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Hexanuclear Cu₃O–3Cu triazole-based units as novel core motifs for high nuclearity copper(II) frameworks†

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The asymmetric 3,5-disubstituted 1,2,4-triazole ligand H₂V (5-amino-3-picolinamido-1,2,4-triazole) by reaction with an excess of Cu(II) perchlorate (Cu : H₂V being 12 : 1) has produced a novel hexanuclear {Cu₆(μ₃-O/H)(HV/V)₃} fragment, with one triangular Cu₃(μ₃-O/H) group connected to three peripheral single Cu(II) ions through a *cis-cis-trans* bridging mode of the ligand, which is the building block of the three structures described here: one hexanuclear, [Cu₆(μ₃-O)(HV)₃(ClO₄)₇(H₂O)₉]·8H₂O (1), one dodecanuclear, [Cu₁₂(μ₃-O)₂(V)₆(ClO₄)₅(H₂O)₁₈](ClO₄)₃·6H₂O (2), and one tetradecanuclear 1D-polymer, {[Cu₁₄(μ₃-OH)₂(V)₆(HV)(ClO₄)₁₁(H₂O)₂₀](ClO₄)₂·14H₂O]_n (3), the last two containing hexanuclear subunits linked by perchlorato bridges. The Cu–Cu av. intra-triangle distance is 3.352(2) Å and the Cu(central)–Cu(bridged external) av. distance is 5.338(3) Å. The magnetic properties of the hexanuclear “Cu₃O–3Cu” cluster have been studied, resulting as best fit parameters: *g* = 2.18(1), *J*(intra-triangle) = -247.0(1) cm⁻¹ and *J*(central Cu^{II} – external Cu^{II}) = -5.15(2) cm⁻¹.

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Introduction

Polynuclear Cu(II) compounds are of interest in biology and in magnetochemistry.¹ The structural and electronic factors that govern exchange coupling have been well established in small di-, tri- and tetrametallic clusters.² More recently, the pursuit of single molecule magnets has focused the attention on ever larger clusters with higher multiplicity ground states.³ In addition, the last few years have witnessed an impressive growth of the literature on 1D, 2D and 3D coordination polymers (CPs) with the aggregates of Cu(II) compounds emerging as a type of subunit whose (self) assemblies may form supramolecular structures.⁴

The rich bridging chemistry of the 1,2,4-triazole ligands towards first-row transition metals has produced multiple nuclearities and topologies.^{5,6} We have previously reported a series of 3-substituted-1,2,4-triazole derivatives which are able to generate trinuclear copper-complexes containing the [Cu₃(μ₃-OH)(trz)₃]ⁿ⁺ core.^{7,8} This specific class of tricopper clusters (with trigonal symmetry) are

receiving great attention for two reasons: (1) because of their magnetic singularity, which involves geometric spin frustration effects, antisymmetric exchange coupling and unusual electron paramagnetic resonance (EPR) response,^{7–9} features which make them relevant as magnetic models to understand the mechanism of action of multicopper enzymatic systems;¹⁰ and (2) as subunits (secondary building units, SBU) of metal–organic frameworks (MOFs, also termed porous coordination polymers, PCPs) which combine magnetism and porosity.^{11,12}

Literature on triangular Cu₃O/OH arrays has basically been focused on oximate (N,O), pyrazole (N,N), 1,2,4-triazole (N,N) and more recently 1,2,3-triazole (N,N) and tetrazole (N,N) bridging groups.¹³ The assembly of triangular units in larger aggregates has been achieved (a) by dimerization of the trimeric units through H-bonds between μ₃-O/μ₃-OH centered triangles,^{14,15a} (b) through bridging counteranions,^{15b,c} (c) by means of bi-topic amines^{15d,e} or carboxylate bridges/bis-carboxylato linkers,^{15f,g} and (d) with the use of carboxylate-functionalized N,N ligands (construction of MOFs).^{16–19}

In oximate systems, some hexanuclear systems²⁰ and a few catena²¹ have been reported to date. In contrast, for the pyrazole family there are many examples of hexacopper complexes and of chains of Cu₃O fragments grown with chlorido, sulfato, perchlorato, thiocyanato, carboxylato or bipyridine bridges.¹⁵

As for the 1,2,4-triazol systems, Cu₃O/OH assemblies are more scarce in number but more diverse than the pyrazole ones,¹³ and the corresponding works could be classified in three groups. (A) The most prolific one comprises a series of

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fascinating 2D and 3D structures mostly obtained from solvothermal synthesis by self-association of bifunctional triazole-carboxylate/carboxylic ligands,^{16–18} triazole-isophthalate ligands,¹⁹ or ternary triazolate-sulfoisophthalate systems.^{11,12} (B) A second group includes the studies which combine triazole ligands with polyoxometalates to render POM-based trinuclear clusters.^{22–24} (C) The third class contains a few examples of polymers made up with simple triazole ligands in which the triangular Cu_3O motifs are bridged by ditopic anions such as sulfonate²⁵ or nitrate,¹⁴ as well as one hexanuclear structure with an unusual $\mu_6\text{-Cl}^-$ anion.²⁶ There are also two special cases with a Cu(II) center linking two Cu_3O units.^{7b,25} Finally, it has been described one related tetrazole hexanuclear copper complex constructed with sulfato bridges.²⁷

In this report we introduce the small polydentate 1,2,4-triazole ligand which not only affords triangular Cu_3O cores but also chelates in *trans* one external Cu(II) center to give an unprecedented $\text{Cu}_3\text{O}\text{-3Cu}$ ($\text{Cu}_3 + \text{Cu} + \text{Cu} + \text{Cu}$) hexanuclear compound with formula $[\text{Cu}_6(\mu_3\text{-O})(\text{HV})_3(\text{ClO}_4)_7(\text{H}_2\text{O})_9]\cdot 8\text{H}_2\text{O}$ (1). Further on, the linkage of two hexanuclear motifs through μ_2/μ_3 -perchlorate anions has yielded one dodecanuclear discrete compound and one tetradecanuclear 1D-coordination polymer formulated as $[\text{Cu}_{12}(\mu_3\text{-O})_2(\text{V})_6(\text{ClO}_4)_5(\text{H}_2\text{O})_{18}](\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$ (2) and $\{[\text{Cu}_{14}(\mu_3\text{-OH})_2(\text{V})_6(\text{HV})(\text{ClO}_4)_{11}(\text{H}_2\text{O})_{20}](\text{ClO}_4)_2\cdot 14\text{H}_2\text{O}\}_n$ (3), respectively. The three structures and the magnetic properties of this new type of hexanuclear cluster are presented.

Experimental

Synthesis of 1, 2 and 3

Synthesis of the ligand H_2V was performed as previously reported.²⁸

A methanolic suspension (20 mL) of H_2V (0.25 mmol, 0.052 g) was stirred for 20 min and then heated with stirring at 50 °C for 10 min (ligand only partially solved). At that point a methanolic solution (5 mL) of $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (3 mmol, 1.111 g) was added dropwise and the mixture stirred for 1 h. The resulting green suspension was filtered off. Additional methanol (2.5 mL) was added to the filtered solution, which was deposited on a crystallizing dish (initial reactants ratio is $\text{H}_2\text{V} : \text{Cu}(\text{II}) = 1 : 12$). Cubic-like green crystals of 1 suitable for X-ray analysis were obtained after *ca.* two months. Yield: *ca.* 60%. IR (ATR, cm^{-1}): 3459(m), 3363(m), 1660(s, sharp), 1617(m), 1588(s, sharp), 1532(s, sharp), 1484(w), 1434(w), 1394(s, sharp), 1307(w), 1266–1241(w), 1054(vs), 985(w, shoulder), 929(w). Anal. calc. for $\text{C}_{24}\text{H}_{55}\text{Cl}_2\text{Cu}_6\text{N}_{18}\text{O}_{49}$ (1) (2009.25): C, 14.35; H, 2.76; N, 12.55, Cl, 12.35. Found: C, 14.00; H, 2.60; N, 11.96; Cl, 11.98. The synthesis was reproduced several times. Some of the crystallizations (the most concentrated, approx. 1 out of 5) rendered crystals of different shapes. The X-ray study revealed that the most abundant, the cubic-like ones, correspond to compound 1 (approx. 55% yield). A few of them, hexagonal-prismatic shaped, correspond to compound 2 (approx. 4% yield). Finally, a third type, big long-prismatic shaped, corresponds to compound 3 (approx. 1% yield).

Crystal structure determination

Crystal data, data collection and structure refinement details for 1, 2 and 3 are summarized in Table 1. Diffraction data were obtained at 100(1) K using a Bruker SMART CCD 1000 (1 and 2) or a Bruker X8 Kappa APEXII (3) diffractometer from crystals mounted on glass fibers. Data were corrected for Lorentz and polarization effects and for absorption following multi-scan type.²⁹ The structures were solved by direct methods and subsequent difference Fourier maps³⁰ and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.³⁰ Hydrogen atoms attached to carbon and nitrogen atoms were placed in geometrically idealized positions and were refined with isotropic displacement parameters constrained to 1.2/1.5 Ueq of the carrier atoms. Molecular graphics were generated with DIAMOND.³¹ For each structure peculiarities of the refinement are indicated in ESI (S1–S3).†

Magnetic measurements

Magnetic susceptibility measurements on polycrystalline samples were carried out with a Superconducting Quantum Interference Design (SQUID) magnetometer in the temperature range of 1.9–300 K under magnetic fields of 250–5000 Gauss. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants. Experimental susceptibilities were also corrected for the temperature independent paramagnetism, $\chi_{\text{TP}} = 60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per copper(II), and for the magnetization of the sample holder. X-Band EPR spectra of polycrystalline samples were recorded at different temperatures with a Bruker ER 200 spectrometer equipped with a helium continuous-flow cryostat.

Results

The ligand

The ligand of the present study, H_2V [5-amino-3(pyridine-2-yl-acetamido)-1,2,4-triazole=5-amino-3-picolinamido-1,2,4-triazole], was obtained from mono-acetylation of the guanazole with picolinic acid.²⁸ In a previous work we reported on a similar ligand, the H_3diV [3,5-bis(picolinamido)-1,2,4-triazole], synthetized by diacetylation of the guanazole (Scheme 1). From the previous H_3diV ligand and with an excess of copper(II) perchlorate a hexanuclear cationic complex of formula $[\text{Cu}_6(\text{HdiV})_2(\text{ClO}_4)_6(\text{H}_2\text{O})_{14}]^{2+}$ was formed, which could be described as a cluster of the “1 + 1 + 2 + 1 + 1” type.³² The ligand H_2V , a 1,2,4-triazole ligand bearing only one chelating arm, studied here as such for the first time, in the presence of Cu(II) forms the Cu_3N_6 nine-membered ring of the $\text{Cu}_3\text{O}(\text{H})$ triangular family.^{7,8} The feature which makes H_2V unique is the bis-chelating nature of the triazole substituent which links in *trans* one additional atom centre, thus resulting in the “3 + 1 + 1 + 1” hexanuclear copper(II) core-motif (Scheme 2). From this building block three different structures have been formed which we present here: one hexanuclear Cu_6 (1), one di-hexanuclear ($2 \times \text{Cu}_6 = \text{Cu}_{12}$) (2), and one 1D-polymer made of dimers linked by pairs of hexamers ($\text{Cu}_2\text{-Cu}_6\text{-Cu}_6\text{-Cu}_2'$, Cu14) (3).



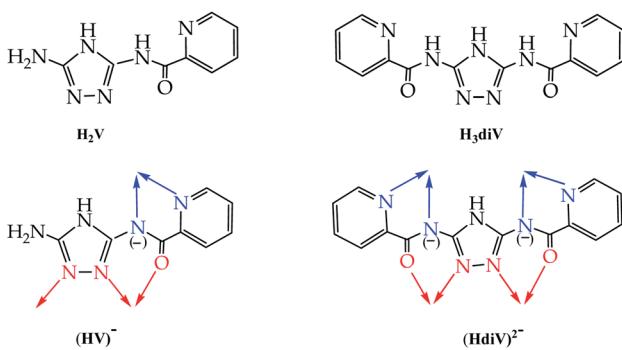
Table 1 Crystal and structure refinement data for 1–3

	1	2	3
Chem. formula	$C_{24}H_{55}Cl_7Cu_6N_{18}O_{49}$	$C_{48}H_{84}Cl_8Cu_{12}N_{36}O_{64}$	$C_{56}H_{113}Cl_{13}Cu_{14}N_{42}O_{95}$
M_r	2009.25	3235.59	4245.29
Cryst. size (mm)	$0.260 \times 0.230 \times 0.220$	$0.240 \times 0.150 \times 0.100$	$0.320 \times 0.260 \times 0.120$
Cryst. syst.	Trigonal	Hexagonal	Monoclinic
Space group	$R\bar{3}:H$	$P6_3/m$	$C2/c$
a (Å)	20.496(3)	20.811(3)	35.294(3)
b (Å)	20.496(3)	20.811(3)	20.8571(17)
c (Å)	33.675(6)	22.620(3)	23.370(3)
α (°)	90	90	90
β (°)	90	90	98.149(5)
γ (°)	120	120	90
V (Å 3)	12 251(4)	8484(3)	17 030(3)
Z, D_c (g cm $^{-3}$)	6, 1.634	2, 1.267	4, 1.656
$h/k/l$	–25/12, 0/25, 0/42	–18/0, 0/21, 0/23	–39/38, 0/23, 0/25
$F(000)$	6060	3240	8520
Absorption coeff. (mm $^{-1}$)	1.865	1.673	2.019
No. of collected/unique rflns	33712/5630	47107/3580	12 143/12 143
R_{int}	0.0498	0.0542	0.0516
No. of data/restraints/params	5630/67/318	3580/13/301	12 143/148/777
R_1/wR_2 ($I > 2\sigma(I)$)	0.1021/0.2846	0.0798/0.2308	0.1198/0.2663
R_1/wR_2 (all data)	0.1521/0.3377	0.1125/0.2547	0.1768/0.2873
Max, min transmission	1.0000, 0.7645	1.0000, 0.7555	1.0000, 0.8926
GOF on F^2	1.049	1.041	1.096
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å $^{-3}$)	1.939, –1.352	1.407, –0.503	3.268, –1.283
CCDC number	1935979	1935980	1935981

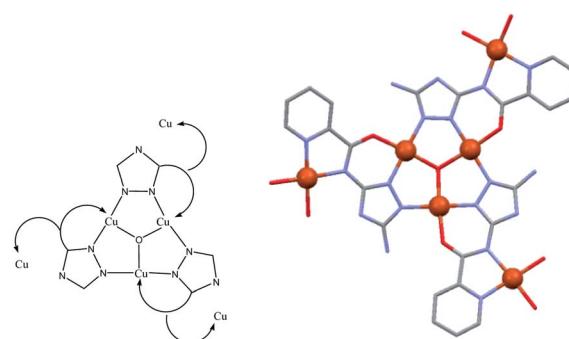
Description of structures

Crystal structure of $[\text{Cu}_6(\mu_3\text{-O})(\text{HV})_3(\text{ClO}_4)_7(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}$ (1). Compound 1 crystallizes in the trigonal system (Table 1). The unit cell contains 6 neutral $[\text{Cu}_6(\mu_3\text{-O})(\text{HV})_3(\text{ClO}_4)_7(\text{H}_2\text{O})_9]$ complexes and 8 water molecules of crystallization (Fig. 1). Table 2 lists selected distances and angles (full list in S4†). The ligand H_2V is deprotonated at the N acetamido group and retains the H atom of the 1,2,4-triazole ring (the H atom is on N4 (N23); this tautomer differs from that present in the reported crystal structure of the ligand).²⁸ The hexanuclear compound includes two type of copper centers, Cu1 and Cu2. There are three Cu(II) ions symmetrically related (Cu1, Cu1a, Cu1b) in a triangular arrangement hold peripherally by N–N triazole

bridges and in the center by a μ_3 -oxo bridge. The coordination environment of these Cu(II) ions is a distorted octahedron, with two N-triazole atoms, one O-carbonyl atom and the central oxo anion in equatorial positions, and two O-perchlorate atoms in the apical ones. There are four coordinating perchlorate anions in total since one of them (Cl1) is tridentate and coordinates simultaneously the 3 copper(II) ions of the $\{\text{Cu}_3\text{O}\}$ core, at a Cu(1)–O(11) distance of 2.63(2) Å. For oximate (N,O), pyrazole (N,N) and 1,2,4-triazole (N,N) systems, it has been described that Td anions (such as sulfate, perchlorate, etc.) often act as tridentate ligands and block three axial coordination sites on the same side of the triangle.^{15b,c,20a,24,25}



Scheme 1 Comparing ligands H_2V and H_3diV : bridging mode of the mono-deprotonated (HV^-) (or the di-deprotonated V^{2-}) (this work) and the di-deprotonated (HdiV^{2-}) ligands.³²



Scheme 2 The quiral “3 + 1 + 1 + 1” hexanuclear copper(II) core-motif (right: Cu atoms in red ball). The average (comp. 1 + comp. 2 + comp. 3) distances are: Cu–Cu(intra-triangle) = 3.352(2) Å, and Cu(central)–Cu(closest external) = 5.338(3) Å.



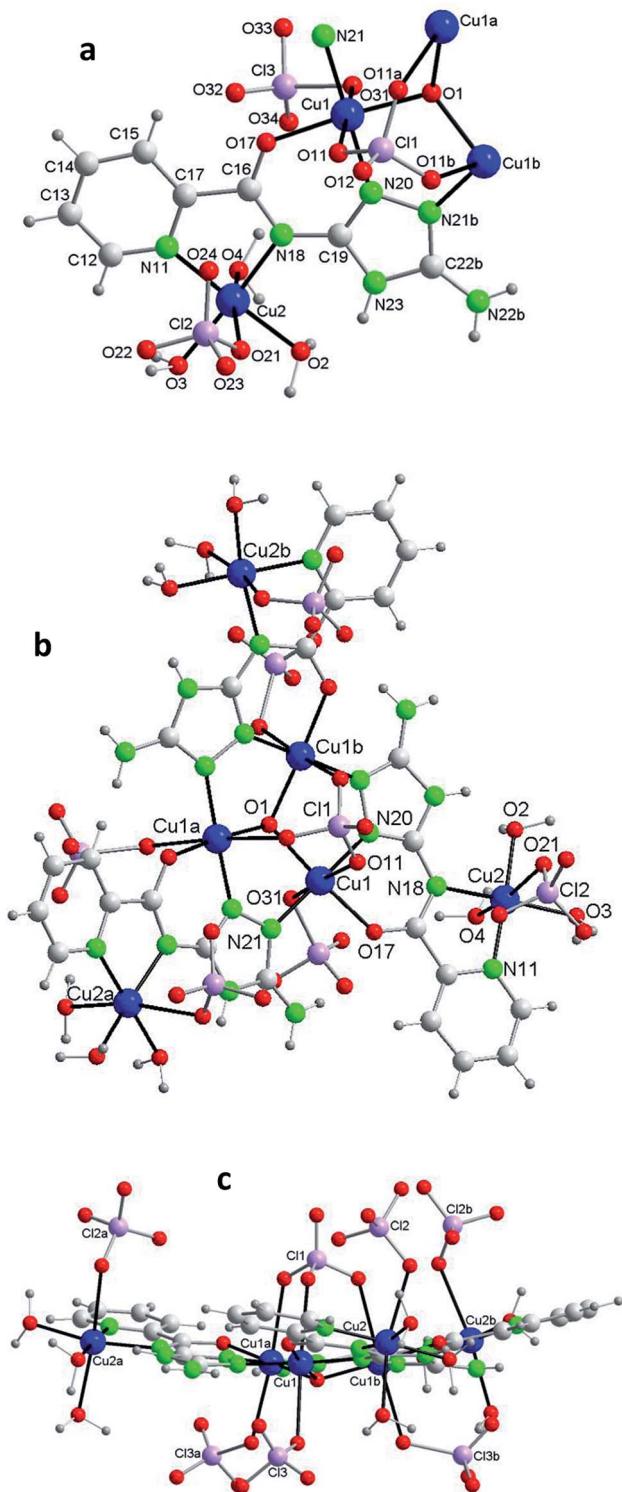


Fig. 1 Compound 1. (a) The asymmetric unit with the labelling [symmetry codes: (a) $-y + 1, x - y + 1, z$; (b) $-x + y, -x + 1, z$]. (b) The hexanuclear compound. (c) The hexanuclear compound (view perpendicular to the c axis). (Water molecules of crystallization omitted for clarity.)

Each of the 3 (HV)⁻ ligands bridges two Cu(II) ions of the Cu₃O group while chelating one of them (bite angle of 86.5(2)^o). Besides, each ligand chelates in *trans* another Cu(II) center, Cu2 (bite angle

of 82.5(2)^o) (Scheme 2, Fig. 1a and b). So, in whole, there are 3 external single Cu(II) atoms (Cu2, Cu2a, Cu2b). This second type of copper center exhibits a very distorted tetragonally octahedral stereochemistry, in which one N-amido, one N-pyridine and two O-water atoms occupy the basal sites and one O-water molecule and one O-perchlorate atom (at 2.47(2) Å) the axial ones.

In the triangular array, the Cu(1)–O(1) distances are of 1.995(3) Å and the Cu(1)–O(1)–Cu(1a) angles of 113.8(2)^o. The central oxygen lies 0.51(1) Å below the plane defined by the three copper atoms. In spite of this deviation of the Cu₃O moiety from planarity, the lack of H-bonding together with the charge balance (and the symmetry of the molecule) lead us to exclude the existence of the central oxygen as OH species (as found in related triangular triazole compounds)^{7,8} instead of O. The intra-triangle Cu1–Cu1 distance, 3.344(2) Å, is in the range observed for related systems.^{7a,8} The Cu1–Cu2 distance is 5.345(2) Å.

A view perpendicular to the c axis shows the {Cu₆(μ_3 -O)(HV)₃} fragment defining a rough plane (Fig. 1c). The hexanuclear unit is chiral although, since in the network there are inversion centers, the bulk solid is racemic (*i.e.* the compound is achiral). Above the plane there are 4 perchlorate anions, three monodentate (towards each of the external Cu(II) centers) and the mentioned tridentate (which bridges the three central Cu(II) atoms); below the plane another 3 monodentate perchlorato ligands complete the octahedral coordination of the three Cu₃O copper atoms. The internal perchlorates together with the axially coordinated water molecules connect one {Cu₆(μ_3 -O)(HV)₃} unit with an upside-down second {Cu₆(μ_3 -O)(HV)₃} unit, of opposite chirality, through H-bonds (Fig. S7†). The O1···O1' distance is 5.208(9) Å. In turn, the external perchlorate anions bind each pair of hexamers with another pair *via* additional H-bonds thus giving chains of pairs of hexanuclear compounds (Fig. S8†).

Crystal structure of [Cu₁₂(μ_3 -O)₂(V)₆(ClO₄)₅(H₂O)₁₈]₂(ClO₄)₃·6H₂O (2). Compound 2 crystallizes in the hexagonal system (Table 1). The unit cell contains 2 cationic [Cu₁₂(μ_3 -O)₂(V)₆(ClO₄)₅(H₂O)₁₂]³⁺ complexes, perchlorate anions and water molecules of crystallization (Fig. 2). Table 2 lists selected distances and angles (full list in S5†). In this case the ligand H₂V is deprotonated both at the N acetamido group and at the triazolato ring (so it is present as V²⁻).

The structure of 2, as that of 1, is based on the hexanuclear {Cu₆(μ_3 -O)(L)₃} block, the main difference between both being that in 2, two hexanuclear units related by one reflection plane (Fig. 2c and S7†) are linked by 3 perchlorate bidentate anions to give a dodecuclear Cu(II) compound (Fig. 2b and d). The O(1)···O(1') distance in 2, of 5.648(18) Å, is somewhat longer than the equivalent O(1)···O(1') distance in paired units of 1 (5.208(9) Å). The deviation of O(1) from the Cu₃ plane is similar (0.52(1) Å). The schematic view of Fig. 2d shows the position of the 8 ClO₄⁻ groups: 2 tridentate external (on a 6-fold axis) and 6 interleaved, 3 of which are bidentate and connect central Cu₃-O atoms from two opposite triangular units, and the other 3 being non-coordinating but contributing to stabilize the dodecuclear species through H-bonds. The 6 enclosed perchlorate anions are placed on a mirror plane which contains the Cl atom and two out of the four O atoms of each perchlorate.

Table 2 Selected bond lengths (Å) and angles (°) for 1–3^{a,b}

	1	2	3
Cu(1)–N(20)	1.909(6)	1.903(6)	1.912(10), 1.910(10), 1.895(10)
Cu(1)–N(21)	1.957(6)	1.947(6)	1.945(10), 1.935(10), 1.955(11)
Cu(1)–O(17)	1.969(6)	1.964(5)	1.968(9), 1.968(9), 1.972(9)
Cu(1)–O(1)	1.995(3)	2.009(3)	1.986(8), 1.994(9), 2.012(8)
Cu(1)–O(31)/O(21)/O(w)	2.501(11)	2.417(7)	2.403(13), 2.385(11), 2.387(17)
Cu(1)–O(11)	2.634(14)	2.506(8)	2.450(12), 2.852(19), 2.546(15)
Cu(1)–Cu(1) ^{#1}	113.8(3)	113.6(2)	114.8(4), 113.1(4), 114.1(4)
Cu(1)–Cu(1) ^{#1}	3.344(2)	3.362(2)	3.335(2), 3.353(2)
O(1)–O(1)'	5.208(9)	5.648(18)	6.816(9)
Cu(2)–O(3)	1.972(8)	1.933(18)AA/2.014(16)BB	1.988(12), 1.965(12), 1.995(11)
Cu(2)–N(11)	1.968(8)	2.009(9)A/1.971(8)B	1.974(12), 1.983(11), 1.960(12)
Cu(2)–O(2)	1.994(8)	2.005(18)AA/2.005(19)BB	1.989(12), 2.003(11), 1.94(15)
Cu(2)–N(18)	2.008(6)	2.011(8)A/2.010(8)B	2.009(11), 2.003(10), 2.007(12)
Cu(2)–O(21)/O(x1)/O(w)	2.470(11)		2.265(18), 2.422(15), 2.258(19)
Cu(2)–O(4)/O(y1)	2.69(3)	2.21(4)AA/2.39(6)BB	2.469(13), 2.456(17), 2.423(14)
Cu(1)–Cu(2)	5.345(2)	5.256(3)A/5.365(3)B	5.361(2), 5.367(2), 5.352(3)
Cu(1)–Cu(1) ^{&3}		6.687(2)	
Cu(1)–Cu(1) ^{&4}		7.485(2)	
Cu(7)–O(77)/Cu(8)–O(103)			1.76(3)/1.88(3)
Cu(7)–N(80)/Cu(8)–N(71)			1.85(3)/1.964(16)
Cu(7)–O(101)/Cu(8)–N(78)			1.94(5)/1.95(3)
Cu(7)–O(102)/Cu(8)–O(104)			2.11(6)/2.00(3)
Cu(7)–O(52)/Cu(8)–O(14)			2.67(2)/2.498(18)
Cu(7)–Cu(8)			5.272(9)

^a For 1: symmetry transformations used to generate equivalent atoms: #1 $-y + 1, x - y + 1, z$, #2 $-x + y, -x + 1, z$. For 2: symmetry transformations used to generate equivalent atoms: &3 $x, y, -z + 1/2$, &4 $-x + y + 1, -x + 1, -z + 1/2$. ^b Labels referred to compound 1 (Fig. 1a and b); for compounds 2 and 3 the distances listed correspond to the equivalent bonds. In italic, labels specific of compound 2; in bold labels specific of compound 3. For complete tables of distances and angles see S4–S6.

A second difference with 1 stands on the lack of any perchlorate on the apical coordination positions of the Cu²⁺ peripheral centers. To be noticed the disorder on these Cu²⁺ atoms (Fig. 2a and S9†). The fragment O(2)–Cu(2)–O(3) of the metal coordination sphere has been assumed to occupy two alternative orientations inclined at an angle of 37(1)° and given an occupancy of 0.5 for each position. Fig. 2b–d display only one out of the two positions for clarity purposes. While the geometry of the central Cu¹⁺ atoms is distorted octahedral, Cu¹(N₂O₂ + O₂) (like in 1), that of the outer Cu²⁺ centers is Cu²⁺(N₂O₂ + O) penta-coordinated. Table 2 compares selected bond angles and distances in the structure of 1 and 2.

A last remarkable feature of the structure of 2 refers to the packing. A view projected on plane ab reveals the existence of wide channels in the network (a 18.631(9) Å void between opposite N4-triazole atoms) (Fig. 2e).

Crystal structure of $\{[\text{Cu}_{14}(\mu_3\text{-OH})_2(\text{V})_6(\text{HV})(\text{ClO}_4)_{11}(\text{H}_2\text{O})_{20} - (\text{ClO}_4)_2 \cdot 14\text{H}_2\text{O}\}_n$ (3). Compound 3 crystallizes in the monoclinic system (Table 1). The intricate structure, a 1D MOF, consists of pairs of hexanuclear units, analogous to those of 1 and 2, linked through polydentate perchlorate anions to dinuclear units formed by two Cu¹⁺ centers *trans*-bridged by one HV[–] ligand, which yield as a whole tetradecanuclear “···Cu₂–(Cu₃O–3Cu)–(Cu₃O–3Cu)–Cu₂···” copper(II) assemblies. The unit cell contains 4 cationic $[\text{Cu}_{14}(\mu_3\text{-O})_2(\text{V})_6(\text{HV})(\text{ClO}_4)_{11}(\text{H}_2\text{O})_{20}]^{2+}$ species, perchlorate anions and guest water molecules (Fig. 3).

and S10†). Table 2 lists selected distances and angles (full list in S6†). In this case the ligand H₂V acts as V^{2–} in the hexanuclear units and as (HV)[–] in the dinuclear ones.

Fig. 3b shows one of those 14Cu species. Fig. 3c and d are alleviated pictures in which water molecules (coordinating/crystallization) and non-coordinating/monodentate perchlorate anions are not displayed to facilitate visualization of the 14Cu centers and the different bridges that connect them (note: Fig. 3b–d contain 14 + 2 Cu).

The 14Cu aggregate contains 8 different (symmetry independent) Cu¹⁺ centers, 9 different (symmetry independent) perchlorate anions and 7 (6V^{2–} + 1(HV)[–]) ligands. Cu1, Cu2, Cu3, Cu4, Cu5 and Cu6, together with 3 ligands and one μ_3 -hidroxo ligand, produce each of the two hexanuclear units, which are symmetry related and of different chirality (see 1 and 2) (Fig. S10†). The 7th (HV)[–] ligand, which acts as *trans*-bichelate, bridges Cu7 and Cu8 to form the dimeric group (Fig. 4). The two hexamers are linked *via* one μ_2 -perchlorato ligand (Cl2) [bonds Cu1–O21(Cl2)O21a–Cu1a], with the O1···O1a distance being 6.816(9) Å, far longer than the equivalent distance in 1 and 2, as expected since in 3 the two hexanuclear units are not properly paired but rather shifted towards each other. One μ_4 -perchlorato ligand (Cl1) which coordinates on apical positions simultaneously Cu1, Cu2 (semi-coordination, 2.852(19) Å, in this case), Cu3 and Cu8 links one hexamer with the dinuclear moiety (Fig. 3a; see also S10†). There is one additional bridge, a second



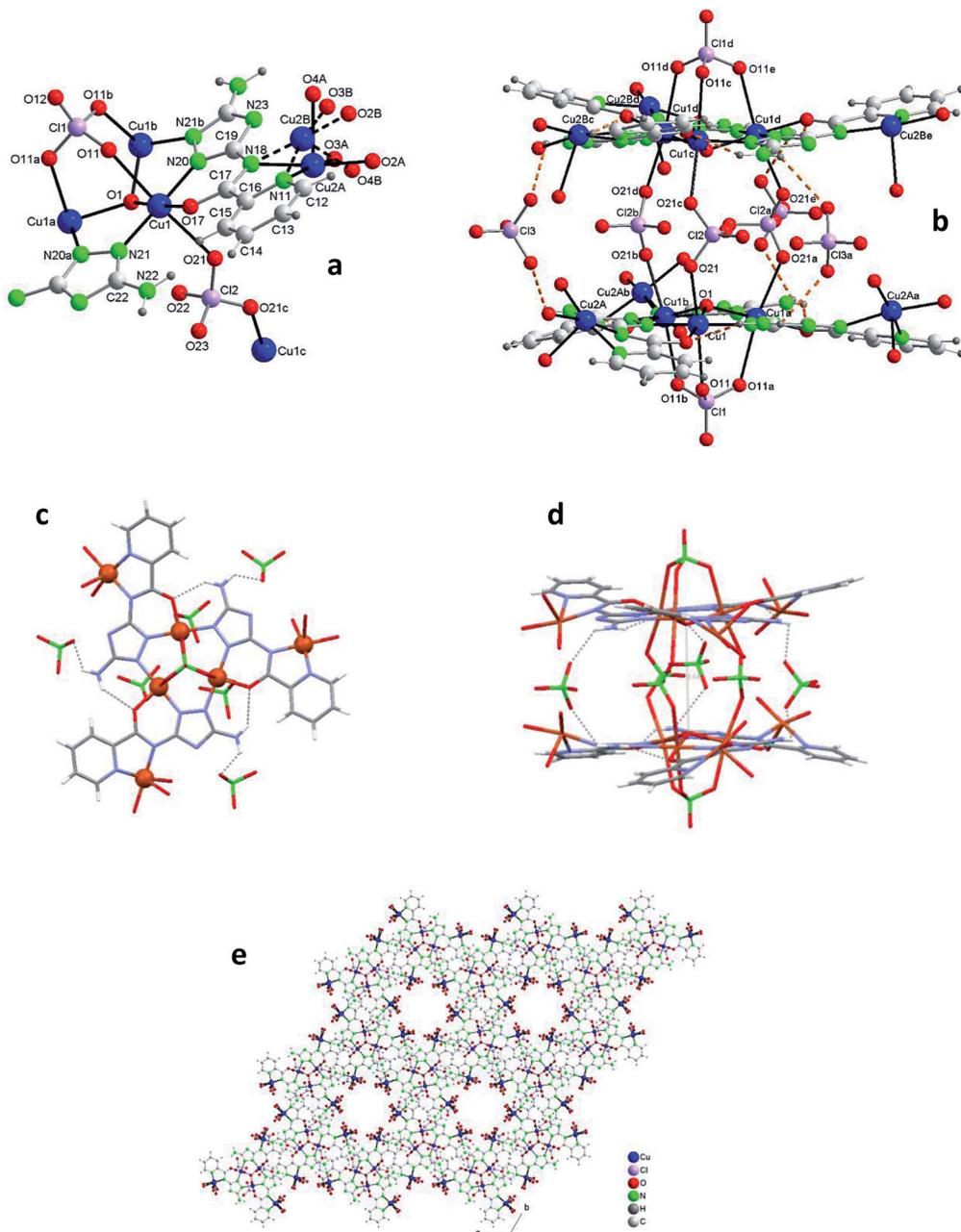


Fig. 2 Compound 2. (a) The asymmetric unit with the labelling and the two alternative orientations for the O(2)–Cu(2)–O(3) fragment [symmetry codes: (a) $-y + 1, x - y, z$; (b) $-x + y + 1, -x + 1, z$ and (c) $x, y, -z + 1/2$]. (b) The dodecanuclear compound (along *a*) (hydrogen bonds shown as orange dashed lines) [symmetry codes: (a) $-y + 1, x - y, z$; (b) $-x + y + 1, -x + 1, z$; (c) $x, y, -z + 1/2$ (d) $-x + y + 1, -x + 1, -z + 1/2$ and (e) $-y + 1, x - y, -z + 1/2$]. (c) Schematic view (projected on plane *ab*) (Cu atoms in red ball; shown selected H-bonds). (d) Schematic view (along *c*) (shown selected H-bonds). (e) Packing (projected on plane *ab*) showing the channels. (Water molecules of crystallization omitted for clarity.)

μ_2 -perchlorato ligand (Cl5) which connects Cu7 with Cu5 [Cu5–O51(Cl5)O52–Cu7]. 4 monodentate perchlorate anions coordinate axially to Cu4 (Cl3, Cl4), Cu5 (Cl6) and Cu6 (Cl7) (Fig. 3c and d). The other 2 perchlorate anions (Cl8 and Cl9) are not coordinating.

The chain grows through (a) another μ_4 -perchlorato ligand (Cl1a) which coordinates the Cu₃-triangular copper centers of the second hexamer (Cu1a, Cu2a, Cu3a), with the Cu8a copper atom of another

dimeric unit (Cu8a, Cu7a), and (b) a new μ_2 -perchlorato ligand (Cl5a) which links Cu5a and Cu7a (Fig. 3b).

In the hexanuclear unit the three ligand planes are visibly deviated from the plane defined by Cu1, Cu2 and Cu3. The large distortion is produced by the polydentate character of the coordinating perchlorate anions. Deviation of the central μ_3 -O1(H) atom toward the triangular Cu₃ plane is 0.498(10) Å (slightly lower than in 1 and 2).

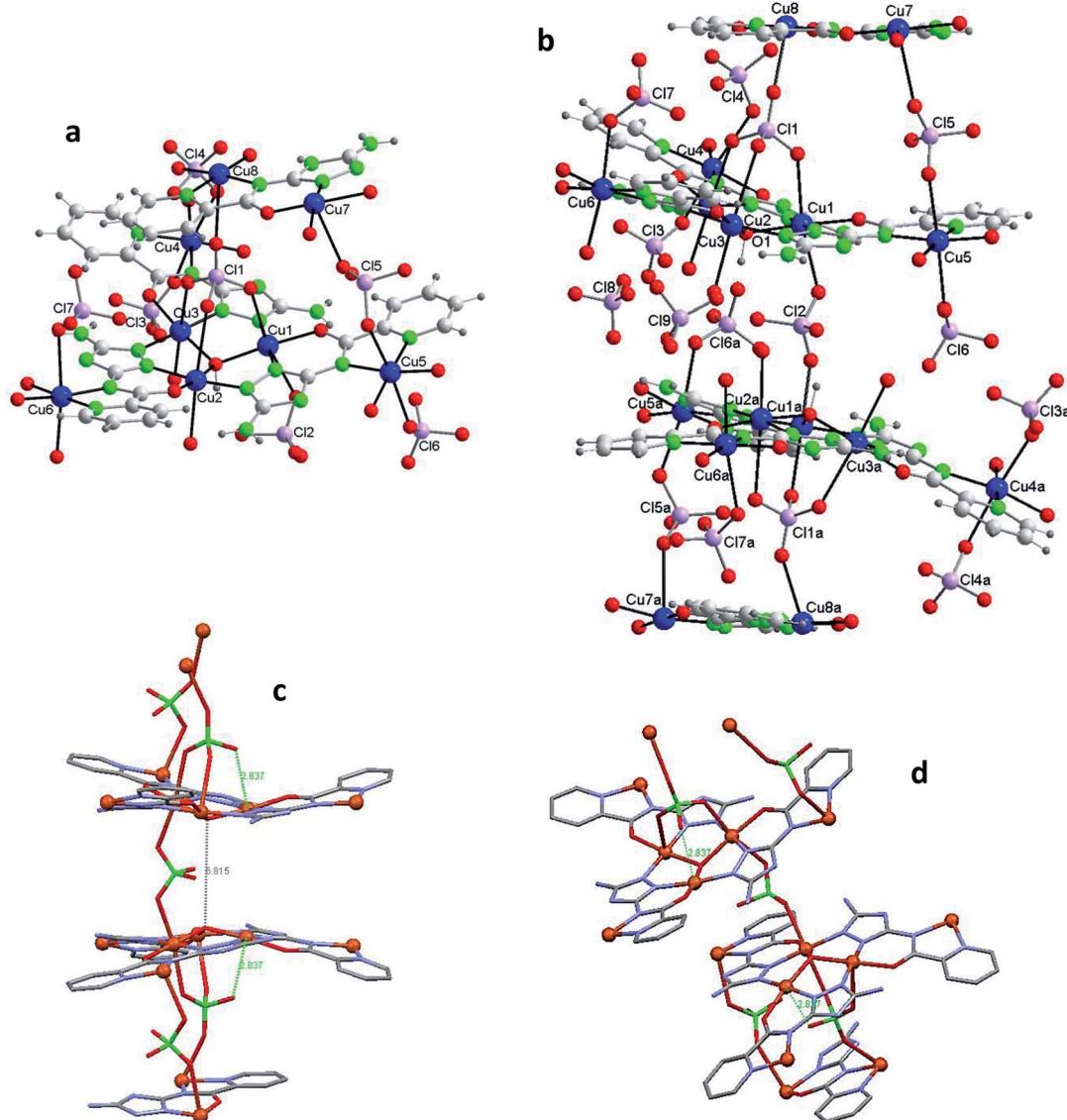


Fig. 3 Compound 3. (a) The asymmetric unit with the labelling (perchlorate anions and water molecules of crystallization omitted for clarity). (b) The tetradeceanuclear compound (along *a*) ($14\text{Cu} + 2\text{Cu}'$ are depicted to show the building of the chain [symmetry code: (a) $-x, y, -z + 1/2$]). (c) Schematic view (along *c*) (Cu atoms in red ball; distances only approx.). (d) Schematic view (approx. along *b*; distances only approx.). (Water molecules of crystallization omitted for clarity.)

As for the coordination geometry of the copper sites, the $6\text{Cu}^{(II)}$ of the hexanuclear arrays display analogous distorted octahedral $\text{N}_2\text{O}_2 + \text{O}_2$ environment but with different ligands on apical positions (Fig. 3b). On axial positions Cu1 presents two polydentate perchlorato ligands; Cu2 and Cu3 one (the) tetradeinate perchlorate anion and one water molecule; Cu4 and Cu5, two perchlorate anions; Cu6 one perchlorate and one water molecule. The $2\text{Cu}^{(II)}$ centers of the dimeric moiety are $\text{NO}_3 + \text{O}$ penta-coordinated (Fig. 4). The basal positions of Cu7 are occupied by the N(triazole) and O(carbonyl) atoms of the ligand, and two O water atoms; the apical ones, by one O perchlorate atom (O52). To end, Cu8 is equatorially coordinated to the N(acetamido) and N(pyridine) atoms of the ligand and to two O water atoms,

and apically to the O14 atom of the Cl1 perchlorate. Bond distances in the coordination polyhedron are listed in Table 2.

Finally to be indicated that in the dimeric unit the $\text{Cu7} \cdots \text{Cu8}$ distance is $5.272(9)$ Å [the average $\text{Cu}(\text{central}) \cdots \text{Cu}(\text{bridged-external})$ distance is $5.360(2)$ Å in the hexanuclear units of 3]. The $\text{Cu8} \cdots \text{Cu8a}$ distance in two consecutive Cu14 units of the chain is $20.387(9)$ Å whereas the $\text{Cu7} \cdots \text{Cu7a}$ distance is $22.117(9)$ Å.

Fig. 5 shows the Cu_3O cores of 1, 2 and 3 with the corresponding coordinating perchlorates (the Cu peripheral centers are not included) to emphasize the different association mediated by the perchlorate anions.

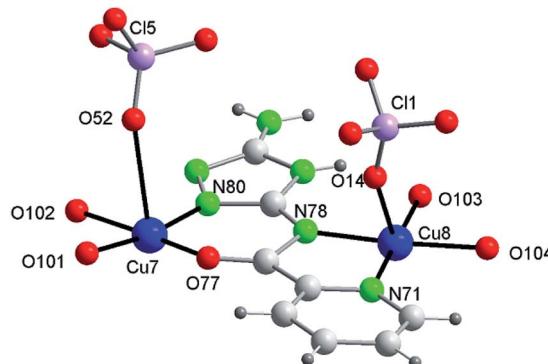


Fig. 4 The dinuclear $[\text{Cu}_2(\text{HV})(\text{ClO}_4)_2(\text{H}_2\text{O})_4]$ fragment of compound 3 with the labelling.

Magnetic studies

The thermal dependence of the $\chi_M T$ product for **1** (χ_M being the magnetic susceptibility per Cu_6 unit) is shown in Fig. 6.

At 300 K the $\chi_M T$ value is $2.05 \text{ cm}^3 \text{ K mol}^{-1}$, which is lower than the value expected for six non-interacting Cu^{II} $S = 1/2$ ions ($\sim 2.4 \text{ cm}^3 \text{ K mol}^{-1}$) with a reasonable g -value.^{2,33} Upon cooling, the $\chi_M T$ product decreases slowly reaching a plateau at $1.75 \text{ cm}^3 \text{ K mol}^{-1}$ between 90 and 60 K. Below ca. 20 K, $\chi_M T$ decreases sharply to achieve a value of $0.70 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K.

From structural analysis (Schemes 2 and 3) this behavior can be rationalized considering two steps. Firstly, the high-temperature region (300–100 K) reveals the presence of a moderate-to-strong antiferromagnetic interaction within the “triangular unit” between the Cu1, Cu2 and Cu3 centers, doubly bridged *via* the central oxo ligand and the peripheral N–N triazolate atoms. This $\{\text{Cu}_3(\mu_3\text{-O}/\text{OH})(\text{N–N})_3\}$ bridging system has already been described as leading to significant antiferromagnetic coupling.^{7–9,33} In previous studies we reported a series of trinuclear compounds of this type built with triazolate ligands which exhibited $\chi_M T$ values of $0.37\text{--}0.40 \text{ cm}^3 \text{ K mol}^{-1}$ in the range 90–60 K.^{7,8} The plateau value of $1.75 \text{ cm}^3 \text{ K mol}^{-1}$ for **1** would roughly correspond to the presence of the Cu_3 triangle plus three almost isolated Cu^{II} additional centers ($0.40 + 1.30$).

Secondly, at lower temperatures (60–2 K), a weaker antiferromagnetic exchange involving the pairs Cu1–Cu4, Cu2–Cu5 and Cu3–Cu6 occurs. This weak antiferromagnetic interaction takes place through the double “NCN + NCO” bridge (Scheme 2), in a *trans*-bridging mode (following literature terminology),³⁴ as observed previously in the “2 + 1 + 1 + 1 + 1” hexanuclear compound $[\text{Cu}_6(\text{HdiV})_2(\text{ClO}_4)_6(\text{H}_2\text{O})_{14}](\text{ClO}_4)_2 \cdot 10\text{H}_2\text{O}$ (**A**).³²

Considering all of these features and the symmetry of the structure (Cu_3 is a perfect triangle) the magnetic data were simulated by means of the following C_3 -symmetric Hamiltonian (eqn 1):²

$$\hat{H} = -J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_3) - j(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_5 + \hat{S}_3\hat{S}_6) + g\beta H \sum_{i=1}^6 \hat{S}_i \quad (1)$$

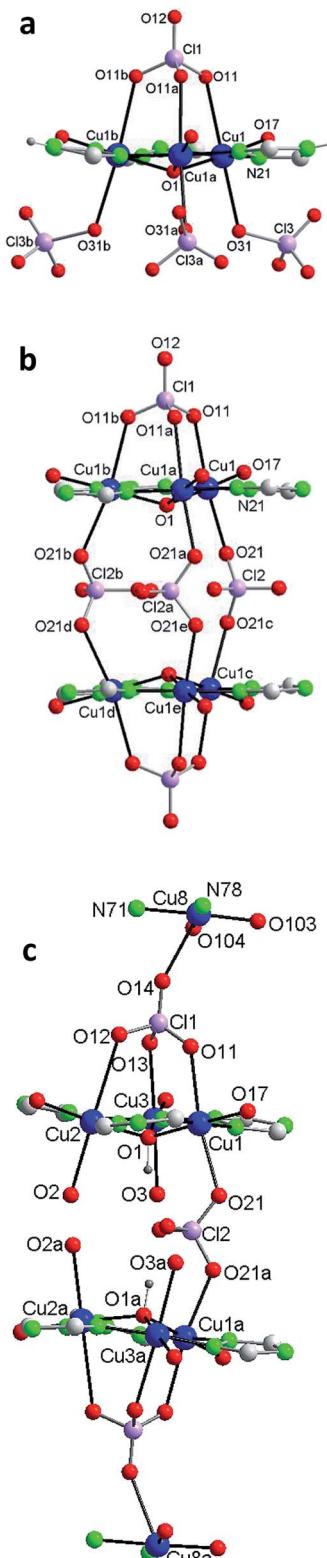


Fig. 5 Detail of the trigonal clusters of Cu atoms in **1** (a), **2** (b) and **3** (c).

Fitting of the magnetic properties of Cu^{II} triangular clusters, example of spin frustrate systems, requires the use of both isotropic and ASE Hamiltonian terms to account for the low temperatures behavior.^{7–9,33} For **1**, however, the experimental



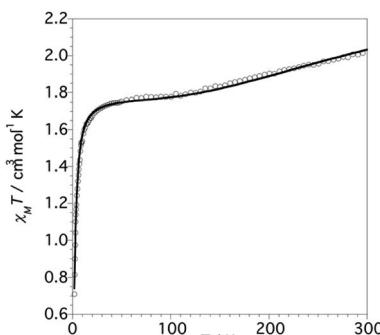


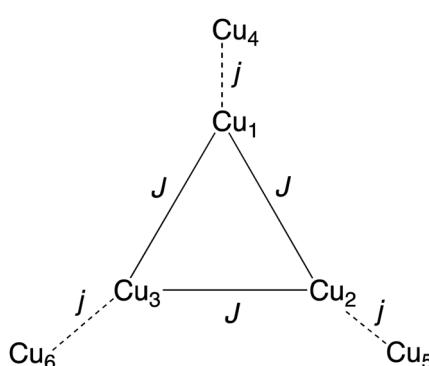
Fig. 6 $\chi_M T$ vs. T plot for complex **1** (values per Cu_6 unit). The solid line corresponds to the best-fit parameters obtained from the Hamiltonian (eqn 1).

data were well reproduced without incorporation of the ASE term into the magneto-chemical analysis. Presumably the ASE is shadowed by the dominant antiferromagnetic interaction within the 3 dimeric Cu(II) units. The resulting best-fit parameters were:

$$g = 2.18(1), J = -247.0(1) \text{ cm}^{-1} \text{ and } j = -5.15(2) \text{ cm}^{-1}.$$

The high symmetry of the structure of **1** must be responsible of the high value of J (-247 cm^{-1}), constant of the AF exchange within the tri-copper triangle, when compared with the values exhibited by the reported analogous triazole trimers ($177\text{--}195 \text{ cm}^{-1}$).⁸ In contrast, the j constant (-5.15 cm^{-1}), corresponding to the AF exchange between the coupled “internal Cu-peripheral Cu” pairs is significantly lower than the one observed for a similar pathway in the hexanuclear compound **A** (-35 cm^{-1}).³² The polydentate character of the perchlorate ligands on axial positions, which induces significant distortion on the equatorial planes of Cu1 (central) and Cu(2) (peripheral), could account for the lower value of j .³⁵

EPR spectra at low T have been recorded in search of the ASE signature. The X-band powder spectrum of **1** at 4 K (Fig. S11†) displays signals at $g_{\parallel} = 2.30$ and $g_{\perp} = 1.61$, the last one being indeed indicative of the existence of ASE ($g < 2.0$).^{8,9}



Scheme 3 The two different antiferromagnetic exchange pathways in the Cu_6 units of **1**.

Conclusions

We have prepared and tested a new simple 1,2,4-triazole ligand, H_2V , capable of yielding with Cu(II) a new building block consisting of hexanuclear Cu(II) clusters with $\text{Cu}_3\text{O}(\text{H})$ core, that is, of the triangular type, but with expanded nuclearity: $\text{Cu}_3\text{O}(\text{H})\text{--}3\text{Cu}$. The hexanuclear units can aggregate in different forms. In the presence of perchlorate anions we have isolated and described three different structures with 6Cu (compound **1**), 12Cu (compound **2**) and 14Cu (compound **3**) of nuclearity. The magnetic properties of the hexanuclear cluster have been studied with **1** and rationalized. Compound **2** combines high nuclearity and a porous 3D structure. Compound **3** is a mixed system (hexanuclear units and dimeric units) in which the dinuclear units link dodecanuclear assembles to afford a one-dimensional coordination polymer. While assemblies of triangular Cu_3O groups have been extensively described the introduction of the $\text{Cu}_3\text{O}\text{--}\text{Cu}_3$ fragment offers a straightforward way to enhance the magnetism of the resulting frameworks/CPs. We plan to explore the possibilities of this hexanuclear Cu(II) scaffold with different anions and anionic linkers.

Conflicts of interest

There are no conflicts to declare.

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