

Synthesis, characterization, and magnetic properties of new complexes based on self-assembled homotrinnuclear units $\text{Cu}^{\text{II}}-\text{Cu}^{\text{II}}-\text{Cu}^{\text{II}}$

Javier Tercero,^a Carmen Diaz,^{*a} Juan Ribas,^a José Mahía,^b Miguel Maestro^b and X. Solans^c

^a *Departament de Química Inorgànica, Universitat de Barcelona, Martí Franquès 1-11, 08028 Barcelona, Spain. E-mail: carme.diaz@qi.ub.es.*

^b *Servicios Xerais de Apoio á Investigación, Facultade de Ciencias, Universidade da Coruña, 15071 A Coruña, Spain*

^c *Departament de Cristal·lografia i Mineralogia, Universitat de Barcelona, Martí i Franquès, sln, 08028 Barcelona, Spain*

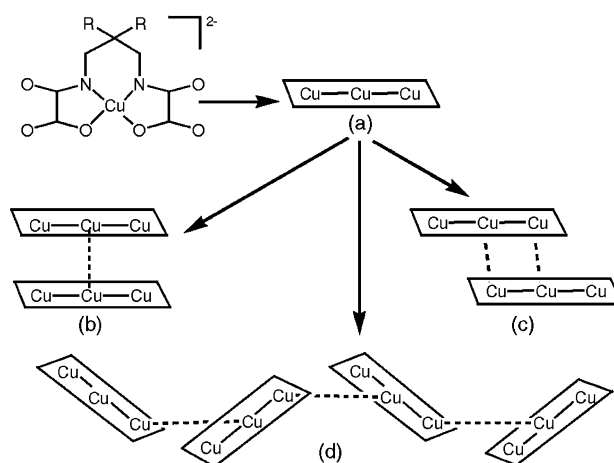
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Three new supramolecular entities of Cu^{II} have been synthesized and characterized: $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (**1**), $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (**2**) and $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{PF}_6)_n \cdot 2n\text{H}_2\text{O}$ (**3**), where pba = 1,3-propanediylbis(oxamato) and tmen = *N,N,N',N'*-tetramethylethylenediamine. The crystal structures of **1** and **2** were solved. Complex **1** is the precursor of **3**; complex **2** is derived from the ClO_4^- analogue of **1**. The two complexes have a central core in common: a trinnuclear Cu^{II} complex with the two terminal Cu^{II} ions blocked by *N,N,N',N'*-tetramethylethylenediamine and with the same environment in the Cu^{II} central atom. In the case of complex **1**, the structure is a double chain of trinnuclear entities linked by hydrogen bonds owing to coordinated water molecules. In the case of complex **2**, the selenocyanate ligands produce intermolecular linkages giving a one-dimensional system. The counter anions PF_6^- and ClO_4^- do not participate directly in the formation of the supramolecular entities. For complex **3** we propose a one-dimensional structure such as found for complex **2**. The magnetic properties of the three complexes were studied by susceptibility measurements vs. temperature; a fit was made by the irreducible tensor formalism (ITO). The values obtained were: $J_1 = -342.1 \text{ cm}^{-1}$, $J_2 = 0.61 \text{ cm}^{-1}$ for **1**, $J_1 = -282.2 \text{ cm}^{-1}$, $J_2 = 2.6 \text{ cm}^{-1}$ for **2** and $J_1 = -245.4 \text{ cm}^{-1}$, $J_2 = 1.3 \text{ cm}^{-1}$ for **3**.

Introduction

We are exploring a strategy to control structure in the solid state, that combines elements of design toward crystal engineering, and the study of magnetic properties. Our goal is to generate supramolecular motifs with structures that can be controlled predictably and altered systematically by design. Our strategy to control molecular arrangement (or packing) uses strong metal–ligand bonds and incorporates more flexible bonds between molecules. This strategy has successfully been applied by us in the preparation of new supramolecular magnetic species, starting from ferrimagnetic molecules, such “metal oxamates” (trinnuclear Cu^{II} cations) or “hetero-metal oxamidates” ($\text{Cu}^{\text{II}}-\text{Ni}^{\text{II}}$ entities). With dinuclear $\text{Ni}^{\text{II}}-\text{Cu}^{\text{II}}$ entities, when the oxamidate is *N,N'*-bis(3-aminopropyl-oxamide)(2⁻), we have reported a series of complexes: some tetranuclear systems with a SCN^- bridging ligand¹ and one-dimensional complexes where the heterodinuclear entities are linked by the nitrite groups acting as a tridentate ligand.² Trinuclear Cu^{II} systems with substituted oxamate(2⁻) ligands (Scheme 1(a)) have a tendency to give several supramolecular structures with short distances between the central Cu^{II} ions of two separate entities forming a hexanuclear-type compound (Scheme 1(b)), hexanuclear systems with hydrogen bonds (Scheme 1(c)), monodimensional systems when the oxamato was 2-hydroxy-1,3-propylenbis(oxamato) (Scheme 1(d));³ and pseudo two-dimensional systems using XCN^- ($\text{X} = \text{S}, \text{Se}$) as bridging ligand.^{4,5} In all compounds that have as base trinnuclear copper(II) systems the two terminal Cu^{II} ions are blocked by *N,N,N',N'*-tetramethylethylenediamine (tmen). The magnetic coupling through the oxamate(2⁻) ligand is well known, the



Scheme 1

coupling is strongly antiferromagnetic, owing to the broad overlap between the magnetic orbitals of the three metal ions and the corresponding molecular orbital of the oxamate bridge.^{6,7} We focused our interest on the association of the “molecular spins” (trinnuclear entities) that takes place when the supramolecular assemblies are formed.

Here we report the synthesis and characterization of three new compounds: $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (**1**), $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (**2**) and $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{PF}_6)_n \cdot 2n\text{H}_2\text{O}$ (**3**), where pba = 1,3-propanediylbis(oxamato) and

tmen = *N,N,N',N'*-tetramethylethylenediamine. The structure of complex **1** is a double chain of trinuclear entities linked by hydrogen bonds. In the case of complex **2**, the intermolecular linkages give a one-dimensional sheet through the selenocyanate ligands. For complex **3** we propose a one-dimensional structure like complex **2**. The magnetic properties of the three complexes were studied by susceptibility measurements vs. temperature. The fit, made by the irreducible tensor formalism (ITO), gave the following values: $J_1 = -342.1 \text{ cm}^{-1}$, $J_2 = 0.61 \text{ cm}^{-1}$ for **1**, $J_1 = -282.2 \text{ cm}^{-1}$, $J_2 = 2.6 \text{ cm}^{-1}$ for **2** and $J_1 = -245.4 \text{ cm}^{-1}$, $J_2 = 1.3 \text{ cm}^{-1}$ for **3**. Compounds **2** and **3** show thermochromism, changing color from green to blue when the temperature is lowered.

Experimental

Materials

Copper(II) perchlorate, copper(II) nitrate, potassium selenocyanate, ammonium hexafluorophosphate and *N,N,N',N'*-tetramethylethylenediamine (tmen) were purchased from Aldrich and used without purification. $\text{Na}_2[\text{Cu}(\text{pba})] \cdot 6\text{H}_2\text{O}$ was synthesized as previously described.⁸ Ethanol was distilled before use.

CAUTION! Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

Synthesis

[Cu₂(H₂O)₂(tmen)₂(μ-Cu(H₂O)(pba))](PF₆)₂ (1**).** An ethanolic solution (5 mL) of *N,N,N',N'*-tetramethylethylenediamine (0.32 g, 2.69 mmol) was added to a stirred solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.650 g, 2.69 mmol) in ethanol (30 mL). An aqueous solution of $\text{Na}_2[\text{Cu}(\text{pba})] \cdot 6\text{H}_2\text{O}$ (0.58 g, 1.36 mmol) was added with constant stirring. An aqueous solution (10 mL) of NH_4PF_6 (0.45 g, 2.76 mmol) was subsequently added with stirring. The resultant solution was filtered to remove any impurity and left to evaporate slowly at room temperature. Dark blue monocrystals suitable for X-ray determination were collected after 2 weeks (yield *ca.* 65%). Found: C, 22.8; H, 4.4; N, 8.4. Calc. for $\text{C}_{19}\text{H}_{44}\text{Cu}_3\text{F}_{12}\text{N}_6\text{O}_9\text{P}_2$: C, 23.26; H, 4.52; N, 8.56%.

[{Cu₂(H₂O)(tmen)₂(μ-Cu(pba))}(μ-SeCN)]_n(ClO₄)_n · 2nH₂O (2**).** To an aqueous solution (30 mL) of $[\{\text{Cu}(\text{tmen})\}_2\{\mu\text{-Cu}(\text{pba})_2\}](\text{ClO}_4)_2$ previously reported⁶ (1.67 g, 2 mmol) an aqueous solution (5 mL) of KSeCN (0.14 g, 1 mmol) was added with constant stirring. The resultant solution was filtered to remove any impurity and left to evaporate slowly at room temperature. Dark green monocrystals suitable for X-ray determination were collected after 3 weeks (yield *ca.* 55%). Found: C, 27.0; H, 4.6; N, 11.1; Cl, 4.1. Calc. for $\text{C}_{20}\text{H}_{44}\text{ClCu}_3\text{N}_7\text{O}_{13}\text{Se}$: C, 26.94; H, 4.52; N, 11; Cl, 3.98%.

[{Cu₂(H₂O)(tmen)₂(μ-Cu(pba))}(μ-SeCN)]_n(PF₆)_n · 2nH₂O (3**).** To an aqueous solution (30 mL) of complex **1** (1.98 g, 2 mmol) were added consecutively KSeCN (0.14 g, 1 mmol) in water (5 mL) and NH_4PF_6 (0.32 g, 2 mmol) in water (10 mL) with constant stirring. The resultant solution was filtered to remove any impurity and left to evaporate slowly at room temperature (yield *ca.* 55%). Despite all efforts no crystals suitable for X-ray determination were obtained. Found: C, 25.8; H, 4.3; N, 10.5. Calc. for $\text{C}_{20}\text{H}_{44}\text{Cu}_3\text{F}_6\text{N}_7\text{O}_9\text{PSe}$: C, 25.63; H, 4.30; N, 10.46%.

Physical measurements

IR spectra (4000–400 cm^{-1}) were recorded from KBr pellets on a Nicolet 520 FT-IR spectrophotometer. Magnetic susceptibility measurements were carried out on polycrystalline

samples with a SQUID apparatus working in the range 2–300 K. Diamagnetic corrections were estimated from Pascal Tables.

X-Ray structure determinations

Diffraction intensity data for single crystals of **1** (blue plate crystal, $0.30 \times 0.20 \times 0.05 \text{ mm}$) and **2** (block green crystal, $0.50 \times 0.25 \times 0.25 \text{ mm}$) were selected and mounted on a Bruker SMART CCD area detector single crystal diffractometer with graphite monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). For **1** the temperature of measurement was 298(2) and for **2** 293(2) and 123(2) K. Absorption corrections were applied using SADABS⁹ (maximum and minimum transmission coefficients 0.911 and 0.599 for **1**; 0.517 and 0.312 for **2** at 293 K and 0.510 and 0.305 for **2** at 123 K).

The structures were solved by direct methods using SHELXS-97¹⁰ for the crystal structure determination and refined by full-matrix least-squares methods on F^2 with SHELXL-97.¹¹ 9066 reflections for **1**, 9939 for **2** (293 K) and 6620 for **2** (123 K) were included in the refinement and 58 restraints for **1**, no restraints for **2** (293 K) and 17 restraints for **2** (123 K) were applied to the 551 parameters for **1**, 418 for **2** (293 K) and 425 for **2** (123 K). For complex **1**, the PF_6^- anions show high thermal parameters and less than ideal geometry. Hydrogen atoms were included in calculated positions and refined in riding mode, except those of the water solvent molecules that were not included. For **2**, hydrogen atoms were included in calculated positions and refined in riding mode. Ionic perchlorate shows high thermal parameters and less than ideal geometry (at 293 K) and also shows high thermal parameters and partial occupancy in two positions (at 123 K). Abbreviated crystal data for **1** and **2** are given in Table 1.

CCDC reference numbers 169868–169870.

See <http://www.rsc.org/suppdata/dt/b1/b107851h/> for crystallographic data in CIF or other electronic format.

Results and discussion

Description of the structure of **1**

The structure of complex **1** consists of double one-dimensional chains derived from $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))]^{2+}$ trinuclear units linked by hydrogen bonds, and hexafluorophosphate ions. A drawing of the cationic part with the atom labeling scheme is given in Fig. 1(a). The main bond distances and angles are given in Table 2.

In the trinuclear unit, oxamato groups bridge the neighboring copper atoms. The terminal copper(II) ions, Cu(1) and Cu(3), have a 4 + 1 environment, the coordination polyhedron can be considered as a square-pyramid with a τ factor value of 0.15 for Cu(1), 0.06 for Cu(2) and 0.08 for Cu(3) ($\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid). Two nitrogen atoms from the tmen ligand and two oxygen atoms from the oxamate form their basal planes. An oxygen atom from a water molecule provides the pentacoordination. The distance of the copper(II) atoms to the basal plane is 0.180 Å for Cu(1), 0.030 Å for Cu(2) and -0.221 \AA for Cu(3). For the central Cu(2) atom the basal plane is formed by two oxygen atoms and two nitrogen atoms from the oxamato ligand, and an oxygen atom from the water molecules provides the pentacoordination. The Cu \cdots Cu separations within the trinuclear unit are Cu(1) \cdots Cu(2) = 5.182 Å and Cu(2) \cdots Cu(3) = 5.215 Å and the Cu(1) \cdots Cu(2) \cdots Cu(3) angle is 173.30°.

A view of the unit cell is shown in Fig. 2(a). The trinuclear entities are self-assembled, *via* hydrogen bonds, in two ways in the *a* and *b* crystallographic directions. In the *a* direction these trinuclear entities are self-assembled through the coordinated water molecules of the three Cu^{II} ions as shown in Fig. 2(b), the contact distances are: O(7) \cdots O(9) = 2.834 Å, and O(8) \cdots O(7) = 2.948 Å. The above described chains are self-

Table 1 Crystallographic data for $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (**1**) and $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (**2**) at 293(2) and 123(2) K

Compound	1	2 at 293(2) K	2 at 123(2) K
Empirical formula	$\text{C}_{19}\text{H}_{44}\text{Cu}_3\text{F}_{12}\text{N}_6\text{O}_9\text{P}_2$	$\text{C}_{20}\text{H}_{44}\text{ClCu}_3\text{N}_7\text{O}_{13}\text{Se}$	$\text{C}_{20}\text{H}_{44}\text{ClCu}_3\text{N}_7\text{O}_{13}\text{Se}$
Formula weight	981.16	895.65	895.65
T/K	298(2)	293(2)	123(2)
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$
$a/\text{\AA}$	10.22180(10)	12.4380(13)	12.4518(11)
$b/\text{\AA}$	13.182	14.4721(14)	14.2871(13)
$c/\text{\AA}$	14.63610(10)	19.130(2)	18.8940(17)
$V/\text{\AA}^3$	1853.39(2)	3443.5(6)	3361.2(5)
Z	2	4	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.774	1.728	1.770
$\mu_{\text{calc}}/\text{mm}^{-1}$	1.903	3.037	3.111
Reflections collected	22103	26835	19416
Independent reflections	9066 [$R_{\text{int}} = 0.0407$]	9939 [$R_{\text{int}} = 0.0587$]	6220 [$R_{\text{int}} = 0.0421$]
Final R indices ^a	$R1 = 0.0472$	$R1 = 0.0326$	$R1 = 0.0319$
$[I > 2\sigma(I)]$	$wR2 = 0.1425$	$wR2 = 0.0674$	$wR2 = 0.0874$
Final R indices	$R1 = 0.0754$	$R1 = 0.0745$	$R1 = 0.0391$
[for all data]	$wR2 = 0.1542$	$wR2 = 0.0756$	$wR2 = 0.0900$

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

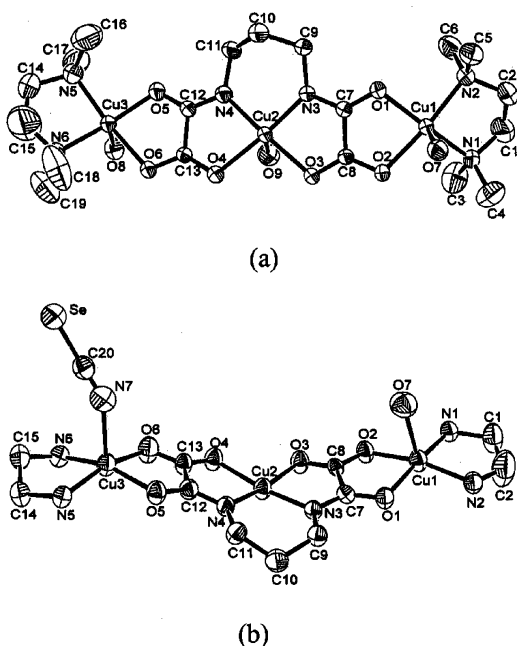


Fig. 1 Drawing of the cationic part of $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (**1**) (a) and $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (**2**) (b) with the atom labeling scheme. Ellipsoids at 50% probability level. The methyl groups are omitted for clarity.

assembled in pairs, in the b crystallographic direction. Each of these trinuclear entities is bridged to two other trinuclear entities of the neighboring chain by six (4 + 2) hydrogen bonds as shown in Fig. 2(c). The four bonds with one of the trinuclear entities are: two between a water molecules O(9) of the central Cu(2) atoms and the oxygen atoms O(6) of the oxamate ligands and the other two between a water molecule O(8) of the terminal Cu(3) atoms and the O(3) of the oxamate ligands, the contact distances are $\text{O}(6) \cdots \text{O}(9) = 2.895 \text{ \AA}$ and $\text{O}(3) \cdots \text{O}(8) = 2.936 \text{ \AA}$. The two bonds with the other trinuclear entity are between O(7) of the terminal Cu(1) atoms and O(4) of the oxamate ligands, the contact distance is $\text{O}(4) \cdots \text{O}(7) = 2.831 \text{ \AA}$. The shortest intermolecular Cu \cdots Cu distances in the a direction are $\text{Cu}(1) \cdots \text{Cu}(2) = 6.628 \text{ \AA}$ (through O(7) and O(9)) and $\text{Cu}(2) \cdots \text{Cu}(3) = 6.520 \text{ \AA}$. In the b direction, the shortest intermolecular Cu \cdots Cu distance is 5.737 \AA .

Table 2 Selected bonds lengths (\AA) and angles ($^\circ$) for $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (**1**)

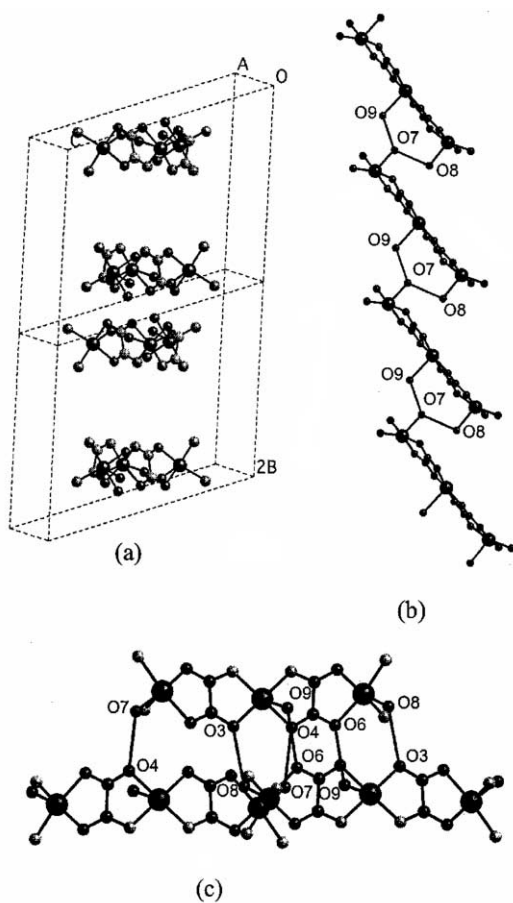
Cu(1)–O(1)	1.953(3)	Cu(2)–O(3)	2.014(3)
Cu(1)–N(2)	2.026(4)	Cu(2)–O(4)	2.040(3)
Cu(1)–N(1)	2.015(4)	Cu(3)–O(5)	1.935(3)
Cu(1)–O(2)	2.026(3)	Cu(3)–N(6)	2.004(4)
Cu(1)–O(7)	2.388(3)	Cu(3)–N(5)	2.027(4)
Cu(2)–N(4)	1.933(3)	Cu(3)–O(6)	2.052(3)
Cu(2)–N(3)	1.929(3)	Cu(3)–O(8)	2.323(3)
O(1)–Cu(1)–N(2)	90.93(13)	N(4)–Cu(2)–O(4)	83.23(13)
O(1)–Cu(1)–N(1)	164.27(14)	N(3)–Cu(2)–O(4)	167.19(13)
N(2)–Cu(1)–N(1)	87.27(15)	O(3)–Cu(2)–O(4)	99.60(11)
O(1)–Cu(1)–O(2)	83.97(11)	O(5)–Cu(3)–N(6)	164.54(15)
N(2)–Cu(1)–O(2)	173.30(13)	O(5)–Cu(3)–N(5)	91.02(15)
N(1)–Cu(1)–O(2)	96.47(13)	N(6)–Cu(3)–N(5)	86.98(17)
O(1)–Cu(1)–O(7)	93.87(12)	O(5)–Cu(3)–O(6)	83.62(12)
N(2)–Cu(1)–O(7)	100.13(13)	N(6)–Cu(3)–O(6)	95.68(13)
N(1)–Cu(1)–O(7)	101.83(13)	N(5)–Cu(3)–O(6)	169.19(15)
O(2)–Cu(1)–O(7)	84.58(11)	O(5)–Cu(3)–O(8)	94.04(13)
N(4)–Cu(2)–N(3)	95.11(14)	N(6)–Cu(3)–O(8)	101.36(14)
N(4)–Cu(2)–O(3)	170.70(14)	N(5)–Cu(3)–O(8)	102.42(16)
N(3)–Cu(2)–O(3)	84.06(12)	O(6)–Cu(3)–O(8)	87.36(12)

Description of the structure of **2**

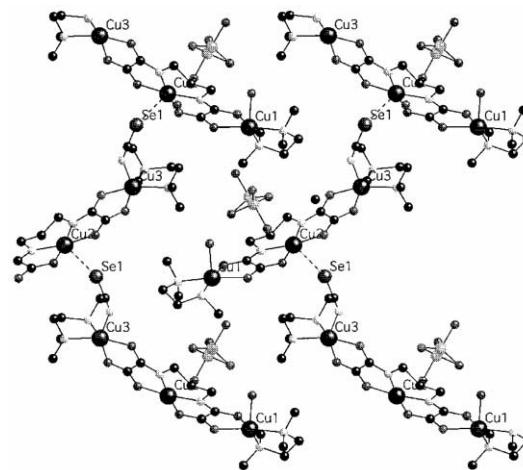
The structure of complex **2** consists of trimeric $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]^+$ units linked *via* an SeCN^- group giving a one-dimensional system separated by ClO_4^- anions. Its structure was solved by X-ray diffraction at two temperatures, 293 K and 123 K, in order to try to explain the change in color with temperature. A drawing of the cationic trinuclear entity with atom labeling scheme is given in Fig. 1(b). The main bond distances and angles are given in Table 3. The three copper(II) ions have 4 + 1 coordination, the coordination polyhedron can be considered as a square-pyramid with a τ factor value of 0.08 for Cu(1), 0.02 for Cu(2) and 0.08 for Cu(3) at 293 K and 0.03 for Cu(1), 0.02 for Cu(2) and 0.00 for Cu(3) at 123 K. For the terminal Cu(1) and Cu(3) ions, the basal planes are formed by two nitrogen atoms from the tmen ligand and two oxygen atoms from the oxamate; the pentacoordination is provided by the oxygen atom from a water molecule for Cu(1) and the nitrogen from the selenocyanate for Cu(3). Two oxygen atoms and two nitrogen atoms from the oxamate ligand form the basal plane for the central Cu(2) atom, and the selenium atom provides the pentacoordination. The distance of the copper(II) atoms to the basal plane is -0.196 \AA for Cu(1), -0.175 \AA for Cu(2) and -0.323 \AA for Cu(3) at 293 K and -0.169 \AA for Cu(1), 0.166 \AA for Cu(2) and -0.296 \AA for Cu(3) at 123 K. The

Table 3 Selected bond lengths (Å) and angles (°) for $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})_n(\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (**2**) at 293(2) and 123(2) K

	293(2) K	123(2) K		293(2) K	123(2) K
Cu(1)–O(1)	1.978(2)	1.836(2)	Cu(2)–O(3)	1.996(2)	1.889(2)
Cu(1)–O(2)	2.013(2)	2.255(3)	Cu(3)–O(5)	1.978(2)	2.175(3)
Cu(1)–N(1)	1.990(3)	1.894(3)	Cu(3)–O(6)	2.026(3)	1.932(3)
Cu(1)–N(2)	2.011(3)	2.240(3)	Cu(3)–N(6)	2.024(3)	2.264(4)
Cu(1)–O(7)	2.328(3)	2.278(3)	Cu(3)–N(5)	2.040(3)	1.917(3)
Cu(2)–N(4)	1.939(3)	1.848(3)	Cu(3)–N(7)	2.233(4)	2.130(4)
Cu(2)–N(3)	1.946(2)	2.155(3)	Se–C(20)	1.815(4)	1.747(4)
Cu(2)–O(4)	1.999(2)	2.159(3)	N(7)–C(20)	1.140(5)	1.112(5)
O(1)–Cu(1)–O(2)	83.70(9)	75.96(10)	N(3)–Cu(2)–O(3)	84.67(10)	76.08(11)
O(1)–Cu(1)–N(1)	170.87(11)	169.55(12)	O(4)–Cu(2)–O(3)	94.81(9)	103.66(10)
O(2)–Cu(1)–N(1)	93.18(10)	101.01(11)	O(5)–Cu(3)–O(6)	84.38(9)	77.94(10)
O(1)–Cu(1)–N(2)	93.22(11)	102.06(11)	O(5)–Cu(3)–N(6)	159.13(11)	163.12(11)
O(2)–Cu(1)–N(2)	166.29(11)	171.33(10)	O(6)–Cu(3)–N(6)	90.54(11)	95.81(12)
N(1)–Cu(1)–N(2)	87.80(12)	79.42(12)	O(5)–Cu(3)–N(5)	92.63(10)	102.75(11)
O(1)–Cu(1)–O(7)	89.88(10)	85.06(11)	O(6)–Cu(3)–N(5)	163.88(12)	163.26(13)
O(2)–Cu(1)–O(7)	90.08(10)	90.17(10)	N(6)–Cu(3)–N(5)	86.66(11)	78.73(12)
N(1)–Cu(1)–O(7)	98.72(11)	105.05(11)	O(5)–Cu(3)–N(7)	104.20(12)	96.40(13)
N(2)–Cu(1)–O(7)	103.30(11)	98.10(11)	O(6)–Cu(3)–N(7)	95.42(12)	101.80(13)
N(4)–Cu(2)–N(3)	94.86(11)	102.01(12)	N(6)–Cu(3)–N(7)	96.41(13)	100.25(13)
N(4)–Cu(2)–O(4)	83.84(10)	76.64(11)	N(5)–Cu(3)–N(7)	100.66(13)	94.76(13)
N(3)–Cu(2)–O(4)	170.35(11)	171.11(11)	C(20)–N(7)–Cu(3)	149.4(3)	146.7(4)
N(4)–Cu(2)–O(3)	169.18(11)	169.81(12)			

**Fig. 2** For $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (**1**): (a) unit cell, (b) view of the self-assembly in the *a* direction and (c) view of the self-assembly in the *b* direction.

trinuclear complexes are linked through the Se-selenocyanate ligand, which is directed towards the central Cu^{II} atom of the neighboring trinuclear entity allowing a chain formation as shown in Fig. 3. The $\text{Cu} \cdots \text{Cu}$ separations within the trinuclear unit are $\text{Cu}(1) \cdots \text{Cu}(2) = 5.175 \text{ \AA}$, $\text{Cu}(2) \cdots \text{Cu}(3) = 5.213 \text{ \AA}$ and the $\text{Cu}(1) \cdots \text{Cu}(2) \cdots \text{Cu}(3)$ angle is 157.36° at 293 K, and $\text{Cu}(1) \cdots \text{Cu}(2) = 5.696 \text{ \AA}$, $\text{Cu}(2) \cdots \text{Cu}(3) = 5.612 \text{ \AA}$ and the $\text{Cu}(1) \cdots \text{Cu}(2) \cdots \text{Cu}(3)$ angle is 159.78° at 123 K.

**Fig. 3** For $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})_n(\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (**2**): projection in the *ac*-plane of the best view of the one-dimensional entities.

The shortest intermolecular $\text{Cu} \cdots \text{Cu}$ distance is *via* the SeCN group, $\text{Cu}(3)$ (terminal) $\cdots \text{Cu}(2)$ (central) = 6.393 \AA (at 293 K) and 6.389 \AA (at 123 K).

Magnetic susceptibility studies

Complex 1. As shown in the crystallographic part (Fig. 2), the trinuclear complexes are linked by hydrogen bonds giving a double chain. The susceptibility measurements are shown in Fig. 4 as $\chi_{\text{M}}T$ vs. T . To fit the experimental data we have assumed a ring of 12 copper(II) atoms, which should describe the behavior of the infinite chain (Fig. 5). The fit to the experimental data was performed according to the following Hamiltonian:

$$H = H_1 + H_2$$

$$H_1 = -J_1(S_1S_2 + S_2S_3 + S_4S_5 + S_5S_6 + S_7S_8 + S_8S_9 + S_{10}S_{11} + S_{11}S_{12})$$

$$H_2 = -J_2(S_2S_4 + S_3S_5 + S_5S_7 + S_6S_8 + S_8S_{10} + S_9S_{11} + S_1S_{11} + S_2S_{12} + S_3S_7 + S_3S_8 + S_1S_9 + S_2S_9 + S_5S_{10} + S_6S_{10} + S_4S_{11} + S_4S_{12})$$

where J_1 corresponds to the coupling through the oxamato bridge, J_2 to the coupling through all the hydrogen bonds. The free parameters were J_1 , J_2 and g (average). The fit

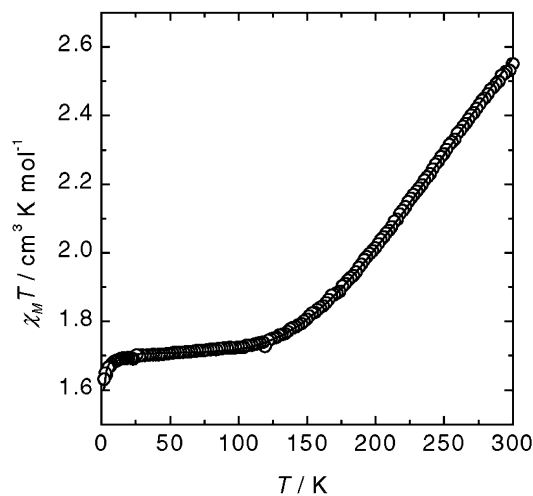


Fig. 4 Experimental and calculated variations of $\chi_M T$ vs. T for $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (1).

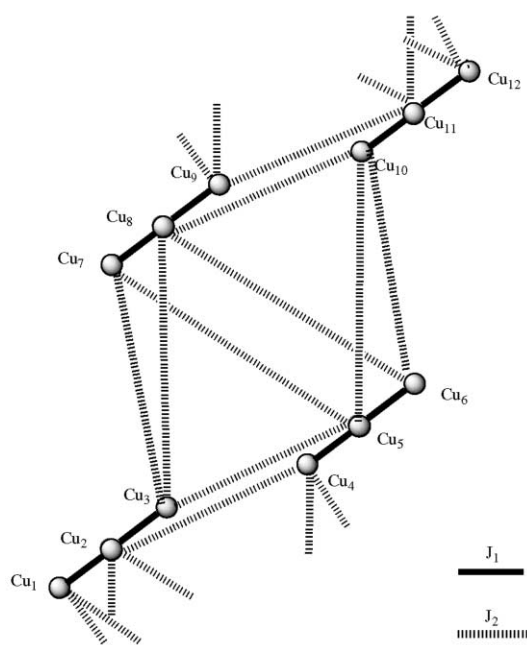


Fig. 5 Scheme of the spin topology assumed to fit the experimental data for $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (1). For different J parameters, see text.

made by the irreducible tensor operator formalism (ITO), using the CLUMAG program,¹² gave the following results $J_1 = -342.1 \text{ cm}^{-1}$, $J_2 = 0.61 \text{ cm}^{-1}$, $g = 2.14$ and $R = 1.28 \times 10^{-5}$.

Complex 2. As can be seen from the crystallographic structure, the chains are formed by trinuclear entities linked by the SeCN group (Fig. 3). For complex 3 we assume the same structure. Such a ligand can transmit an additional magnetic interaction between the trinuclear entities, giving rise to two possible different forms of the ground state at low temperatures. These two forms are shown in Fig. 6. If the magnetic interaction between these two entities was weakly ferromagnetic, the resulting total spin value would tend to zero at low temperatures, so the $\chi_M T$ curve would decrease and also tend to zero at these temperatures. In contrast, if the coupling was weakly antiferromagnetic, $\chi_M T$ would tend to infinity at low temperatures. The susceptibility measurements for complex 2 and 3 are shown in Figs. 7 and 8, respectively, as $\chi_M T$ vs. T . To fit the experimental data we have assumed a ring of twelve copper(II) atoms, which should describe the behavior of the

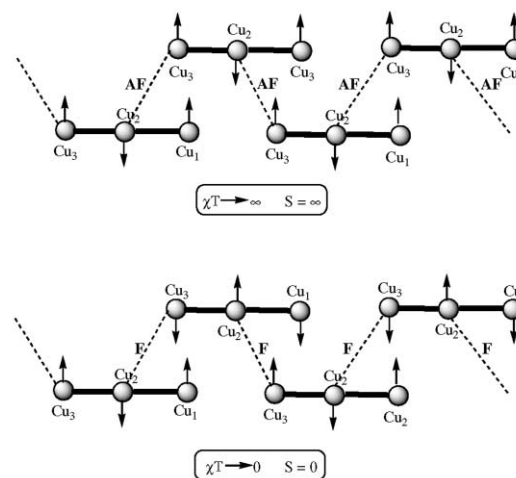


Fig. 6 Scheme of the spin topology assuming ferro- or antiferromagnetic coupling between the trinuclear $[\text{Cu-Cu-Cu}]$ entities in $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (2).

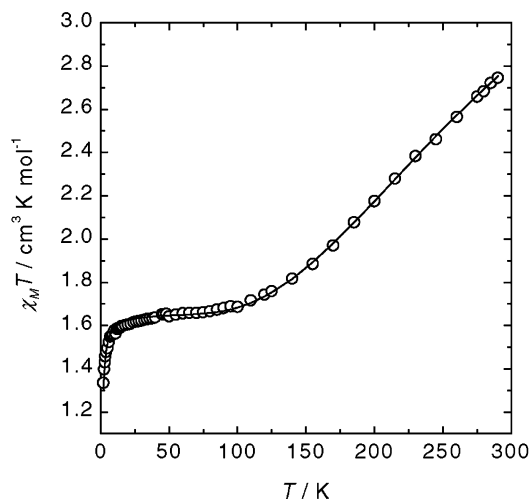


Fig. 7 Experimental and calculated variations of the $\chi_M T$ vs. T for $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (2).

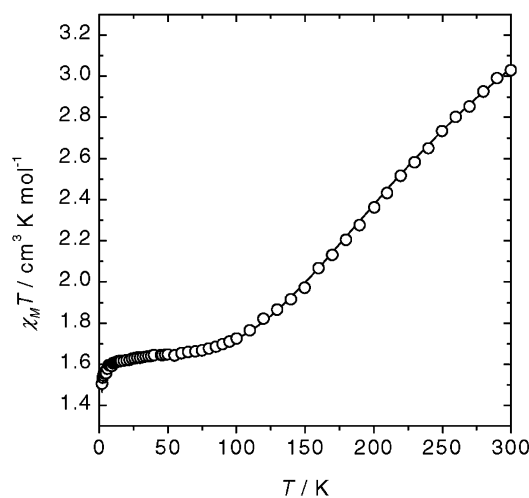


Fig. 8 Experimental and calculated variations of the $\chi_M T$ vs. T for $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]_n(\text{PF}_6)_n \cdot 2n\text{H}_2\text{O}$ (3).

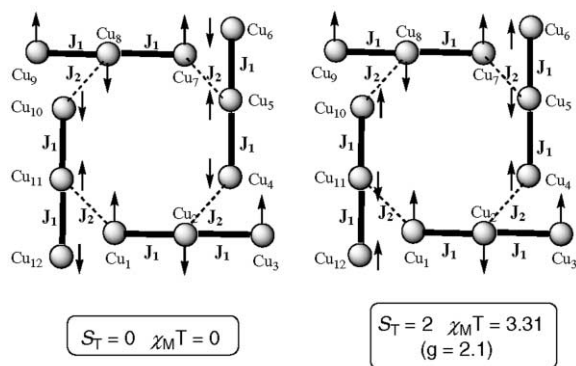
infinite chain with negligible uncertainty (Fig. 9). The fit of experimental data was performed according to the following Hamiltonian:

$$H = -J_1(S_1S_2 + S_2S_3 + S_4S_5 + S_5S_6 + S_7S_8 + S_8S_9 + S_{10}S_{11} + S_{11}S_{12}) - J_2(S_2S_4 + S_3S_7 + S_8S_{10} + S_{11}S_1)$$

Table 4 Main molecular parameters affecting the intramolecular antiferromagnetic coupling for **1** and **2** and related complexes

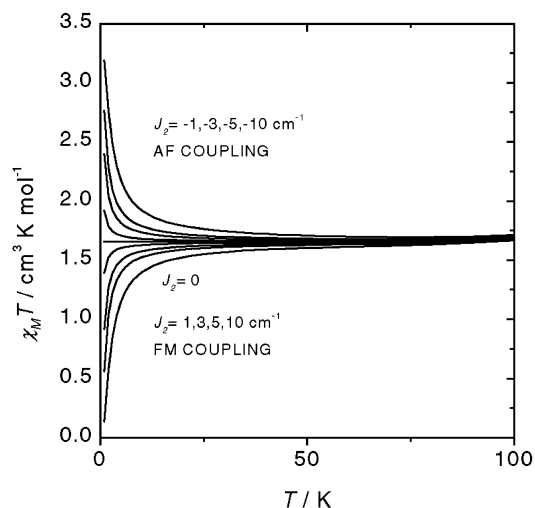
	J/cm^{-1}	CuCuCu $^\circ$	Deviation $^a/\text{\AA}$			τ descriptor for five coordination b			Ref.
			Cu1	Cu2	Cu3	Cu1	Cu2	Cu3	
1	-342.1	173.30	0.180	0.030	-0.221	0.15	0.06	0.08	This work
2 (293 K)	-282.2	157.36	-0.196	-0.175	-0.323	0.08	0.02	0.08	This work
(1)	-312.1	165.15	0.202	-0.110	0.207	0.03	0.02	0.01	3
(2)	-333.9	169.14	-0.145	0.075	0.186	0.07	0.07	0.08	3
(3)	-335.9	173.90	-0.221	0.024	0.246	0.02	c	0.20	3

a Deviation of the copper(II) ions from the mean plane created by the four basal atoms. b τ is 0 for square pyramid and 1 for trigonal bipyramid. c The environment for Cu II is square planar.

**Fig. 9** Scheme of the spin topology assuming intermolecular ferro- (a) or antiferro-magnetic (b) coupling for a ring of twelve copper(II) atoms.

where J_1 corresponds to the coupling through the oxamato bridges and J_2 to the coupling through the SeCN bridge. The free parameters were J_1 , J_2 and g (average). The fit made by the irreducible tensor operator formalism (ITO) using the CLUMAG program gave the following results: $J_1 = -282.2 \text{ cm}^{-1}$, $J_2 = 2.6 \text{ cm}^{-1}$, $g = 2.10$ and $R = 2.02 \times 10^{-4}$ for complex **2** and $J_1 = -245.4 \text{ cm}^{-1}$, $J_2 = 1.3 \text{ cm}^{-1}$, $g = 2.10$ and $R = 2.67 \times 10^{-4}$ for complex **3**.

Finally, to compare the theoretical magnetic behavior for the two extreme cases represented in Fig. 9, a simulation of $\chi_M T$ vs. T , using the same formalism, was performed, fixing the J_1 value as -275 cm^{-1} and the g value as 2.1 and varying the values of J_2 (coupling through the SeCN bridge) between -10 and 10 cm^{-1} . As expected, with these small J_2 values the variation of $\chi_M T$ vs. T is manifested only at low temperatures (Fig. 10). When J_2 coupling is antiferromagnetic, $\chi_M T$ vs. T , increases at lower temperatures tending to $S = 2$ (4 electrons; $\chi_M T = 3.31 \text{ cm}^3$

**Fig. 10** Theoretical curves obtained by the CLUMAG program (see text) for different J_2 values. In all cases J_1 and g were constant: $J_1 = -275 \text{ cm}^{-1}$ and $g = 2.1$.

$\text{mol}^{-1} \text{ K}$ assuming $g = 2.1$); when J_2 coupling is ferromagnetic $\chi_M T$ vs. T , decreases at lower temperatures tending to zero.

Thermochromic behavior

As indicated above, complexes **2** and **3** show thermochromic behavior: at room temperature their color is green and upon lowering the temperature the color becomes blue. Differential scanning calorimeter (DSC) measurements were carried out from room temperature to $-160 \text{ }^\circ\text{C}$. Both complexes show a change in the slope of the curve at $-133.9 \text{ }^\circ\text{C}$ for **2** and $-141.3 \text{ }^\circ\text{C}$ for **3** associated with the color changes. In order to interpret this feature the structure of **2** was solved at 293(2) K and 123(2) K. As shown in Table 3 there is a clear change in the distances and angles in the coordination sphere of each Cu II ion. Considering each Cu II ions as isolated, extended Hückel calculations were made, varying distances and angles according to the observed variations and, explicitly, assuming both geometries. With this hypothesis, the calculated d-d transitions between the corresponding MO would tend to lower energies, while the experimental behavior is the opposite. Thus, this cannot be the reason for the observed thermochromic behavior. This behavior must be due to the transition between MO of the full trinuclear entity. According to the literature the thermochromism can be associated with phase transitions in the solid phase, changes in the environment around the metal ions, geometrical distortions, isomerizations, etc.¹³ On the other hand, in trinuclear Ni-Cu-Ni complexes¹⁴ the magnetic exchange can give new forbidden transitions, activated by an exchange mechanism. At room temperature the visible spectra of **2** and **3**, in acetonitrile solution, show a band centered at ca. 620 nm. Its bandwidth avoids seeing any forbidden transition. Finally, we have observed, recently, that all trinuclear Cu-Cu-Cu complexes prepared by us show the same thermochromic behavior.³ Owing to their different self-assembled features we can conclude that this characteristic is intrinsic to the trinuclear entity.

Conclusions

(a) Structural features. In this work we have synthesized the complex $[\{\text{Cu}_2(\text{H}_2\text{O})(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})_n](\text{ClO}_4)_n \cdot 2n\text{H}_2\text{O}$ (**2**) starting from $[\text{Cu}_2(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))](\text{ClO}_4)_2$ previously reported by us.⁶ In order to prepare the analogous complex with PF_6^- (**3**) instead of ClO_4^- , we have synthesized $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{tmen})_2(\mu\text{-Cu}(\text{H}_2\text{O})(\text{pba}))](\text{PF}_6)_2$ (**1**). In the trinuclear starting product the change of counter anion has produced an important effect: with the perchlorate there is neither coordination nor crystallization water molecules, this precludes the self-assembly process reported in this work for the new hexafluorophosphate complex, **1**, through hydrogen bonds owing to the coordinated water molecules.

In previous work,⁵ we reported the synthesis and characterization of a pseudo-two-dimensional neutral complex $[\{\text{Cu}_2(\text{tmen})_2\text{SeCN}(\mu\text{-Cu}(\text{pba}))\}(\mu\text{-SeCN})]$, starting from $[\text{Cu}_2(\text{tmen})_2(\mu\text{-Cu}(\text{pba}))](\text{ClO}_4)_2$ with SeCN^- and stoichiometry 1 : 1; changing this stoichiometry to 2 : 1, the new one-dimensional complex **2** has been obtained in which the presence of ClO_4^- counter anions impedes the pseudo-two-dimensionality.

(b) Magneto-structural correlations. As previously reported⁶ the most antiferromagnetic coupling occurs when the trinuclear entity is completely planar assuming that all copper(II) ions are in the center of the square-planar coordination: this is an ideal case. In Table 4 we have gathered some structural differences between the complexes reported in this work and those previously reported with the same trinuclear bases.³ The most important one lies in the angle formed by the three Cu^{II} ions. This angle in complex **2** is the smallest found for these systems (157.36°) and, thus, the antiferromagnetic coupling is, also, the smallest ($J = -282.2 \text{ cm}^{-1}$).

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