

## SYNTHESIS AND CRYSTAL STRUCTURES OF THREE NEW CYANIDO-BRIDGED HETEROMETALLIC COMPLEXES

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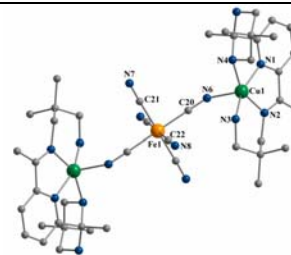
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Received March 4, 2015

Three new isostructural cyanido-bridged heterometallic complexes,  $[\{Cu(L)\}_2\{M(CN)_6\}]$  ( $M = Fe^{II}$ ,  $Ru^{II}$  and  $Os^{II}$ ), have been synthesized and crystallographically characterized (L is a Schiff-base ligand derived from the 1:2 condensation of 2,6-diacetylpyridine with 2,2-dimethyl-1,3-diaminopropane, followed by the cycloaddition of one of the amino groups to the neighbouring azomethinic group with the formation of a 1,3-diazacyclohexane ring). The  $[M(CN)_6]^{4-}$  metalloligands connects two  $\{Cu(L)\}$  fragments through two *trans* cyanido groups.



### INTRODUCTION

Since the initial report on Prussian Blue analogues,<sup>1</sup> and stimulated by the synthesis of room temperature molecule based magnets,<sup>2</sup> homoleptic cyanido complexes, such as  $[M(CN)_6]^{n-}$  ( $M = V^{II}$ ,  $Cr^{III}$ ,  $Fe^{II}$ ,  $Fe^{III}$ ,  $Ru^{III}$  or  $Os^{III}$ ), have been widely used as building-blocks (metalloligands) for the construction of oligonuclear complexes, and coordination polymers with various topologies and interesting magnetic properties.<sup>3</sup> The nuclearity of the desired cyanido bridged complexes and the dimensionality of the coordination polymers can be controlled through ancillary ligands that block several coordination sites of the assembling cation or to the cyanido metalloligand.<sup>4</sup> Scheme 1 illustrates the formation of trinuclear complexes when a pentadentate blocking ligand is attached to the assembling cation. The Schiff bases are among the most popular complexing agents in coordination chemistry. They can be obtained in high yields,

and, by choosing the appropriate carbonyl and primary amine precursors, the number and the relative position of donor atoms can be easily controlled.

Herein, we report on the synthesis and structural characterization of three new heterobimetallic trinuclear complexes,  $[Cu_2M^{II}]$  ( $M = Fe, Ru, Os$ ) incorporating  $[M(CN)_6]^{4-}$  units. A new tetradentate Schiff base derived from the 1:2 condensation of 2,6-diacetylpyridine with 2,2-dimethyl-1,3-diaminopropane is employed as a blocking ligand.

### EXPERIMENTAL

#### Materials and methods

Chemicals were purchased from commercial sources and the  $(AsPh_4)_3[Ru(CN)_6] \cdot 2H_2O$  and  $(PPh_4)_3[Os(CN)_6] \cdot 6H_2O$  precursors were prepared according to the literature.<sup>5</sup>  $(PPh_4)_3[Ru(CN)_6]$  has been obtained by adapting the synthesis reported in the literature. The trinuclear complexes have been synthesized using a similar method: the mononuclear species

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is generated *in situ* by adding the copper(II) salt into an alcoholic solution of the Schiff-base. The subsequent addition of the  $[\text{M}(\text{CN})_6]^{3-}$  metalloligands ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $(\text{PPh}_4)_3[\text{Ru}(\text{CN})_6]$ , and  $(\text{PPh}_4)_3[\text{Os}(\text{CN})_6]$ ) affords the three complexes. The IR spectra reveal the formation of the Schiff-base ligand (with bands in the  $1600\text{ cm}^{-1}$  region) and confirm the presence of the cyanido groups with bands in the range  $2000 - 2100\text{ cm}^{-1}$ .

**Synthesis of  $[\{\text{Cu}^{\text{II}}(\text{L})\}_2\{\text{Fe}^{\text{II}}(\text{CN})_6\}]$  (**1**):** to an ethanolic solution (10 mL) containing 2,6-diacetylpyridine (0.01g, 0.061 mmol) and 2,2-dimethyl-1,3-diaminopropane (0.012g, 0.12 mmol), a solution of  $\text{CuCl}_2$  (0.01g, 0.061 mmol) in 5 mL of ethanol was added and stirred for 1h at  $50\text{ }^\circ\text{C}$ , then 15 mL of an aqueous solution of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (0.012g, 0.036 mmol) was added. The clear green solution was left in the dark undisturbed. After 2 days crystals suitable for X-Ray diffraction were obtained. IR: KBr,  $\text{cm}^{-1}$ : 2046, 1619, 1593, 1467, 1202, 828.

**Synthesis of  $[\{\text{Cu}^{\text{II}}(\text{L})\}_2\{\text{M}^{\text{III}}(\text{CN})_6\}]$ ;  $\text{M}^{\text{III}} = \text{Ru}$  (**2**), and **Os** (**3**)** The  $\text{Ru}^{\text{III}}$  and  $\text{Os}^{\text{III}}$  analogues were synthesized in a water-methanol mixture as follows: to a methanolic solution (10 mL) containing 2,6-diacetylpyridine (0.01g, 0.061 mmol) and 2,2-dimethyl-1,3-diaminopropane (0.012 g, 0.12 mmol),  $\text{Cu}(\text{ClO}_4)_2$  (0.01g, 0.061 mmol) in 10 mL of water was added and stirred for 1h at  $50\text{ }^\circ\text{C}$ , then 10 mL of water-methanol (1:1) solution of  $(\text{PPh}_4)_3[\text{M}^{\text{III}}(\text{CN})_6]$  ( $\text{M}^{\text{III}} = \text{Ru}^{\text{III}}$ ,  $\text{Os}^{\text{III}}$ ) (0.051g, 0.04 mmol) was added. Green crystals, suitable for X-Ray diffraction, were formed in 2 days. IR: KBr,  $\text{cm}^{-1}$ : 2055, 1593, 1470, 1206, 828.

#### Physical measurements and X-Ray crystallography

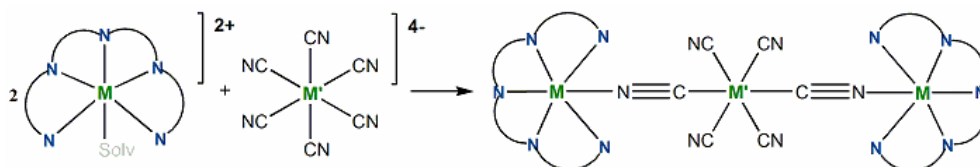
IR spectra (KBr pellets) were recorded on a Tensor 37 spectrophotometer in the  $4000\text{--}400\text{ cm}^{-1}$  region and UV-Vis spectra were recorded with a Jasco V-670 spectrophotometer. The X-Ray diffraction analysis for compound **1** was performed on a Xcalibur, Eos diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The crystal was kept at  $200.00(10)\text{ K}$  during data collection. Using Olex2,<sup>6</sup> the structure was solved with the ShelXS structure solution program and refined with the ShelXL<sup>7</sup> refinement package using Least Squares minimisation. X-Ray crystallographic data for **2** and **3** were collected on a Bruker APEX II Quazar diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The structure of **2** was solved using Superflip<sup>8</sup> and refined by full-matrix least squares techniques based on  $F^2$  using SHELXL-2014/7. All atoms, except hydrogen, were refined anisotropically.

Additional information about the refinement process can be found in the `_refine_special_details` section of the cif files. A summary of the crystallographic data and the structure refinement for crystals **1** and **2** is given in Table 1. CCDC reference numbers: Crystal 1: 1062937; crystal 2: 1062938.

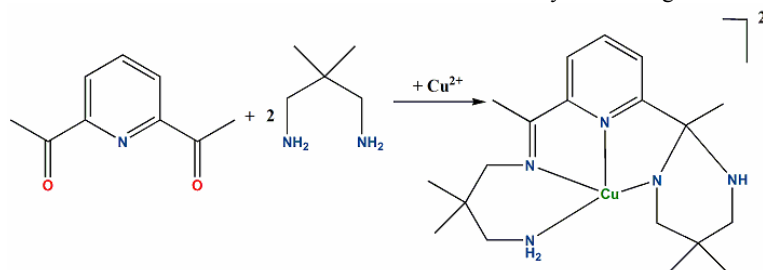
## RESULTS AND DISCUSSION

Three new trinuclear complexes:  $[\{\text{Cu}(\text{L})\}_2\{\text{M}(\text{CN})_6\}]$  ( $\text{M} = \text{Fe}^{\text{II}}$ ,  $\text{Ru}^{\text{II}}$ ,  $\text{Os}^{\text{II}}$ ) were isolated in the self-assembly process involving hexacyanometallates metalloligands, and the complex cation  $[\text{Cu}(\text{L})]^{2+}$ . The formation of discrete complexes is assured by attaching the co-ligand to the assembling cation. In the present study we have employed a Schiff-base ligand obtained from the condensation of 2,6-diacetylpyridine with 2,2-dimethyl-1,3-diaminopropane, followed by a cycloaddition of one of the amino groups to the neighbouring azomethinic group with the formation of a 1,3-diazacyclohexane ring (Scheme 2).

The new compounds were characterized by IR and UV-Vis spectroscopy and by X-Ray diffraction. During the reaction, the  $\text{M}^{\text{III}}$  ions were reduced, resulting in diamagnetic  $[\text{M}(\text{CN})_6]^{4-}$  species. The IR spectra of all three compounds show the characteristic band of the Schiff-base ligand  $\nu_{\text{C=N}} = 1620\text{ cm}^{-1}$ . The presence of a strong peak in the  $2055\text{ cm}^{-1}$  region confirms the presence of the  $[\text{M}(\text{CN})_6]^{4-}$  fragments,  $2060\text{ cm}^{-1}$  for  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $2050\text{ cm}^{-1}$  for  $[\text{Ru}(\text{CN})_6]^{4-}$ , and  $2040\text{ cm}^{-1}$  for  $[\text{Os}(\text{CN})_6]^{4-}$ . The solid-state electronic spectra were recorded for all three compounds. The broad bands with tails at long wavelengths are assigned to the  $\text{Cu}^{\text{II}}$  ion in a square pyramidal geometry:  $630\text{ nm}$  for compound **1** ( $\text{Cu}_2\text{Fe}$ ),  $650\text{ nm}$  for compound **2** ( $\text{Cu}_2\text{Ru}$ ), and  $690\text{ nm}$  for compound **3** ( $\text{Cu}_2\text{Os}$ ) (Fig. 1).<sup>9</sup>



Scheme 1 – General reaction scheme for the construction of discrete cyanido-bridged trinuclear complexes.



Scheme 2 – The formation of the  $[\text{Cu}(\text{L})]^{2+}$  complex cation employed in the present study.

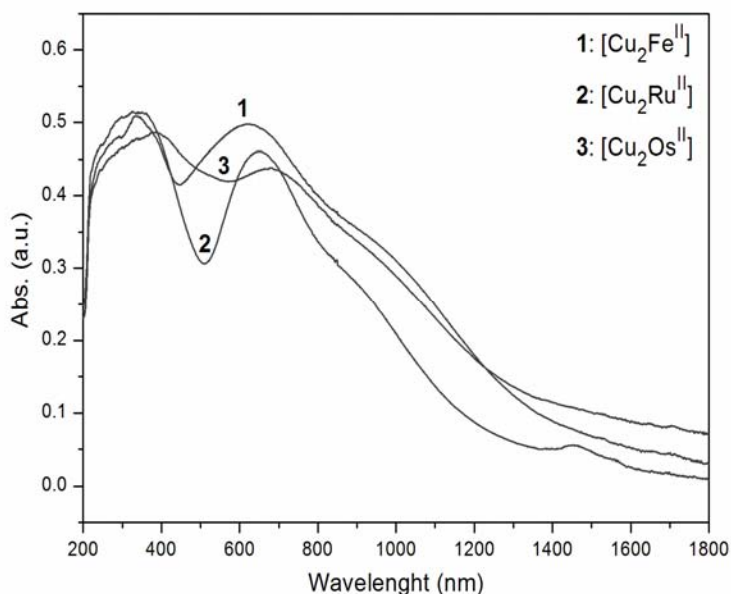
Fig. 1 – The solid-state electronic spectra for complexes **1**, **2**, and **3**.

Table 1

Crystallographic data, details of data collection and structure refinement parameters for compounds **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>44</sub> H <sub>108</sub> Cu <sub>2</sub> FeN <sub>16</sub> O <sub>20</sub>	C <sub>45</sub> H <sub>106</sub> Cu <sub>2</sub> RuN <sub>16</sub> O <sub>19</sub>
Formula weight	1364.39	1403.60
Temperature/K	200.00(10)	120(2)
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	11.7797(5)	11.7873(4)
<i>b</i> /Å	12.6693(6)	12.6699(4)
<i>c</i> /Å	12.8142(6)	12.8632(4)
$\alpha$ /°	67.442(5)	67.7440(10)
$\beta$ /°	89.379(4)	88.669(2)
$\gamma$ /°	73.390(4)	73.0100(10)
<i>V</i> /Å <sup>3</sup>	1681.81(14)	1692.01(9)
<i>Z</i>	1	1
<i>D</i> <sub>calc</sub> /mg/mm <sup>3</sup>	1.347	1.377
$\mu$ /mm <sup>-1</sup>	0.915	0.917
Crystal size/mm <sup>3</sup>	0.80 × 0.20 × 0.020	0.17 × 0.05 × 0.02
$\theta_{\min}$ , $\theta_{\max}$ (°)	3.46 to 50.06	2.57 to 25.32
Reflections collected	11518	78248
Independent reflections	5906 [ <i>R</i> <sub>int</sub> = 0.0244]	6158 [ <i>R</i> <sub>int</sub> = 0.0421]
Data/restraints/parameters	5906/0/379	6158/4/402
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0365	0.0359
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.0999	0.1009
GOF <sup>c</sup>	1.048	1.080
Largest diff. peak/hole/e Å <sup>-3</sup>	0.62/-0.71	0.94/-0.49

<sup>a</sup> $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ , <sup>b</sup> $wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right\}^{1/2}$ , <sup>c</sup> GOF =  $\left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$ , where *n* is the number of reflections and *p* is the total number of parameters refined.

The crystal structures for complex **1** (Cu<sub>2</sub>Fe) and **2** (Cu<sub>2</sub>Ru) were determined by X-Ray diffraction on single crystals. They crystallize in the *P*-1 space group with similar cell parameters (Table 1). Compound **3** (Cu<sub>2</sub>Os) is isostructural with **1** and **2**, as shown by the determination of the

unit cell on a single-crystal (*a* = 11.874, *b* = 12.7614, *c* = 13.0389 Å;  $\alpha$  = 67.405,  $\beta$  = 88.877,  $\gamma$  = 72,894°, *V* = 1734.08 Å<sup>3</sup>). Since these complexes are isomorphous, only the structure of complex **1** will be discussed in detail.

According to X-Ray crystallography, the crystal structure of **1** is built up of neutral trinuclear complexes  $[\{\text{CuL}\}_2\{\text{Fe}(\text{CN})_6\}]$  and solvate water molecules in 1:20 ratio. The trinuclear complex results from two  $\{\text{Cu}^{\text{II}}(\text{L})\}^{2+}$  units bridged by the  $[\text{M}(\text{CN})_6]^{4-}$  metalloligand, which involves two *trans* cyano groups (Fig. 2). The bond distances and angles for compounds **1** and **2** are gathered in Table 2.

The coordination geometry of  $\text{Cu}^{\text{II}}$  is square-pyramidal. The basal plane of the  $\text{Cu}^{\text{II}}$  ion is formed by four nitrogen atoms arising from the Schiff-base ligand, while the axial position is occupied by the CN group. The Cu - N<sub>basal</sub> distances vary between 1.9442(2) and 2.087(2) Å. The apical Cu - N distance is slightly longer: 2.089(2) Å. The intra-trimer Cu...Cu distance is 9.665 Å and the Cu...Fe distance is 4.833 Å.

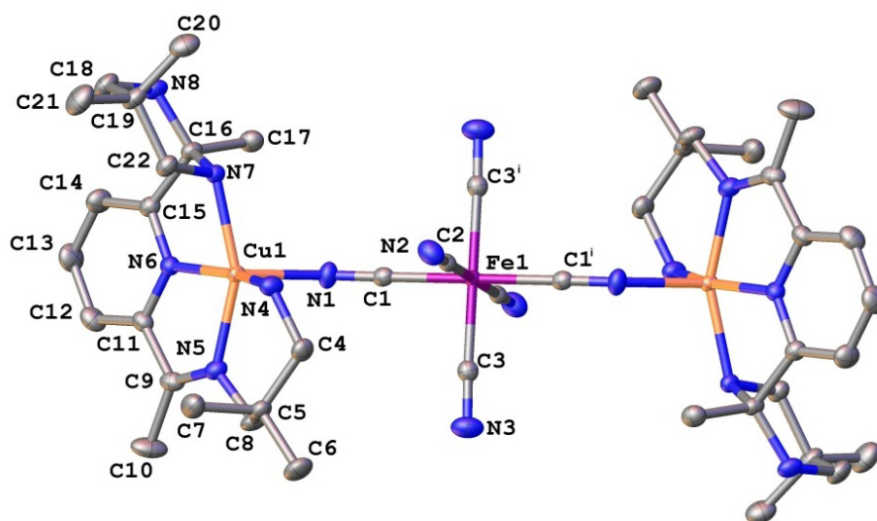


Fig. 2 – Perspective view of the trinuclear  $[\{\text{CuL}\}_2\{\text{Fe}(\text{CN})_6\}]$  complex. Symmetry code: (i)  $2 - x, 1 - y, 1 - z$ .

Table 2

Selected bond distances and angles for compounds **1** and **2**

Compound	<b>1</b> ( $\text{Cu}_2\text{Fe}$ )	<b>2</b> ( $\text{Cu}_2\text{Ru}$ )
Bond lengths(Å)	Cu1 - N1 = 2.089(2) Cu1 - N4 = 1.996(2) Cu1 - N5 = 2.025(2) Cu1 - N6 = 1.944(2) Cu1 - N7 = 2.087(2) Fe1 - C1 = 1.896(2) Fe1 - C2 = 1.924(2) Fe1 - C3 = 1.908(2)	Cu1 - N1 = 1.943(2) Cu1 - N2 = 2.028(2) Cu1 - N3 = 2.091(2) Cu1 - N5 = 1.993(3) Cu1 - N6 = 2.093(3) Ru1 - C20 = 2.043(3) Ru1 - C21 = 2.022(3) Ru1 - C22 = 2.014(3)
Angles (°)	N4 - Cu1 - N1 = 94.88(9) N4 - Cu1 - N5 = 96.62(8) N4 - Cu1 - N7 = 97.46(8) N5 - Cu1 - N1 = 95.67(8) N5 - Cu1 - N7 = 155.62(8) N6 - Cu1 - N1 = 108.21(8) N6 - Cu1 - N4 = 156.83(9) N6 - Cu1 - N5 = 79.56(8) N6 - Cu1 - N7 = 79.67(7) N7 - Cu1 - N1 = 102.84(8) N1 - C1 - Fe1 = 177.8(2) N2 - C2 - Fe1 = 178.9(2) N3 - C3 - Fe1 = 177.7(2) C1 - Fe1 - C2 = 89.1(1) C1 - Fe1 - C3 = 90.7(1)	N1 - Cu1 - N3 = 79.78(10) N3 - Cu1 - N6 = 102.77(10) N6 - Cu1 - N5 = 95.53(11) N5 - Cu1 - N2 = 96.63(10) N2 - Cu1 - N1 = 79.65(10) N1 - Cu1 - N6 = 106.96(10) N3 - Cu1 - N5 = 97.51(10) N6 - Cu1 - N2 = 95.20(10) N5 - Cu1 - N1 = 157.42(11) N2 - Cu1 - N3 = 155.87(10) N7 - C21 - Ru1 = 177.8(3) N8 - C20 - Ru1 = 178.8(3) N6 - C22 - Ru1 = 177.2(3) C22 - Ru1 - C21 = 90.69(12) C22 - Ru1 - C20 = 88.55(11)

The square-pyramidal geometry is supported by the value of  $\tau$  parameter (singular structure parameter).<sup>10</sup> For compound **1** the value of the  $\tau$  parameter equals 0.02 ( $\tau = (\beta - \alpha)/60$ , where  $\beta$  and  $\alpha$  are the N6 - Cu1 - N4 and, respectively, N5 - Cu1 - N7 angles).

The Fe<sup>II</sup> atom is coordinated by six carbon atoms arising from the cyanido ligand and displays an octahedral geometry. The Fe - C distances (1.896(2) Å - 1.924(2) Å) fall in the normal range for low spin cyanido complexes of iron(II).<sup>11</sup>

In the crystal **1** there are multiple possibilities for non-covalent interactions, since different fragments can play the role of proton donors or proton acceptors. As the result, all the components

of the structure are assembled via an extensive network of intermolecular N-H...O, O-H...O and O-H...N hydrogen bonding (Table 3). The main crystal structure motif can be described as a three-dimensional supramolecular architecture (Fig. 3). It is noteworthy, that the solvate water molecules by themselves are self-assembling into the 2D supramolecular layers sustained only by O-H...O bonds without the participation of the trinuclear complexes (Fig. 4). The parallel packing of these layers in the crystal, that occur through non-bonding interaction, with the trinuclear  $[\{\text{CuL}\}_2\{\text{Fe}(\text{CN})_6\}]$  molecular complexes, leads to the formation of channels, which are accomodating the  $\{\text{Cu}^{\text{II}}(\text{L})\}^{2+}$  units.

Table 3

H-bonds parameters in the crystal structure 1

<i>D-H...A</i>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	<i>D-H...A</i>	Symmetry code
O9w-H...O10w	0.85	2.13	2.817(3)	137.1	<i>x, y, z</i>
O10w-H...O9w	0.85	2.00	2.818(8)	160.0	1 - <i>x</i> , 1 - <i>y</i> , - <i>z</i>
O10w-H...O4w	0.83	2.09	2.736(4)	134.7	-1 + <i>x</i> , -1 + <i>y</i> , <i>z</i>
O2w-H...O1w	0.85	2.00	2.847(3)	170.8	1 - <i>x</i> , 1 - <i>y</i> , - <i>z</i>
O2w-H...O1w	0.85	2.09	2.875(3)	152.8	2 - <i>x</i> , 2 - <i>y</i> , - <i>z</i>

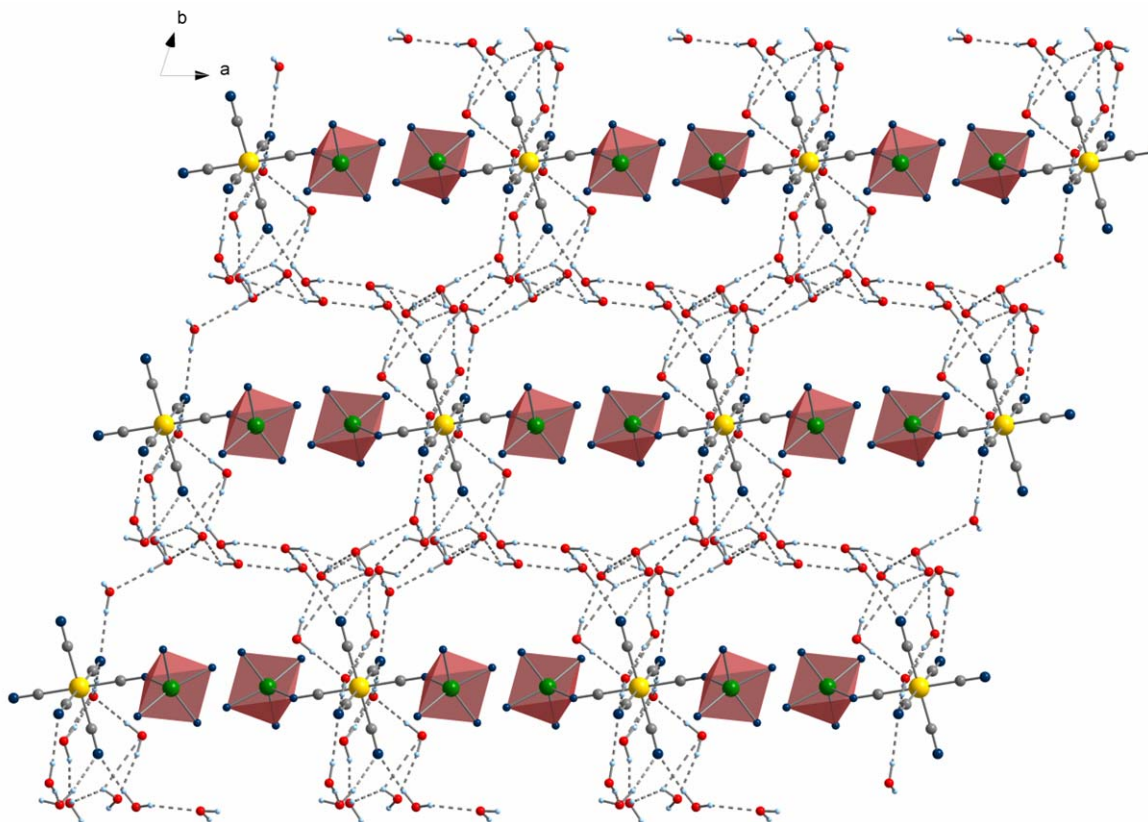


Fig. 3 – Packing diagram for compound **1**. View along the crystallographic *c* axis. The Schiff-base ligand coordinated to copper atoms was omitted for clarity.



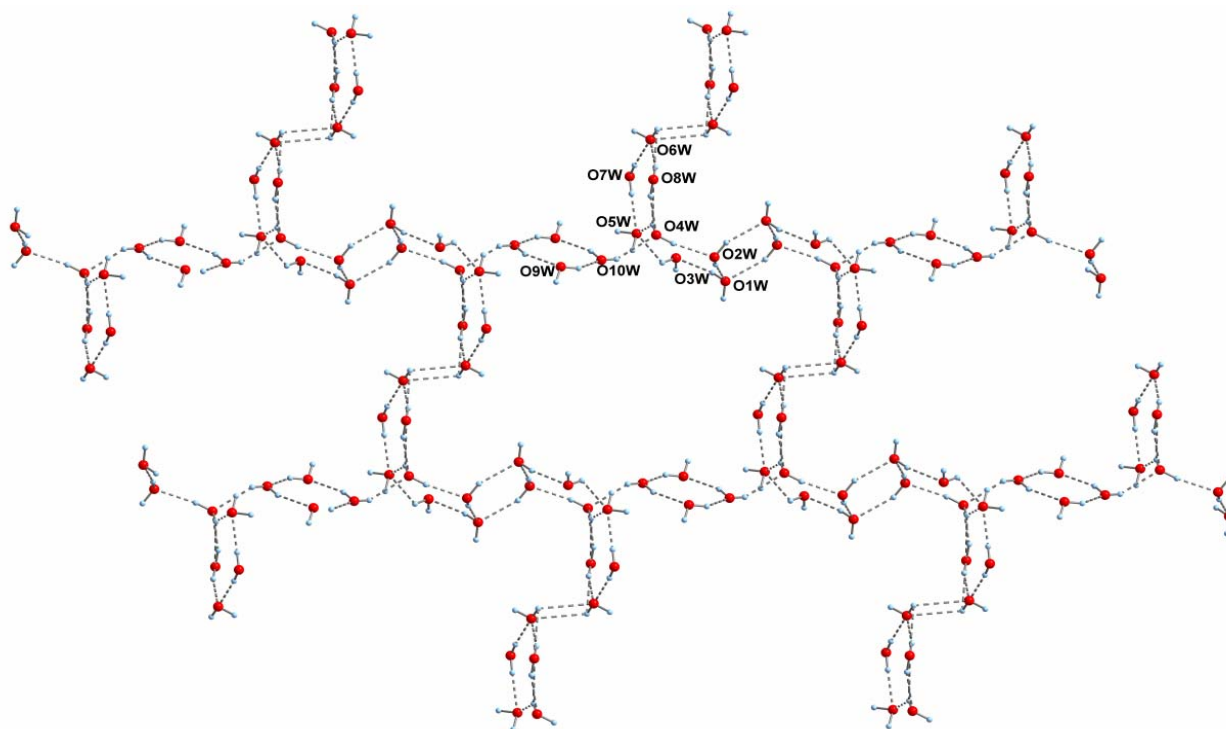


Fig. 4 – H-bond interactions established between the water molecules in crystal 1.

## CONCLUSIONS

In summary, three new heterometallic complexes,  $[\{Cu(L)\}_2\{M(CN)_6\}]$ ,  $M = Fe^{II}$ ,  $Ru^{II}$  and  $Os^{II}$ , were prepared using a Schiff base derived from the 1:2 condensation of 2,6-diacetylpyridine with 2,2-dimethyl-1,3-diaminopropane as a blocking ligand. Interestingly, during the condensation reaction, a cycloaddition of one primary amine group to the  $-C=N-$  bond is observed, resulting in a 1,3-diazacyclohexane ring. The three compounds are isostructural and were characterized by IR and UV-Vis spectroscopy and by X-Ray diffraction. The presence of the co-crystallized water molecules leads to the formation of a complex 3D architecture supported by hydrogen-bond interactions.

*Acknowledgements:* We are grateful to the UEFISCDI (project PN-II-ID-JRP-RO-FR-2011-2-0034) for financial support.

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