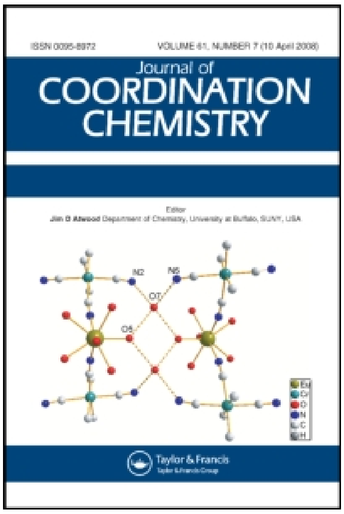

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A new cyanido-bridged $[\{CL\}_2(\mu\text{-NC})_2\text{Mo}^{IV}(\text{CN})_6]$ pentanuclear complex (L^{2-}=bicompartmental macrocyclic ligand): synthesis, spectral, and structural characterization

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To cite this Article Visinescu, Diana , Sutter, Jean-Pascal , Duhayon, Carine , Madalan, Augustin M. , Jurca, Bogdan and Andruh, Marius(2011) 'A new cyanido-bridged $[\{CL\}_2(\mu\text{-NC})_2\text{Mo}^{IV}(\text{CN})_6]$ pentanuclear complex (L^{2-}=bicompartmental macrocyclic ligand): synthesis, spectral, and structural characterization', Journal of Coordination Chemistry, 64: 1, 93 — 104, First published on: 28 November 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.536914

URL: http://dx.doi.org/10.1080/00958972.2010.536914

Journal of Coordination Chemistry
Vol. 64, No. 1, 10 January 2011, 93–104

A new cyanido-bridged $[\{Cu^{II}_2L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6]$ pentanuclear complex (L^{2-} = bicompartmental macrocyclic ligand): synthesis, spectral, and structural characterization

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(*Received 13 July 2010; in final form 4 October 2010*)

An unprecedented pentanuclear hetero-bimetallic complex has been obtained by a self-assembling process between $\{Cu_2L\}^{2+}$ binuclear cationic units and $[Mo(CN)_8]^{4-}$ anions. The compound with the formula $[\{Cu^{II}_2L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6(CH_3OH)_{1.5}(H_2O)_{0.5}]\cdot[\{Cu^{II}_2L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6(CH_3OH)_2]\cdot 5H_2O\cdot 7.5CH_3OH$ (**1**) (H_2L = binucleating Schiff-base obtained by condensation of 2,6-diformyl-4-methylphenol with 1,3-propylenediamine), **1**, crystallizes in $P\bar{1}$ triclinic space group and consists of two pentanuclear species, $[\{Cu^{II}_2L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6(CH_3OH)_{1.5}(H_2O)_{0.5}]$ (**A**), $[\{Cu^{II}_2L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6(CH_3OH)_2]$ (**B**) and solvent. In each unit, two $\{Cu_2L\}^{2+}$ cations are bridged by one octacyanidomolybdate, *via* two *cis*-cyanido groups. Non-covalent channel motifs are developed through a complex network of supramolecular interactions (hydrogen bonds, π–π stacking interaction) involving **A** and **B** units and lattice solvent molecules.

Keywords: Bicompartmental ligands; Hetero-bimetallic complexes; Copper; Octacyanidometallates; Cyanido-bridged complexes

1. Introduction

Since the pioneering work of Robson [1], bicompartmental Schiff-base ligands have opened wide possibilities in rational synthesis of polynuclear complexes [2]. The proximity of the coordination sites makes them suitable molecular models in biomimetic chemistry or magnetochemistry [2]. Recently, it has been shown that these complexes can be used as tectons in obtaining high-nuclearity clusters or coordination polymers [3–12]. This ability arises from several important properties of

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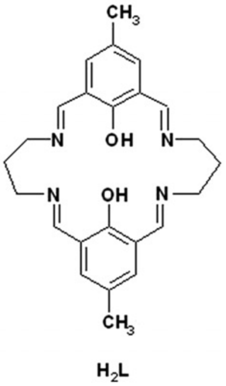
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2010.536914



Scheme 1. Schematic representation of ligand H_2L.

complexes with compartmental ligands: (1) high stability in solid state/solution; (2) solubility in common solvents; and (3) the existence of labile axial ligands (solvent molecules or anions) which can be replaced by bridging ligands. At the same time, a crucial role in the assembly processes of multimetallic complexes, starting from binuclear building blocks, is played by the inner metal ions. Thus, phenoxo-bridged homobimetallic complexes with Robson-type ligands in combination with divergent organic ligands have generated rich metallosupramolecular chemistry [4–6]. The self-assembly process of stable 3d-3d′ or 3d-4f hetero-bimetallic complexes with compartmental ligands with organic and/or metal-containing spacers (usually anionic complexes acting as ligands) have offered a straightforward route to supramolecular heterospin systems with interesting properties [7–12].

The [2+2] macrocyclic Schiff-base compartmental ligands present some synthetic advantages, higher stability, and also higher structural flexibility, which explain the popularity of their corresponding homo- and heterometallic complexes [2c]. Focusing on symmetric macrocyclic ligands, $[Cu_2L(H_2O)_2]^{2+}$ cation (H_2L = binucleating Schiff-base obtained by the condensation of 2,6-diformyl-4-methylphenol with 1,3-propylenediamine; see scheme 1) has been reacted with both organic anion [6] and negatively charged paramagnetic complexes with potentially bridging ligands [12]. For example, in reaction with acetylenedicarboxylate, the labile coordination sites (occupied by water molecules) were substituted with carboxylato oxygens, developing copper(II)-based 1-D coordination polymers [6]. An extensive network, built by $[Cu_2L(H_2O)_2]^{2+}$ and $[Fe^{III}(CN)_6]^{3-}$ ionic units interconnected through hydrogen bonds, showed that the ligand/hydrogen-acceptor duality of cyanide may direct the reaction toward supramolecular systems [12].

Octacyanidometallate anions are intensively used as tectons in crystal engineering [13]. Their geometry varies between three ideal configurations: square antiprism D_{4d}, dodecahedron D_{2d}, and bicapped trigonal prism C_{2v}. This structural versatility is responsible for the diversity of network topologies made from $[M(CN)_8]^{4-}$ (M = Mo, W) and hydrated/chelated 3d or 4f metal ions [14, 15]. Moreover, this flexibility of shape and the non-cubic geometric of the $[M(CN)_8]^{4-}$ units make it a desirable linker to grow cluster compounds of large nuclearity [14, 15]. Taking into account these characteristics, we have envisaged combination between bimetallic complexes with compartmental ligands and octacyanidometallates to construct heterotrimetallic 3d-4f-4(5)d cluster and chain compounds [16]. As an extension of this approach, we now consider the preparation of new 3d-3d-4(5)d hetero-bimetallic systems.

Herein, we report the synthesis, crystal structure, and spectroscopic properties of a cyanido-bridged Cu^{II}–Mo^{IV} complex formed by the reaction of $[Cu_2L(H_2O)_2]Cl_2 \cdot 6H_2O$ and $K_4[Mo^{IV}(CN)_8]$.

2. Experimental

Chemicals were purchased from commercial sources and all manipulations were performed using materials as received. The starting materials, $[Cu_2L]Cl_2 \cdot 6H_2O$ and $K_4[Mo^{IV}(CN)_8] \cdot 2H_2O$, were prepared as outlined in the literature [1b, 17]. IR spectra (KBr pellets) were recorded with a FTIR Bruker Tensor V-37 spectrophotometer. UV-Vis spectra (diffuse reflectance technique) were recorded with a JASCO V-670 spectrophotometer using MgO as a standard. The temperature dependence of the molar magnetic susceptibility of **1** was investigated from 5 to 300 K in an applied magnetic field of 0.1T on a Cryogenic SQUID magnetometer.

2.1. *Synthesis*

Compound **1** has been obtained as follows: an aqueous solution (10 mL) of $K_4[Mo(CN)_8] \cdot 2H_2O$ (40 mg, 0.052 mmol) was layered, in a test tube, with a methanolic solution (10 mL) containing $[Cu_2L]Cl_2 \cdot 6H_2O$ (12.6 mg, 0.026 mmol). X-ray quality green crystals of **1** are obtained after several days. Yield: 80%. Anal. Calcd for $C_{122}H_{157}N_{32}O_{24.5}Cu_8Mo_2$: C, 46.27; H, 4.96; N, 14.16 (**1**). Found: C, 46.92; H, 4.73; N, 14.51 (**1**). IR (cm^{-1}): 3417 (m), 2925 (w), 2104 (m), 1637 (s), 1572 (m), 1449 (m), 1329 (m), 1199 (m), 818 (w).

The crystals were measured on an Oxford Diffraction XCALIBUR diffractometer (Mo-Kα radiation monochromator). The structures were solved by direct methods and refined by full-matrix least-squares based on F. All non-solvent molecules and non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using CRYSTALS crystallographic software package [18]. The hydrogens were located in a difference map, but those attached to carbon were repositioned geometrically. The hydrogens were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98 Å, N–H in the range 0.86–0.89 Å, N–H to 0.86 Å, O–H = 0.82 Å) and Uiso(H) (in the range 1.2–1.5 times Ueq of the parent atom), after which the positions were refined with riding constraints. The maximum positive residual electron density is located at 0.98 Å from Cu(102) ($x = 0.130$, $y = 0.566$, $z = 0.891$), probably due to an imperfect absorption correction. Many water and methanol molecules appear to be highly disordered and it was difficult to model their positions and distribution reliably. Therefore, the SQUEEZE function of PLATON [19] was used to try to minimize the contribution of the electron density in the solvent region from the intensity data. The crystallographic data and other pertinent information are given in table 1.

Table 1. Crystal data and details of the structure determination for **1**.

Empirical formula	$C_{122}H_{157}Cu_8Mo_2N_{32}O_{24.5}$
Formula weight	3164.04
Temperature (K)	180
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	14.541(1)
b	22.761(1)
c	24.589(1)
α	67.451(6)
β	79.901(5)
γ	82.781(5)
Volume (Å^3), Z	7384.1(8), 2
Calculated density (g cm^{-3})	1.423
Absorption coefficient (mm^{-1})	1.364
θ range for data collection (°)	2.8–29.1
Reflections collected	69,260
Unique reflection	39,079 [R(int) = 0.056]
Nb parameters	1627
Reflections used	16,440
Final R indices [$I > 1.6\sigma(I)$][a]	$R_1 = 0.0789$, $wR_2 = 0.0881$
Goodness-of-fit on F^2	1.121
$\Delta\rho$, maximum, minimum (e Å^{-3})	−1.52 and 3.25

[a] $R_1 = \sum \| F_o| - |F_c\| / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + F_c^2)/3$.

3. Results and discussion

3.1. *Synthesis and spectral properties of 1*

Self-assembly between $[Cu_2L]^{2+}$ and $[Mo(CN)_8]^{4-}$, in a molar ratio 2 : 1, leads to very stable green single crystals of cyanido-bridged hetero-bimetallic complex **1**.

The infrared spectrum of **1** reveals signatures of the imine moieties from the Schiff-base ligand and the cyanido groups from $[Mo(CN)_8]^{4-}$. A single broad absorption at *ca* 2104 cm^{-1} results from overlap of the bridging and terminal ν_{CN} vibrations. These low ν(CN) frequencies, which usually are attributed to isolated octacyanidometallates, have also been observed for cyanido-bridged complexes assembled from $[Mo(CN)_8]^{4-}$ and Cu(II) complexes bearing electron-withdrawing Schiff-bases [20]. This phenomenon has been explained by the strong electronic effect of the Schiff base (electron-withdrawal from copper(II) center to terminal ligands) which enhances back donation to the cyanide bridge and compensates the kinematic coupling (the increase of ν(CN) frequencies) [13]. The strong intensity band at 1637 cm^{-1} is assigned to stretching of the iminic bond ($\nu_{C=N}$). Skeletal vibrations of the aromatic rings, representing C=C stretching, absorb at 1570 cm^{-1} [21].

Figure 1 shows the visible electronic spectra of **1**, which exhibits two main bands assigned to $\{Cu_2L\}^{2+}$ and $[Mo(CN)_8]^{4-}$ ions. The first absorption, with maximum at *ca* 670 nm, is assigned to d–d transitions of square-pyramidal or elongated octahedral Cu(II) chromophores [22]. The second band is less monotonous, with maximum at 380 nm and several shoulders at *ca* 460 and 290 nm. A supplementary shoulder is also visible at 255 nm. These absorptions are tentatively assigned to metal-to-ligand charge-transfer (MLCT) and d–d transitions within $[M(CN)_8]^{4-}$ units [23, 24]. Taking into account that the intraligand transitions within the macrocyclic compartmental ligand,

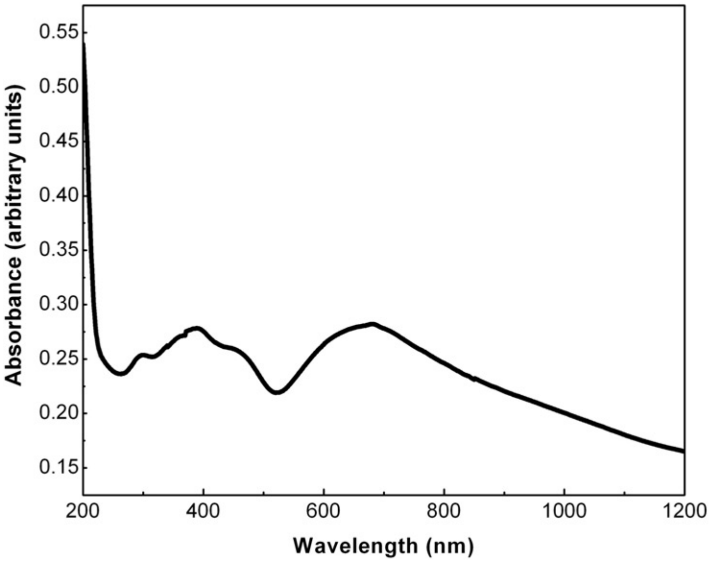


Figure 1. UV-Vis spectrum for **1**.

π–π* (azomethinic chromophores), may also give rise to absorption bands in the 350–380 nm region [25], it is likely that the observed band comprises both the intraligand and the octacyanidometallate specific transitions.

3.2. *Crystal structure of* $[\{Cu_2^{II}L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6(CH_3OH)_2]\cdot[\{Cu_2^{II}L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6(CH_3OH)_{1.5}(H_2O)_{0.5}]\cdot 5H_2O\cdot 7.5CH_3OH$ *(1)*

Compound **1** crystallizes in the $P\bar{1}$ triclinic space group and consists of two neutral cyanido-bridged pentanuclear hetero-bimetallic aggregates, $[\{Cu_2^{II}L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6(CH_3OH)_{1.5}(H_2O)_{0.5}]$ (**A**) and $[\{Cu_2^{II}L\}_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6(CH_3OH)_2]$ (**B**), and crystallized water and methanol (figure 2). The main distances and angles are given in table S1 (Supplementary material).

For each aggregate, one octacyanidomolybdate fragment bridges two $\{Cu_2L\}$ moieties, through two *cis*-cyanido groups, in a bent fashion (Cu(1)–Mo(1)–Cu(3) = 97.652(2)° in **A**, Cu(101)–Mo(2)–Cu(103) = 104.269(2)° in **B**). The copper(II) ions exhibit a distorted square-pyramidal geometry, with basal planes described by the O_2N_2 donors from the Schiff-base compartmental ligand. The trigonal distortion degree of a square-pyramidal geometry can be described by the τ parameter ($\tau = [(\theta - \varphi)/60] \times 100$), where θ and φ are the angles between the donor atoms and the Cu(II) ion forming the diagonals of the basal plane in a square-pyramidal geometry [26]. Values of τ parameters for the eight copper(II) centers range between 0.5% and 6.66% (Supplementary material, table S2), which confirm the slight distortion of the copper(II) polyhedra. For Cu(1) and Cu(3) in **A** (Cu(101) and Cu(103) atoms in **B**), the apical coordination position is occupied by the cyanide groups. The Cu–$N_{cyanide}$ bond lengths are Cu(1)–N(1) = 2.198(7) and Cu(3)–N(2) = 2.134(8) Å in **A** (Cu(101)–N(102) = 2.236(8) and Cu(103)–N(101) = 2.151(8) Å in **B**). A methanol in **A** and a water

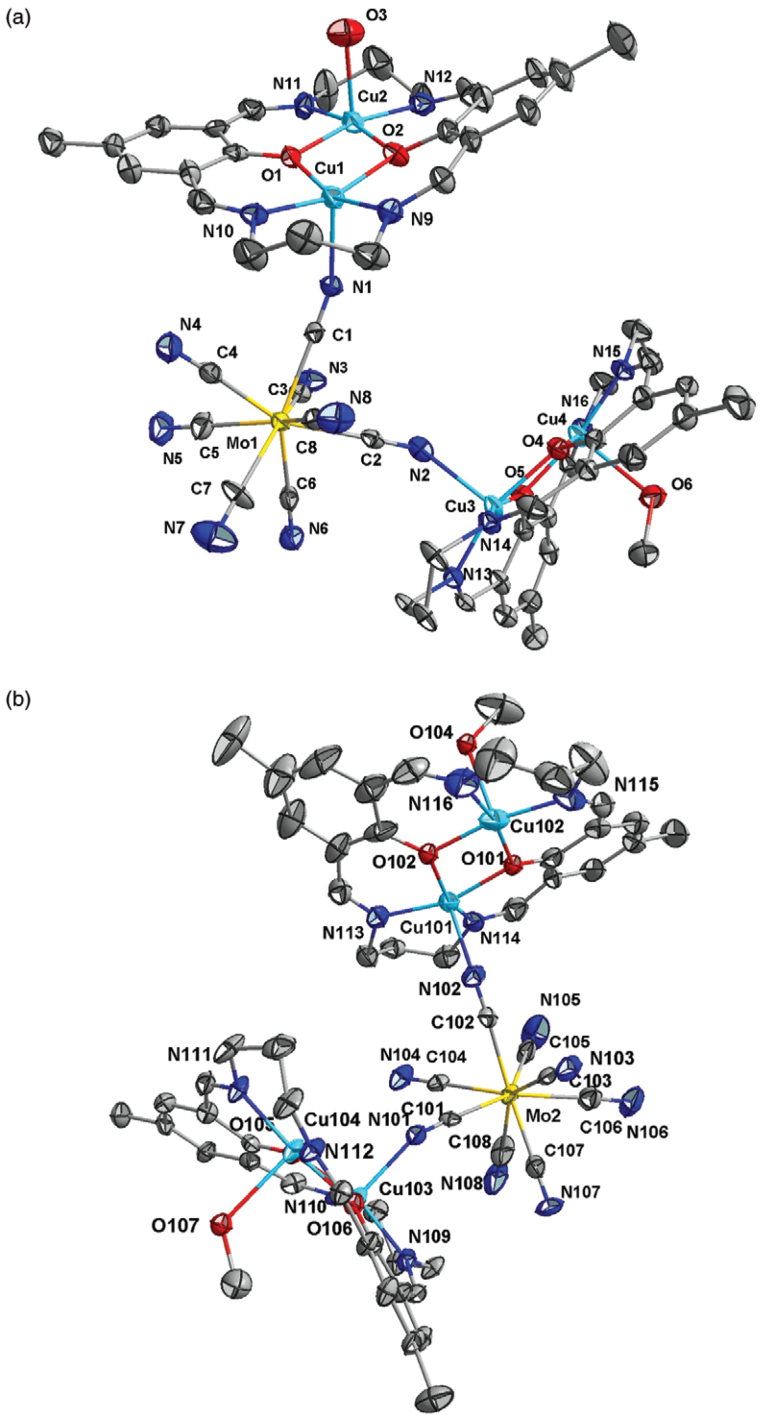


Figure 2. Perspective drawings of the independent crystallographically independent units: (a) **A** and (b) **B** in crystal **1**, along with atom labeling (hydrogens are not shown and thermal ellipsoids are plotted at the 50% probability level).

molecule in **B** are axially coordinated to Cu(2) and Cu(104), respectively. The equatorial Cu–N and Cu–O distances and the corresponding angles fall in the normal range [27], Cu–N bond lengths varying between 1.946(7) and 1.9797(7) Å for **A** (1.943(7) to 1.991(7) Å for **B)**, respectively, and the Cu–O links ranging from 1.964(6) to 2.002(6) Å for **A** (1.935(8) to 2.002(7) Å for **B)**. The distances between the cyanido-bridged copper(II) ions are Cu(1)$\cdots$Cu(3) = 7.9700(19) Å (**A**) and Cu(101)$\cdots$Cu(103) = 8.3071(19) Å (**B**).

The Mo–C distances range from 2.144(9) to 2.179(8) Å in **A** and from 2.134(9) to 2.181(11) Å in **B**, while the C–N bond lengths vary between 1.142(10) and 1.160(12) Å in **A** (1.105(14) and 1.159(12) Å in **B**). A striking structural aspect lies in the non-linearity of Mo–C–N–Cu linkage. Although the Mo–C–N angles are close to 180° (from 175.3(7)° to 179.3(8)° in **A** and from 174.5(10)° to 179.9(8)° in **B**), the two Cu–N–C bond angles are significantly bent: Cu(1)–N(1)–C(1) = 151.1(7)° and Cu(3)–N(2)–C(2) = 150.5(6)° in **A** (Cu(103)–N(101)–C(101) = 144.5(7)° and Cu(101)–N(102)–C(102) = 149.4(7)° in **B**). In octacyanidomolybdate-based complexes, the original dodecahedral structure (D_{2d}) of $K_4[Mo^{IV}(CN)_8]$ [28] usually rearranges itself into a more stable square antiprism geometry (D_{4d}) [13, 29]. Analysis of the coordination polyhedra of the cyanidometallate cores in **1** by Continuous Shape Measures (CShM) analysis [30], carried out with SHAPE [31], have revealed that the shape of the two Mo sites is close to square antiprism.

The macrocyclic ligands are not planar, being twisted with dihedral angles of 22.437(5)° and 34.079(6)° in **A** and of 29.840(8)° and 31.408(5)° in **B**. The intramolecular copper(II)–copper(II) distances *via* phenoxo-bridges are Cu(1)–Cu(2) = 3.1160(14) Å and Cu(3)–Cu(4) = 3.0846(12) Å for **A**, Cu(101)–Cu(102) = 3.1024(16) Å and Cu(103)–Cu(104) = 3.0708(12) Å in **B**, while the copper(II)–molybdenum(IV) distances across cyanido-links are Cu(1)–Mo(1) = 5.3142(13) Å and Cu(3)–Mo(1) = 5.2740(14) Å for **A**, Cu(101)–Mo(2) = 5.3694(13) Å and Cu(103)–Mo(2) = 5.1518(15) Å for **B**.

The independent crystallographic pentanuclear units, **A** and **B**, are further involved in assembly of two separated, non-covalent double chains following distinct hydrogen-bond pathways and developed along the *c*-axis (figure 3). The interatomic distances associated with hydrogen bonds are given in table 2. Terminal cyanide groups, coordinated and crystallized water and methanol, inter-connect the neighboring cyanido-bridged $\{Cu_4^{II}Mo^{IV}\}$ units through N$\cdots$H–O and O–H$\cdots$O type hydrogen bonds. All terminal cyanido groups are hydrogen acceptors toward water and methanol. Details of the packing diagram are depicted in figure S1 (Supplementary material), showing the different hydrogen bonding patterns of the **A** and **B** complexes. The **A** unit is five-connected to vicinal $\mathbf{A^e}$, $\mathbf{B^b}$, and $\mathbf{B^c}$ neutral entities following the non-covalent sequences $O(3)\cdots O(215)^d\cdots N(5)^e$, $O(3)^f\cdots O(215)^b\cdots N(5)$, $N(4)\cdots O(213)^a\cdots O(207)^a\cdots N(106)^c$, $N(3)\cdots O(201)^f\cdots O(107)^b$, and $O(6)\cdots O(204)\cdots N(103)^b$, respectively (figure S1(a) in Supplementary material). **B** unit is interlinked to only two neighboring **A** complexes, in which two hydrogen-bond paths, $N(3)^b\cdots O(201)^f\cdots O(107)^b$ and $N(103)\cdots O(204)^b\cdots O(6)^b$, connect the $\mathbf{A^b}$ and **B** complexes, while the larger non-covalent five-atoms fragment, $N(106)\cdots O(207)^h\cdots O(213)^h\cdots N(4)^c$, joins the $\mathbf{A^c}$ and **B** units, as shown in figure S1(b), Supplementary material (symmetry codes: (^{a}) = $1 - x, 1 - y, 1 - z$; (^{b}) = $-x, 1 - y, 1 - z$; (^{c}) = $-x, 1 - y, 2 - z$; (^{d}) = $x, 1 + y, z$; (^{e}) = $-x, 2 - y, 1 - z$, (^{h}) = $-1 + x, y, 1 + z$). Isolated hydrogen-bonds are established also between the remaining CN^- groups and

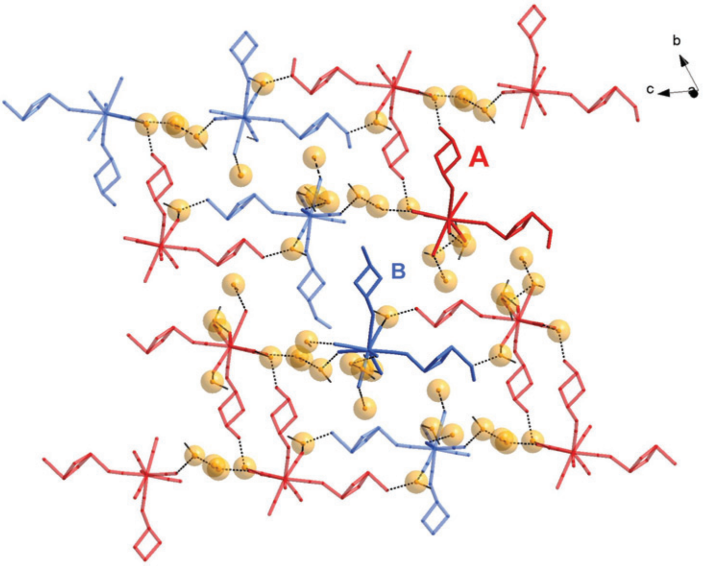


Figure 3. Perspective view of the two independent hydrogen-bond double chains built from complexes **A** and **B**. The macrocyclic Schiff-base ligands, except the phenoxo-bridges, were omitted for clarity; lattice solvent molecules are represented as space filling.

Table 2. Selected intermolecular contacts (Å) in **1**.

O(3)$\cdots$O(215)^{d}	2.6587(3)
O(213)$^{a}\cdots$O(212)^{a}	2.6530(3)
O(213)$^{a}\cdots$O(207)^{a}	2.6989(2)
O(203)$^{b}\cdots$O(205)^{b}	2.7280(2)
O(107)$\cdots$O(201)^{a}	2.6319(1)
O(204)$\cdots$O(6)^{b}	2.6503(1)
O(212)$\cdots$O(213)	2.6530(3)
O(207)$\cdots$O(213)	2.6989(2)
N(5)$^{e}\cdots$O(215)^{d}	2.7726(3)
N(4)$\cdots$O(213)^{a}	2.7914(2)
N(106)$^{c}\cdots$O(207)^{a}	2.7263(1)
N(7)$\cdots$O(206)^{a}	2.8701(1)
N(6)$\cdots$O(203)^{b}	2.7975(1)
N(105)$\cdots$O(211)^{g}	2.6928(3)
N(3)$^{b}\cdots$O(201)^{a}	2.7178(1)
O(204)$^{b}\cdots$N(103)^{b}	2.7012(1)
N(108)$\cdots$O(208)^{g}	2.8458(1)
N(107)$\cdots$O(214)^{g}	2.8156(1)
N(104)$\cdots$O(216)^{g}	3.0375(1)
N(106)$\cdots$O(207)^{h}	2.7263(1)
N(4)$^{c}\cdots$O(213)^{h}	2.7914(2)
N(8)$\cdots$O(202)	2.7849(1)
N(103)$^{b}\cdots$O(204)	2.7012(1)
N(107)$\cdots$O(214)^{g}	2.8156(1)

Symmetry codes: (^{a}) $= 1-x,\ 1-y,\ 1-z$; (^{b}) $= -x,\ 1-y,\ 1-z$; (^{c}) $= -x,\ 1-y,\ 2-z$; (^{d}) $= x,\ 1+y,\ z$; (^{e}) $= -x,\ 2-\mathrm{y},\ 1-z$; (^{g}) $= x,\ y,\ 1+z$; (^{h}) $= -1+x,\ y,\ 1+z$.

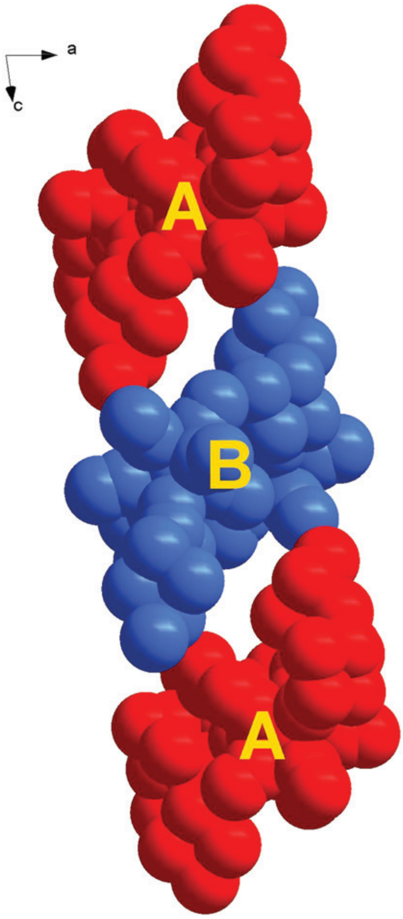


Figure 4. Space-filling representation of the crystal packing along the *b*-axis in **1**, highlighting the supramolecular channels built by **A** and **B** units assembled by hydrogen bonds.

dangling lattice water and/or methanol molecules (figure 3 and table 2). The intermetallic separations imposed by hydrogen bonds are Mo(1)···Mo(2)^c = 12.1571(13) Å, Cu(2)···Mo(1)^e = 7.5822(15) Å, Cu(4)···Mo(2)^b = 7.7707(15) Å and Cu(104)···Mo(1)^b = 7.3950(14) Å.

The resulting **A**–**B** (in *bc*-plane) and **A**–**A** (in *ab*-plane) units form rings within the chain, leading to supramolecular channels propagated parallel to the *b*-axis (figure 4).

Weak inter-ring stacking interactions occur between the phenolic fragments of neighboring **A** and **B** units and contribute to the stabilization of supramolecular architecture (the centroid–centroid distance is 3.5316(2) Å, while the angles between the normal to each benzene ring and the centroid–centroid vector are 19.481(2)°) (figure 5).

Magnetic properties reveal, for **1**, a very weak magnetic susceptibility (χ_M) at 300 K, resulting from a strong antiferromagnetic interaction between the two Cu(II) ions of a

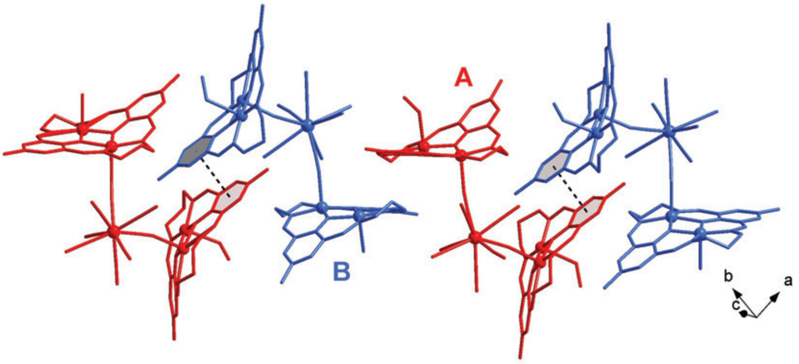


Figure 5. Details of the crystal packing showing π–π stacking interactions (dashed lines) between **A** and **B** phenolic rings.

Schiff-base complex. For such binuclear units, exchange interactions of the order of -700 to $-800\,\mathrm{cm}^{-1}$ have been reported [27].

4. Conclusions

Synthesis of a pentanuclear {3d–4d} complex has been achieved by self-assembling pre-existing binuclear complexes with an octacyanidometallate unit. The cyanido-bearing precursors, including tetra-, hexa-, and octacyanidometallate derivatives, are susceptible to develop extended structures in reaction with solvated 3d metal ions and some very recent examples support these presumptions [32–34]. The example presented in this article illustrates a quite promising route for preparation of heteropolynuclear species with discrete structures, in which the preformed and stable bimetallic cations, $\{Cu_2L\}^{2+}$, are a capping moiety and impede development of polymers. Various combinations of spin carriers and topologies can be anticipated by extending this methodology to the heterobinuclear complexes (with compartmental ligands), yielding unprecedented magneto-structural properties.

Supplementary material

CCDC 763286 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors gratefully acknowledge the CNCSIS (PNII – IDEI-1912/2009).

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