CH_3OH)_{1.5}(H_2O)_{0.5}]$ (L′ = binuclear Schiff-base), in which water and methanol are terminal groups without extension in the structure [20].

### 3.4. *Magnetic properties*

For diamagnetic $[Fe(CN)_5NO]^{2-}$ and $[Ni(CN)_4]^{2-}$ [21], magnetic studies allow evaluation of Cu(II)-Cu(II) interaction. The magnetic behaviors of **1** and **4** in the form $\mu_{eff}$ *versus T* plots are sketched in figure 5 ($\mu_{eff}$ being the effective magnetic moment of two complexes). At 300 K, the $\mu_{eff}$ values for **1** and **4** are 1.82 and 1.62 $\mu_B$, respectively, which are less than the spin-only value of 2.45 $\mu_{eff}$ $\mu_B$ for two isolated Cu(II) ions ($S = 1/2$), indicating magnetic exchange occurs [14]. With lowering temperature, both complexes exhibit similar magnetic behavior. From 300 to 60 K, $\mu_{eff}$ of both complexes gradually decrease. With further decrease in temperature, $\mu_{eff}$ values decrease abruptly to reach minimal values of 0.41 and 0.15 $\mu_B$ at 2 K, respectively. These behaviors suggest an overall antiferromagnetic coupling between Cu(II) ions.

## 4. Conclusions

An N,O-donor pyrazole derivative has been used to construct cyano-bridged heterometallic complexes. Subtle changes observed in the structures of **1**–**6** show the solvent effect. Different lattice solvents in **1** and **2** result in different crystallization. Coordination water in **3** and **5** prevent extending and 0-D structures are formed. A unique 2-D $6^3$-network in **6** is observed for the first time in silver cyanides. Magnetic measurements show overall antiferromagnetic coupling in **1** and **4**.

## Supplementary material

CCDC no. 761955–761960 (**1**–**6**) contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk).

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