CrystEngComm



View Article Online

PAPER



Cite this: DOI: 10.1039/c7ce01230f

Study of the complex formation between the [Cu(bpca)]⁺ secondary building unit and the aromatic N donors 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) and 1,3-bis(4-pyridyl)propane (bpp)⁺

Eloisa O. Ribeiro,^a Nathália R. de Campos,^a Antônio C. Doriguetto, ¹/₁₀^a Wdeson P. Barros,^b Marcos A. Ribeiro, ¹/₁₀^c Elgte E. B. De Paula,^d Humberto O. Stumpf, ¹/₁₀^e Francesc Lloret,^f Miguel Julve ¹/₁₀^f and Maria V. Marinho ¹/₁₀*^a

Two new complexes of the formula $[{Cu(bpca)}_2(\mu-tppz)](NO_3)_2 \cdot 5H_2O$ (1) and $[Cu(bpca)(H_2O)(ClO_4)(\mu-tppz)](NO_3)_2 \cdot 5H_2O$ (1) and $[Cu(bpca)(H_2O)(ClO_4)(H_2O)(ClO_4)(\mu-tppz)](NO_3)_2 \cdot 5H_2O$ (1) and $[Cu(bpca)(H_2O)(ClO_4)(H_2O)(ClO_4)(H_2O)(ClO_4)(H_2O)(ClO_4)(H_2O)(ClO_4)(H_2O)(ClO_4)(H_2O)(ClO_4)(H_2O)(H_$ bpp)Cu(bpca)(H₂O)₂]ClO₄·H₂O (2) [tppz = 2,3,5,6-tetra(2-pyridyl)pyrazine and bpp = 1,3-bis(4pyridyl)propane] have been prepared by the reaction of the [Cu(bpca)]⁺ [Hbpca = bis(2pyridylcarbonyllimide] building block and the tppz and bpp N donors. An unusual coordination mode of the tppz ligand was observed in 1, which functions as a bis(bidentate) ligand to two copper(II) atoms each coordinated to a nitrogen atom of the pyrazine moiety and a pyridyl nitrogen atom. This compound presents a layered structure of alternating anionic (ca. 1.6 Å) and cationic (ca. 10 Å) slices, providing the opportunity to obtain isomorphic structures by exchanging the counterion, the solvent or both of them. As in 1, each bpca group in 2 is the end-cap ligand being coordinated to the copper(11) ion through its three nitrogen atoms in equatorial positions. The supramolecular layers in 2 are filled by the disordered water molecules and one of the perchlorate groups where the volume occupied by the disordered water can be considered as a void of 91.9 Å³. Additionally, the very weak antiferromagnetic couplings observed in 1 [J = -0.16] and 2 [J = -0.41 cm⁻¹] can be understood by simple orbital symmetry considerations about the type and orientation of the magnetic orbital at each copper(11) ion in both compounds which provide a clear picture of the poor ability of the involved bridges in mediating electronic effects between the paramagnetic centers

Received 5th July 2017, Accepted 12th August 2017

DOI: 10.1039/c7ce01230f

rsc.li/crystengcomm

Introduction

The organic 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpyt) and 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpymt) molecules are very stable

in relation to hydrolysis, with drastic conditions being required for the occurrence of their hydrolytic reaction (temperatures of about 150 °C and the presence of a concentrated mineral acid).¹ However, in the seventies, Lerner and Lippard found that copper(II) salts promote the hydrolysis of both triazines in aqueous solution and under mild conditions to afford the 2-arylformamide molecule and the [bis(2-arylcarbonyl)amido]copper(II) complex [aryl = pyridyl (tpyt) and pyrimidyl (tpymt)].² Later, only two other metal ions have been found to promote this hydrolysis, namely rhodium(III) and cobalt(II) for tpyt and tpymt, respectively.^{3,4} Remarkably, the crystal structures of compounds of the formula $[Cu(bpca)(pca)]X \cdot nH_2O$ [pca = 2-picolinamide and X = $CF_3SO_3^{-}$ (n = 0) and ClO_4^{-} (n = 1)allowed the nature of the two main products of the copper(II)assisted tpyt hydrolysis to be established because both are present as ligands in them.^{5,6} The structures determined by X-ray diffraction of the mononuclear complexes [Cu(bpca)(H₂O)₂]- $NO_3 \cdot 2H_2O_7^7$ [Cu(bpcam)(H₂O)₃]NO₃ \cdot 2H₂O₅² and [Cu(bpcam)- $(H_2O)_2$ ClO₄⁸ [bpca = bis(2-pyridylcarbonyl)amidate and bpcam = bis(2-pyrimidylcarbonyl)amidate] show that the bis(2-

^a Instituto de Química, Universidade Federal de Alfenas, Alfenas, MG 37130-001, Brazil. E-mail: mvmarinho09@gmail.com

^b Instituto de Química, Departamento de Química Inorgânica, Universidade Estadual de Campinas, Campinas, SP 13083-970, Brazil

^c Departamento de Química, Universidade Federal do Espírito Santo, Vitória, ES 29075-910, Brazil

^d Instituto Federal de Educação, Ciência e Tecnologia do Sul de Minas Gerais, Pouso Alegre, MG 37550-000, Brazil

^e Departamento de Química – ICEx, Universidade Federal de Minas Gerais, Belo Horizonte, MG 31270-901, Brazil

^fInstituto de Ciencia Molecular/Departament de Química Inorgànica, Universitat de València, C/Catedrático José Beltrán 2, 46980-Paterna, València, Spain

[†] Electronic supplementary information (ESI) available: XPRD measurements (Fig. S1 and S2), crystallographic tables (Tables S1–S3), TG and DTA curves (Fig. S3), crystallographic drawings (Fig. S4–S9). CCDC 1559171–1559172. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c7ce01230f

arylcarbonyl)amidate ligands coordinate to the copper(π) ion as tridentate ligands, the six- or five coordination at the copper(π) ion being achieved by three or two water molecules, respectively. Based on the fact that these coordination water molecules are easy leaving groups and also the presence of two peripheral carbonyl groups to be used as donors, they have received great attention as building blocks in different synthetic routes to construct di-,^{8,9} tri-¹⁰ tetra-^{10b,11} and hexanuclear¹² species as well as one-dimensional compounds, ^{9i,j,l,10b,12,13} whose structures and magnetic properties were thoroughly investigated.

In the context of these studies concerning the use of the bpca-containing copper(π) complex as a building block in designing polynuclear systems and having in mind the richness and variety of the crystal structures based on pyridyl ligands such as 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) and 1,3-bis(4-pyridyl)propane (bpp),^{14–16} we have explored the possible complex formation between [Cu(bpca)]⁺ and these aromatic N donors (see Scheme 1). The results that we have obtained are presented herein and they concern the preparation, thermal study and structural characterization of two compounds of formula [{Cu(bpca)}₂(μ -tppz)](NO₃)₂·5H₂O (1) and [Cu(bpca)(H₂O)(ClO₄)(μ -bpp)Cu(bpca)(H₂O)₂]ClO₄·H₂O (2) together with the study of their magnetic properties as a function of the temperature.

Experimental

Materials

Copper(II) nitrate trihydrate, tpyt, bpp and ethanol were purchased from commercial sources and used as received. The tppz ligand was prepared according to a previously reported procedure¹⁷ with some modifications: α -pyridoin (10 g, 47 mmol) and ammonium acetate (45 g, 580 mmol) were mixed and slowly heated to 180 °C in an oil-bath with a reflux air condenser. The mixture soon became molten and a very intense brown-green colour developed. The heating was maintained for a further three hours, with occasional shaking. After this time, the mixture was cooled to room temperature. Ethanol was added and the yellow solid formed was collected by filtration. Its recrystallization from a pyridine/ toluene mixture afforded a colourless crystalline solid. M. p. 284 °C. Yield: 30%. IR/cm⁻¹: 3052 [ν (C–H)], 1590, 1568, 1483 [ν (C=C) + ν (C=N)], 1288, 1273 [δ (C–H)_{pyridyl}].

 $[Cu(bpca)(H_2O)_2]NO_3\cdot 2H_2O$ and $[Cu(bpca)]ClO_4$ were prepared according to procedures reported elsewhere^{5,7} as follows: a green coloured suspension was obtained by adding an aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.388 g, 1.6 mmol) or $[Cu(H_2O)_6](ClO_4)_2$ (0.593 g, 1.6 mmol) to an aqueous suspension of tpyt (0.250 g, 0.8 mmol) for $[Cu(bpca)(H_2O)_2]NO_3$ $\cdot 2H_2O$ and $[Cu(bpca)]ClO_4$, respectively. Heating at 100 °C



(1)

(2)

Scheme 1 Schematic representation of the [Cu(bpca)]⁺ building block and its reaction with the tppz and bpp ligands.

with stirring for 30 min yielded a dark blue solution. Evaporation of the solvent at room temperature produced blue polyhedra of $[Cu(bpca)(H_2O)_2]NO_3 \cdot 2H_2O$ and blue needles of $[Cu(bpca)]ClO_4$.

Warning. Perchlorate salts containing organic ligands are potentially explosive. We worked in solution on the mmol scale and the products were obtained by slow evaporation of the mother solutions in a hood at room temperature.

Preparation of the complexes

[{Cu(bpca)}₂(μ-tppz)](NO₃)₂·5H₂O (1). An ethanolic solution (5 ml) of the tppz ligand (0.016 g, 0.035 mmol) was poured into a warm solution (70 °C) of [Cu(bpca)(H₂O)₂]NO₃ ·2H₂O (0.033 g, 0.070 mmol) in water (10 ml). The resulting green mixture was kept under continuous stirring for an hour and a half. Slow evaporation of the solution at room temperature gave blue crystals of 1 suitable for single crystal X-ray diffraction experiments. They were collected on filter paper, washed with a small amount of cold water and dried in the open air. Yield *ca.* 50%. Anal. calc. for C₄₈H₄₂Cu₂N₁₄O₁₅ (1) (%): C, 48.77; H, 3.58; N, 16.59. Found: C, 48.75; H, 3.54 N, 16.50. IR/cm⁻¹: 3406 [ν(O–H)], 3075 [ν(C–H)_{arom}], 1713 [ν(C=O)_{imide}], 1626, 1598, 1476, 1444 [ν(C=C/C=N)_{tppz}], 1381, 1364 [ν(NO₃)], 1297, 1251 [δ(C–H)], 1154 [ν(C–C)], 758, 701, 632 [δ(C–H)].

[Cu(bpca)(H₂O)(ClO₄)(μ-bpp)Cu(bpca)(H₂O)₂]ClO₄·H₂O (2). An ethanolic solution (5 ml) of the bpp ligand (0.010 g, 0.035 mmol) was added to a warm aqueous solution (70 °C, 15 ml) of [Cu(bpca)]ClO₄ (0.040 g, 0.070 mmol). The resulting green mixture was kept under continuous stirring for an hour and a half. Slow evaporation of the solution at 19 °C gave single crystals of 2 as blue-greenish squares. They were collected on filter paper, washed with a small amount of cold water and dried in the open air. Yield *ca.* 75%. Anal. calc. for $C_{37}H_{38}Cl_2Cu_2N_8O_{16}$ (2) (%): C, 42.37; H, 3.65; N, 10.68. Found: C, 42.20; H, 3.60; N, 10.60. IR/cm⁻¹: 3516, 3348 [ν(O-H)], 3106, 3075 [ν(C-H)_{arom.}]; 2940, 2864 [ν(C-H)_{aliph.}]; 1709 [ν(C=O)_{imide}], 1620, 1598, 1572, 1475, 1450 [ν(C=C/C=N)_{bpp}], 1297, 1264 [δ(C-H)], 1159 [ν(C-C)], 1084, 1068, 1049, 1024 [ν(ClO₄)], 755, 706, 618 [δ(C-H)].

Physical measurements

Melting points were determined using a Mettler melting point apparatus (Mettler-Toledo, Leicester, UK) and are uncorrected. IR spectra were recorded on a Thermo Scientific IS50 FT-IR spectrophotometer in the wavenumber range of 4000–400 cm⁻¹ with an average of 144 scans and 4 cm⁻¹ spectral resolution using an attenuated total reflection (ATR) apparatus. Elemental analyses were carried out using a CHNS-O Elemental Analyzer (model Perkin Elmer 2400) (IQ-USP). Thermogravimetry (TG) and differential thermal analysis (DTA) were performed and the results were obtained simultaneously with the same modulus employing a thermobalance (model EXSTAR SII TG/DTA 7000) in the temperature range 35–1100 °C, using alumina crucibles containing samples of approximately 3 mg under a flow of N₂ (100 mL min⁻¹) at a heating rate of 10 °C min⁻¹. The TG/DTA equipment was calibrated using an indium standard for the temperature and an alumina calibration weight for mass. Powder diffraction data were obtained on a powder X-ray diffractometer (model Ultima IV, Rigaku, Japan) using a Cu-K α tube (λ = 1.5418 Å) at a voltage of 40 kV and a current of 30 mA in the 2θ range 5-40°. Magnetic susceptibility measurements were carried out on polycrystalline samples in the temperature range 3.0-300 K using a Quantum Design SQUID susceptometer and using an applied dc magnetic field of 0.1 T. Corrections for the diamagnetism of the constituent atoms by using Pascal's constants were estimated as -586×10^{-6} (1) and $-505 \times$ 10⁻⁶ cm³ mol⁻¹ (2) [per dicopper(II) unit].¹⁸ Corrections for the temperature-independent paramagnetism $[60 \times 10^{-6} \text{ cm}^3]$ mol^{-1} per mol of copper(II) ions] and the sample holder (a plastic bag) were also applied.

X-ray data collection and structure refinement

X-ray crystallographic data for 1 and 2 were collected with a Bruker Apex II Duo diffractometer equipped with a CCD area detector and using Enhance Source Mo-K α radiation (λ = 0.71073 Å) with a graphite monochromator. The values of the temperature for the data collection were 293(2)(1) and 150(2)(2) K. Data integration and scaling of the reflections for compounds 1 and 2 were performed using the ApexII suite. Final unit cell parameters were based on the fitting of all reflection positions. Analytical absorption corrections were performed using Bruker SADABS^{19,20} with a multi-scan procedure and the space group identification was done with XPREP.²¹ The structures of compounds 1 and 2 were solved by direct methods using the SHELXT program.²² The positions of all atoms for each compound could be unambiguously assigned on consecutive difference Fourier maps. Refinements were performed using SHELXL²³ based on F^2 through a full-matrix least-squares routine. All non-hydrogen atoms except those of the disordered water molecules in 2 were refined with anisotropic atomic displacement parameters. Positional disorder observed in 2 for the non-coordinated water molecule was reliably modelled as follows: the disorder was refined over six site occupancy factors with 0.334(3), 0.278(3), 0.111(3), 0.095(3), 0.131(3), and 0.100(6) occupancy for the O16, O17, O18, O19, O20, and O21 positions, respectively. The occupancy factor of the disordered positions was assigned as free variables and a linear restraint (SUMP SHELXL²³ instruction) was applied to them, restraining the sum of six site occupation factors to be equal to 1.00. The same isotropic displacement parameters are used for all disordered positions. The positions of the hydrogen atoms of all the water molecules (except those of the disordered ones in 2 which were neither found nor geometrically positioned) were calculated by the Nardelli method²⁴ and they were included as fixed contributions according to the riding model.²⁴ A summary of the crystal data and refinement conditions for 1 and 2 is given in Table 1. Selected bond lengths and angles are grouped in Table S1 (ESI \dagger) (1) and Table S2 (2) (ESI \dagger) whereas the hydrogen

bonds are listed in Tables S3 (ESI[†]) (1) and Table 2 (2). The Mercury software²⁵ was also used to calculate the X-ray powder diffraction patterns from both the unit cell parameters and the atomic positions obtained from the single crystal structure analysis. Anyway, the experimental and calculated powder X-ray diffraction (PXRD) patterns regarding the two complexes (see Fig. S1 and S2 in the ESI[†]), show a good match, each pattern confirming that the obtained structure from the single crystal is equal to that of the bulk. CCDC-1559171 and 1559172 contain the supplementary crystallographic data for 1 and 2, respectively.

Results and discussion

Synthesis, spectroscopy and thermal characterization

The copper(\mathfrak{n})-assisted hydrolysis of the tpyt molecule in aqueous solution affords the mononuclear $[Cu(bpca)(H_2O)_2]^+$ species which has been used as a building block in the preparation of a great variety of polynuclear copper(\mathfrak{n}) complexes.^{10–13*a,b,d,e*} In fact, the stability of this precursor in solution together with the easy replacement of the coordinated water molecules by better donors such as organic linkers are at the origin of this rewarding synthetic route. Having in mind these characteristics, we have explored the reactivity of the $[Cu(bpca)(H_2O)_2]NO_3 \cdot 2H_2O$ and $[Cu(bpca)]ClO_4$ building blocks *versus* the tppz and bpp nitrogen donors as spacers, the result being the dicopper(\mathfrak{n}) complexes 1 and 2.

The infrared spectra of 1 and 2 exhibit a strong absorption around 1710 cm⁻¹ which is characteristic of the $v(C==O)_{imide}$

Table 1 Crystallographic details for 1 and 2					
Compound	1	2			
Formula	C48H42Cu2N14O15	C37H38Cl2Cu2N8O16			
Formula weight	1182.06	1046.72			
Crystal system	Monoclinic	Triclinic			
Space group	Сс	ΡĪ			
<i>a</i> (Å)	22.185(4)	12.7715(5)			
b (Å)	18.725(4)	13.2527(5)			
<i>c</i> (Å)	23.730(5)	14.5883(5)			
α (°)	90	116.240(1)			
β (°)	102.68(3)	101.360(1)			
γ (°)	90	95.472(1)			
$V(Å^3)$	9618(3)	2124.1(1)			
Z/Z'	4/2	2/1			
Wavelength (Å)	0.71073	0.71073			
<i>T</i> (K)	293(2)	150(2)			
D_{calc} (Mg m ⁻³)	1.633	1.637			
Absorp. coef. (mm^{-1})	0.973	1.209			
F(000)	4848	1068			
Theta range (°)	1.44 to 25.35	1.62 to 29.17			
Reflections collected	127 033	101 800			
Independent reflections	17 639	11 053			
-	$[R_{int} = 0.0959]$	$[R_{int} = 0.0238]$			
Completeness to θ_{\max} (%)	93.3	100.0			
Data/restraints/parameters	17 639/2/1438	11 053/10/617			
Goodness of fit on F^2	1.037	1.043			
$R, \mathrm{w}R[I > 2\sigma(I)]$	0.0438, 0.0834	0.0392, 0.0995			
R, wR (all data)	0.0665, 0.0915	0.0542, 0.1129			
Largest diff. peak and	0.557 and -0.493	1.200 and -0.733			
hole (e $Å^{-3}$)					

Table 2 Hydrogen bonds for **2** (Å, \circ)^{*a,b*}

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D····A)	<d-h-a< th=""></d-h-a<>
O5−H5a···O14 ^{vii}	0.88(1)	1.91(1)	2.782(2)	177(3)
O5-H5b···O3 ^v	0.88(1)	1.88(1)	2.737(2)	166(3)
$014-H14b\cdots02^{i}$	0.87(1)	1.92(1)	2.773(2)	167(3)
014-H140.00000000000000000000000000000000000	0.87(1) 0.88(1)	2.14(2) 2.06(1)	2.830(2) 2.929(4)	135(2) 175(4)
015–H15b…O9 ^{vi}	0.88(1)	2.05(1)	2.920(4)	172(3)

^{*a*} D = donor and A = acceptor. ^{*b*} Symmetry code as in Fig. 8 and 11: (i) -x + 1, -y + 1, -z + 1; (ii) -x + 1, -y - 1, -z; (v) -x + 1, -y + 2, -z + 1; (vi) x, y - 1, z - 1; (vii) x, y + 1, z.

vibration, its presence unambiguously supporting the hydrolysis of the tpyt molecule to afford the bpca ligand.^{2b,5-7} The occurrence of the v(CC/CN) stretching vibrations in the ranges 1638–1450 cm⁻¹ (1) and 1620–1450 cm⁻¹ (2) suggests the coordination of the aromatic nitrogen donors to the copper(π) ion. The broad absorption band in both IR spectra between 3600 and 3200 cm⁻¹ is due to the presence of water molecules involved in an extensive network of hydrogen bonds. Finally, the strong absorptions in the ranges 1389–1351 cm⁻¹ (1) and 1090–1025 cm⁻¹ (2) indicate the presence of nitrate and perchlorate groups, respectively.²⁶ These spectroscopic features for 1 and 2 were confirmed by their X-ray structures (see below).

The results of the thermogravimetric/differential thermal analysis (TG/DTA) studies for compounds 1 and 2 are shown in Fig. S3a and b (ESI[†]), respectively. The TG curve of 1 under a N₂ atmosphere shows a first mass loss in the temperature range of 26-100 °C which has been attributed to the release of five water molecules (observed 7.48%; calculated 7.61%). An endothermic peak is observed at 91 °C in the DTA curve which is attributed to the loss of water molecules. 1 is thermally stable between 100 and 293 °C with three successive weight losses being observed at higher temperatures which are most likely due to the release of two nitrate anions plus the thermal decomposition of the tppz and one mol of the bpca organic ligand (observed 57.09%; calculated 62.48%). The exothermic step in the DTA curve at 334 °C corresponds to them. The heating process continues and an amount of residue, most likely copper(II) oxide, was obtained at 1040 °C.

Two consecutive weight losses were observed for 2 in the temperature range 40–209 °C in good agreement with the crystal structure of the complex, where solvent molecules are present. The TG curve shows weight losses in two steps relative to 6.82% of the total mass which correspond to endothermic processes in the DTA curve at 76 and 209 °C. They are most likely related to the removal of four water molecules (calculated 6.88%). An exothermic event associated to the release of perchlorate anions plus the thermal decomposition of the bpca and bpp ligands (observed 78.39%; calculated 81.17%) can be observed at 323 °C. The heating process continues at high temperature where a small amount of residue can be observed, which was attributed to 2 CuO (observed 15.52%; calculated 15.20%)



Fig. 1 Perspective drawings of the crystallographically independent dicopper(n) units of 1 with partial atom numbering (the whole numbering scheme is shown in Fig. S4, ESI \dagger). The hydrogen atoms involved in the intermolecular C-H…O type interaction (double dashed lines) are represented as arbitrary radius spheres whereas the ellipsoids of the non-hydrogen atoms are at the 50% probability level. The remaining hydrogen atoms, water molecules of crystallization and nitrate counterions were omitted for the sake of clarity.



Fig. 2 (a) An overlaying view of the two dicopper(II) entities present in the asymmetric unit of **1**. (b) A perspective view showing the orientation of the dinuclear units, nitrate counterions and water molecules in relation to the pseudo-inversion symmetry (black dot) identified in the structure. Green dashed lines highlight the units related by the pseudo-inversion symmetry.

Description of the structures

 $[{Cu(bpca)}_2(\mu\text{-tppz})](NO_3)_2 \cdot 5H_2O (1). \ \text{Compound 1 crystal-lizes in the non-centrosymmetric space group Cc with two$



Fig. 3 View of **1** showing the packing of the dinuclear units (cationic layer). The two non-symmetry related dicopper(II) units are distinguished by the colour scheme (blue *vs.* green). Intermolecular copper-copper distances are indicated. Hydrogen atoms, water molecules and nitrate anions were omitted for the sake of clarity.

crystallographically independent dicopper(II) entities (Z' = 2)in the asymmetric unit. A perspective view of the two discrete $[{Cu(bpca)}_2(\mu-tppz)]^{2+}$ dinuclear units that built up the asymmetric unit of 1 are shown in Fig. 1. The asymmetric unit of 1 is completed by four nitrate counterions and ten uncoordinated water molecules (Fig. S4, ESI†). Overlying the two dinuclear units using Mercury²⁵ showed them to be very similar (Fig. 2) and related by an inversion orthogonal transformation with a root mean square deviation of 0.1718 Å between homologous atoms (maximum distance of 0.3930 Å). The pseudo-inversion center relating the two dinuclear units is located at (ca. 0.50, 0.83, 0.53) fractional coordinates (and at equivalent by symmetry positions of the Cc space group) of the unit cell. These facts suggest that the crystal could belong to the centrosymmetric supergroup C2/c (also identified as a potential space group by systematic extinction analysis), with just one dinuclear unit per asymmetric unit. However, trial attempts to solve the structure in C2/c were unsuccessful despite the affine transformation relating the two moieties coinciding with this space group. Closer scrutiny showed this not



Fig. 4 (a) View of the packing of the water molecules and nitrate anions (anionic layer) projected onto the *ab* plane in **1**. The crystallographically independent water/nitrate molecules/anions are distinguished by the colour scheme and highlighted by a dotted circle. (b) View of **1** showing the packing onto the *ac* plane, the cationic (dinuclear units) and anionic (water/nitrate molecules/anions) layers being highlighted. The two crystallographically independent dinuclear units (blue *vs.* green) and the water/nitrate molecules/anions are differentiated by the colour scheme. Least-squares planes through the upper and lower limit of the anionic layer are also shown. The approximate values of the thickness of the cationic and anionic layers are indicated. Hydrogen atoms were omitted for the sake of clarity.

to be the case because part of the hydration water molecules and nitrate anions break the crystallographic inversion symmetry of the C2/c space group (Fig. 2b). The two dinuclear units and two [those containing the N27 and N28 nitrogen atoms (Fig. 2b)] of the four nitrate groups are related by the pseudo-inversion centers present in the structure. On the other hand, the two remaining nitrate anions (those containing the N26 and N29 nitrogen atoms) are not inversion-related groups breaking the crystallographic inversion symmetry that would result in the whole symmetry being consistent with C2/c. Interestingly, two of the ten water molecules present in the structure [those containing the O12 and O16 oxygen atoms (Fig. 2b)] are in the two positions generated from that of the two non-centrosymmetric nitrate anions operating by the pseudo-inversion center. Analyzing the intramolecular structure of the dicopper(π) units, one can see that tppz adopts the bis-bidentate γ coordination mode acting as donor at each side through the pyrazine and one adjacent pyridyl nitrogen atoms (Fig. 1). The four crystallographically independent copper(π) ions (Cu1, Cu2, Cu3 and Cu4) are five-coordinate in distorted square pyramidal surroundings. The values of the trigonality parameter (τ) are 0.06 (Cu1), 0.11 (Cu2), 0.08 (Cu3) and 0.09 (Cu4) (τ is equal to 0 or 1 for ideal square pyramidal or trigonal bipyramidal, respectively).²⁷ A pyridyl nitrogen of the tppz molecule and three nitrogen atoms from a tridentate bpca ligand build the basal plane whereas a pyrazine nitrogen of the tppz fills the apical position in all of them. The basal Cu–N distances vary in the range 1.894(5)–2.013(5) Å (Table S1, ESI†), their values being shorter than the apical Cu–N interactions



Fig. 5 View of **1** projected onto the *ab* plane showing the hydrogen bonds between the cationic and the anionic supramolecular layers. The donor…acceptor separations are highlighted by dotted cyan lines.

[2.329(4), 2.360(5), 2.318(5) and 2.330(4) Å for Cu1–N5, Cu2–N6, Cu3–N17 and Cu4–N19, respectively] as expected due to the Jahn–Teller effect for the copper(n) ion. The copper(n) ions are shifted by 0.129(3) (Cu1), 0.125(3) (Cu2), 0.114(3) (Cu3) and 0.124(3) Å (Cu4) from the mean basal plane towards the apical site. The copper–copper separations within each tppz-bridged dicopper(n) unit are 6.846(2) [Cu1…Cu2] and 6.820(2) Å [Cu3…Cu4].

Dealing with the packing of 1, it is also observed in Fig. 1 that the crystallographically independent dinuclear units are connected by two bifurcated C-H···O type interactions involving the O3, O4, O5 and O6 carbonyl oxygens of the peripheral bpca ligands and the C31 and C56 pyridyl carbon atoms of the bridging tppz ligands atoms as acceptors and donors, respectively. Indeed, additional supramolecular dimerization between adjacent dicopper(π) units occurs along the [100] direction in the same way through O1, O2, O7 and O8 carbonyl oxygens from the bpca ligands and C13 and C79 pyridyl carbon atoms of the bread of the b

bon atoms of the tppz molecules (Fig. S5, ESI[†]). In this way, a supramolecular chain results along the crystallographic a axis with alternation of the shortest intermolecular coppercopper contacts [Cu4···Cu1 = 5.000(2) Å and Cu2···Cu3 = 4.999(2) Å] (Fig. 1). Additional contributions to the stabilization of the pseudo-centrosymmetric entity and consequently to the supramolecular chain along the [100] direction arise from weak π -stacking interactions between the pyridyl rings of the bpca ligands (Fig. S6, ESI[†]). The separation between the least-squares planes through neighbouring bpca rings is ca. 3.3 Å (Fig. S6, ESI⁺). Parallel supramolecular chains growing along the [100] direction are connected by van der Waals forces along the crystallographic b axis generating a supramolecular 2D network (Fig. 3). The shortest intermolecular Cu···Cu distances (···Cu3···Cu1···Cu3··· or ···Cu4···Cu2···Cu4···) along the b axis are twice longer (ca. 9.6 Å) than those (ca. 6.8 and 5.0 Å for the intra- and inter-dinuclear units, respectively) along the crystallographic a axis (Fig. 3). Finally, one can see how the cationic layers containing the dinuclear units (Fig. 3) and the anionic layers containing water/nitrate molecules/anions (Fig. 4a) are stacked along the c axis (Fig. 4b). Therefore, a remarkable feature of this structure is the layered structure alternating anionic (ca. 1.6 Å) and cationic (ca. 10 Å) slices opening the opportunity to obtain isomorphic structures by exchanging the counterion, the solvent or both.

In spite of the considerable number of water molecules of crystallization in the structure of 1 (1:5 dicopper(II) unit to water molar ratio), just one $O_{acceptor} \cdots O_{donnor}$ distance involving the dinuclear units and the water molecules is expected to result in a O-H···O type hydrogen bond. The expected interaction would have the O3 carbonyl-oxygen atom from the bpca as acceptor and the O13 water oxygen atom as do-nor (O3···O13 = 2.890(8) Å) (Fig. 5). However, the final refinement shows that the hydrogen atoms of this water molecule are not positioned towards O3. Indeed, this water molecule



Fig. 6 View of **1** projected onto the *ab* plane showing the network of hydrogen bonds involving the water molecules and the nitrate anions (supramolecular anionic layer). The crystallographically independent water/nitrate molecules/anions are differentiated by the colour scheme as in Fig. 4a. The donor…acceptor separations are highlighted by dotted cyan lines.



Fig. 7 Perspective view of the asymmetric units of **2** with partial atom numbering. The hydrogen atoms of the water molecule are represented as arbitrary radius spheres and the ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. The longer $Cu \cdots O$ interactions are represented as double dashed lines. The hydrogen atoms attached to the carbon atoms and the disordered water molecule of crystallization were omitted for the sake of clarity.

could also be involved in two other hydrogen bonds with another water molecule of crystallization (O14) and the O21 nitrate oxygen [O13...O14 = 2.837(8) Å and O13...O21 = 2.997(9) Å]. A complex network of hydrogen bonds is expected to be formed among the water molecules of crystallization and the nitrate counterions, contributing to the stabilization of the anionic/hydrated layer in the crystal packing (Table S3 (ESI[†]) and Fig. 6). However, the hydrogen bond geometries found in this refinement in terms of donor-H distances and donor-H…acceptor angles could not be the real ones, since it was not possible to find the positions of the hydrogen atoms of the water molecules by Fourier-difference procedures. This limitation is quite probable due to the number of nonhydrogen atoms in the asymmetric unit in addition to the presence of metal atoms. In this way, the positions of the hydrogen atoms of all the water molecules had to be calculated by the Nardelli method.^{24a} Therefore, only the donor…acceptor distances involving oxygen atoms of nitrate (acceptor) and water (either donor or acceptor) close enough to be considered a hydrogen bond are included in Table S3 (ESI⁺).

 $[Cu(bpca)(H_2O)(ClO_4)(\mu-bpp)Cu(bpca)(H_2O)_2]ClO_4 \cdot H_2O$ (2). The structure of 2 is constituted by cationic bpp-bridged dicopper(II) units with end-cap bpca ligands, non-coordinate perchlorate and water molecules of crystallization (Fig. 7). One of the two copper(II) ions (Cu1) achieves six-coordination with two weakly coordinated water molecules in the axial positions. Differently, the six-coordination of Cu2 is completed by a coordinated water molecule and a semicoordinated perchlorate group filling the axial sites. Both basal coordination planes around the copper(II) cations on the dinuclear unit are defined by the three nitrogen donor atoms from each tridentate bpca ligand and one nitrogen atom from bpp that adopts the bis-monodentate coordination mode. The basal

bond distances at Cu1 and Cu2 cover the range 1.942(2)-2.033(3) Å (Table S2, ESI^{\dagger}). The values of the axial Cu1···O_w interactions which are shown as double dashed lines in Fig. 7 are 2.522(3) (Cu1...O15) and 2.674(2) Å (Cu1...O14). In the case of Cu2, the axial interaction with the perchlorate anion $[Cu2\cdots O6 = 2.649(2) \text{ Å}]$ is somewhat longer than that with the water molecule $[Cu2\cdots O5 = 2.369(2) \text{ Å}]$ and it could not be viewed as a coordination bond.²⁸ This being so, the environment at Cu1 could be considered as distorted square planar (see N-Cu-N and N-Cu-O angles in Table S2, ESI†), while Cu2 would exhibit a distorted square pyramidal geometry ($\tau = 0.27$), the apical position occupied by the O5 water molecule. This markedly longer apical Cu-O distance was also observed in the mononuclear complex [Cu(bpca)(Phpr)- (H_2O)]·3/2H₂O with Phpr = 3-phenylpropionate [Cu(1)–O(1W) = 2.365(2) Å].^{10b} The two [Cu(bpca)]⁻ units in 2 are connected through the bpp ligand which adopts a TG conformation (where T = *trans* and G = *gauche*) with a value for the N···N distance of 9.071(3) Å in agreement with the definition of Carlucci et al. about the different conformations that can be reached by using this ligand in its polymeric structures [N…N values in the ranges 9.1-10.1, 8.6-9.2, 3.9-5.3 and 6.7-8.6 Å for TT, TG, GG and GG' conformations, respectively.^{16b,d} The Cu1…Cu2 separation across the bpp bridge is 12.396(1) Å.

Looking at the crystal packing of 2, a centrosymmetric supramolecular dimer stabilized by hydrogen bonds involving one of the water molecules (O14) as donor and two bpcaoxygen atoms ($O2^{ii}$ and $O4^{i}$) as acceptors (Fig. 8a and Table S2, ESI†) is present as the main building block. The supramolecular dimers are interconnected by translational symmetry, once again having O14 as hydrogen donor (O14–H14a) and the bpca-oxygen O4 as acceptor, generating a supramolecular







(b)

Fig. 8 (a) Perspective view of a fragment of the supramolecular double chain in 2 running parallel to the [021] direction. (b) A view of the interconnection between the supramolecular double chains in 2 along the crystallographic *c* axis. The hydrogen atoms involved in the intermolecular hydrogen bonds (double dashed lines) are represented as arbitrary radius spheres and the thermal ellipsoids of the non-hydrogen atoms are at the 50% probability level. The remaining hydrogen atoms, the disordered water molecule, and one of the perchlorate counterions were omitted for the sake of clarity [symmetry code as in Table 2: (i) -x + 1, -y + 1, -z + 1; (ii) -x + 1, -y - 1, -z; (iii) x, y - 2, z - 1; (iv) -x + 1, -y, -z; (v) -x + 1, -y + 2, -z + 1; (vi) x, y - 1, z - 1; (vii) x, y + 1, z].

double chain along the [021] direction (Fig. 8a, Table S2, ESI†). Parallel double chains are also interlinked along the crystallographic *c* axis through intermolecular hydrogen bonds by means of two water molecules (O5 and O15) as donors [O5 has either O3^v (bpca-oxygen atom) or O14^{vii} (water oxygen) as acceptors, whereas O9^{vi} (perchlorate oxygen atom) is the acceptor of O15 (see Fig. 8b and Table S2, ESI†)]. This leads to a supramolecular 2D network parallel to the (100) plane depicting a wavy periodicity of the dicopper(II) cations within the double chains along the [021] direction (Fig. 9a). It is important to note that this packing defines the shortest intermolecular copper–copper separation (values in the range 6.777–8.388 Å) (Fig. 9b).

The stacking of these supramolecular layers along the crystallographic *a* axis gives rise to channels parallel to the [021] direction which are filled by the disordered water molecules and one of the perchlorate groups (C11) [see Fig. 10 and S7 (ESI[†])]. These channels are also arranged in a layered structure parallel to the (100) plane alternating with the layers of the bpp-bridged dicopper(π) cations (Fig. S8,

ESI†). It is observed that each disordered water molecule moiety is surrounded by six perchlorate anions in a hexagonal arrangement (Fig. S8, ESI†). In fact, the volume occupied by the disordered water can be considered as a void, which is defined as empty space in the unit cell that is large enough to hold a spherical "probe" of the given radius.²⁵ The void volume occupied by the disordered water molecules is 91.9 Å³ (about 4.3% of the unit cell of 2 calculated using the contact surface approach with grid spacing and a probing-sphere radius of 0.7 and 1.1 Å, respectively) (Fig. S9, ESI†). Fig. 11 shows that the disordered water molecule and the perchlorate anion contribute to the packing through intermolecular hydrogen bonds involving hydrogen bond acceptors/donors (O3, O5 and O15) of the dicopper(n) unit (see also Table 2).

Magnetic properties

The magnetic properties of 1 and 2 in the form of a $\chi_M T$ product *versus T* plot [χ_M being the magnetic susceptibility







Fig. 9 (a) View of 2 projected onto the bc plane highlighting the wavy-shape of the supramolecular double chains along the [021] direction that generates the 2D network parallel to the (100) plane. Molecules related by inversion symmetry are differentiated by the colour scheme (magenta vs. cyan). The hydrogen atoms, disordered water molecules and one of the perchlorate counterions were omitted for the sake of clarity. (b) Intraand intermolecular copper-copper distances in 2 where only the copper(u) ions are shown.

per dicopper(II) unit] are shown in Fig. 12. At room temperature, $\chi_{\rm M}T$ for 1 and 2 is equal to 0.83 cm³ mol⁻¹ K, a value which is as expected for two magnetically isolated spin doublets ($S_{Cu} = 1/2$) with g = 2.10. Upon cooling, $\chi_M T$ remains constant until 40 K and further decreases very slightly to attain values of 0.81 (1) and 0.80 $\text{cm}^3 \text{ mol}^{-1}$ K (2) at 3.0 K. This behaviour is typical of a very weak antiferromagnetic interaction between the copper(π) ions.

Given the dinuclear structure of 1 and 2, we analysed their magnetic data through a simple Bleaney-Bowers expression for a dicopper(π) unit [eqn (1)]²⁹

$$\chi_{\rm M} = (2N\beta^2 g^2/kT)/[3 + \exp(-J/kT)]$$
(1)

the spin Hamiltonian being defined by eqn (2)

$$\boldsymbol{H} = -J\boldsymbol{S}_{1}\cdot\boldsymbol{S}_{2} + g\beta H(\boldsymbol{S}_{1} + \boldsymbol{S}_{2})$$
(2)

where J is the magnetic coupling parameter, g is the average Landé factor of the copper(II) ions and N, β and k have their usual meanings. Least-squares best-fit parameters are J =



Fig. 10 View of 2 showing the stacking of layers along the crystallographic a axis as well as the channel structure filled by the disordered water molecules (in red) and one of the perchlorate counterions (in blue). Hydrogen atoms were omitted for the sake of clarity.



Fig. 11 A view of **2** projected onto the *ab* plane showing the hydrogen bond network involving water molecules and perchlorate anions (anionic layer). The crystallographically independent water/perchlorate molecules/anions are differentiated by the colour scheme as in Fig. S7a (ESI \dagger). The donor…acceptor interactions are highlighted by dotted cyan lines [symmetry code as in Table 2: (vi) x, y – 1, z – 1].

-0.16 (1) and -0.41 cm⁻¹ (2) and g = 2.10 (1 and 2) with $R = 6.7 \times 10^{-6}$ (1) and 4.5×10^{-6} (2), R being the agreement factor defined as $\sum_i [(\chi_M T)_{obs}(i) - (\chi_M T)_{calcd}(i)]^2 / \sum_i [(\chi_M T)_{obs}(i)]^2$.

The very weak antiferromagnetic couplings observed in 1 and 2 can be understood by simple orbital symmetry considerations about the type and orientation of the magnetic orbital at each copper(n) ion in 1 and 2 which provide a clear picture of the poor ability of the involved bridges in mediating electronic effects between the paramagnetic centers. In the case of compound 1, the unpaired electron at each copper(n) ion is delocalized in the basal plane of the square pyramid $[d(x^2-y^2)$ type magnetic orbital], the spin density on the apical position (N5, N6, N17 and N19 at Cu1, Cu2, Cu3 and Cu4, respectively) being very small. Consequently, the overlap between the two magnetic orbitals of each dicopper(n) unit by this axial pathway across the pyrazine ring of the tppz bridge is expected to be very poor and then the magnetic coupling



Fig. 12 $\chi_M T$ vs. T plot for 1 (blue circles) and 2 (green squares). Best-fit curves through eqn (1) (see text) are shown as solid lines.

would be negligible.³⁰ Previous studies of tppz-containing dicopper(II) complexes, where the tppz adopts the bistridentate coordination mode with the exchange pathway involving equatorial bonds at the copper(II) ions, showed values of -J in the range 20–61 cm⁻¹.^{14*a*-*h*} The bis-bidentate bridging mode of the tppz in 1 connecting apical positions of the copper(II) ions through the pyrazine ring accounts for its poorer ability to mediate magnetic interactions in this compound. As far as compound 2 is concerned, although the possible intramolecular exchange pathway involves the equatorial Cu1-N4 and Cu2-N5 bonds (the unpaired electron at each copper(II) ion being delocalized in the equatorial plane), the great distance between the copper(II) ions through the extended bpp ligand (ca. 12.4 Å) allows one to predict a very weak intramolecular magnetic interaction, if any. Finally, the small magnetic couplings observed for 1 and 2 have to be considered as the higher ones for the intramolecular magnetic interaction, the values of the shortest intermolecular coppercopper separation [ca. 5.0 (1) and 6.8 Å (2)] being shorter than those of the intramolecular ones [ca. 6.8 (1) and 12.4 Å (2)].

Conclusions

In summary, we have reported the synthesis and spectroscopic, thermal, structural and magnetic characterization of two new copper(II) compounds. Our synthetic strategy is based on the simultaneous use of the [bis(2pyridylcarbonyl)amido]copper(II) metalloligand and tppz and bpp as spacers to provide the dicopper(II) compounds [{Cu(bpca)}₂(μ -tppz)](NO₃)₂·5H₂O (1) and [Cu(bpca)(H₂O)-(ClO₄)(μ -bpp)Cu(bpca)(H₂O)₂]ClO₄·H₂O (2). Two crystallographically independent tppz-bridged dicopper(II) units occur in 1 with values of the copper–copper separation across the bis-bidentate tppz ligand of 6.846(2) (Cu1/Cu2) and 6.820(2) Å (Cu3/Cu4). They are interconnected by non-classical hydrogen bonds and additional weak π - π type stacking interactions contributing to the stabilization of the structure. A

remarkable feature of the structure of 1 is its supramolecular layered structure alternating anionic (ca. 1.6 Å) and cationic (ca. 10 Å) slices opening the opportunity to obtain isomorphic structures by exchanging the counterion, the solvent or both. The structure of 2 consists of bpp-bridged dicopper(II) units where the bis-monodentate bpp ligand adopts a TG conformation (T = trans and G = gauche), the intramolecular copper-copper distance being 12.3957(6) Å. An extensive network of hydrogen bonds involving the coordinated water and some of the crystallization water molecules, the carbonyl oxygen atoms of the bpca ligand and one oxygen atom of the coordinated perchlorate leads to a supramolecular 2D network in 2, with the disordered water molecules and the noncoordinated perchlorate being located in the interlayer voids. Thermal studies of 1 revealed the loss of five water molecules up to 91 °C, the anhydrous phase being stable between 100 and 293 °C, while in 2, the loss of the crystallization and coordinated water molecules occurred in two steps at 40 and 209 °C, and the resulting anhydrous phase is stable in the temperature range 194-255 °C. Very weak antiferromagnetic couplings are observed in 1 and 2 through the bis-bidentate tppz and bis-monodentate bpp bridges, these spacers appearing as very poor mediators of magnetic interactions between the copper(II) ions linked by them.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the Brazilian agencies CAPES (AUXPE -PNPD 2347/2011), CNPq (48723/2014-0 and 308162/2015-3), FINEP (Ref. 134/08), and FAPEMIG (Projects APQ-00273-14 and PPM-00533-16) and the Spanish agencies Ministerio Español de Economía y Competitividad (Projects CTQ2013-44844P and CTQ2016-75068P) and Unidad de Excelencia María de Maetzu (Project MDM-2015-0538) for financial support. We also thank CNPq (H. O. S and A. C. D.) and FAPEMIG (N. R. C.) for research fellowships. This work is a collaboration research project of members (ACD and MVM) of the Rede Mineira de Química (RQ-MG) supported by FAPEMIG (Project: CEX – RED-00010-14). W. P. B. acknowledges the FAPESP (2015/22379-7).

References

- 1 E. M. Smolin and L. Rapoport, *S-Triazines and Derivatives*, Interscience, New York, 1959, p. 163.
- 2 (a) E. I. Lerner and S. J. Lippard, J. Am. Chem. Soc., 1976, 98, 5397; (b) E. I. Lerner and S. J. Lippard, Inorg. Chem., 1977, 16, 1537.
- 3 (a) P. Paul, B. Tyagi, M. M. Bhadbhade and E. Suresh, J. Chem. Soc., Dalton Trans., 1997, 2273; (b) P. Paul, B. Tyagi,
 A. Bilakhiya, M. M. Bhadbhade, E. Suresh and G. Ramachandraiah, Inorg. Chem., 1998, 37, 5733; (c) P. Paul, B. Tyagi, A. K. Bilakhiya, M. M. Bhadhade and E. Suresh, J. Chem. Soc., Dalton Trans., 1999, 2009.

- 4 D. A. Safin, P. M. J. Szell, A. Keller, I. Korobkov, D. L. Bryce and M. Murugessu, *New J. Chem.*, 2015, **39**, 7147.
- 5 A. Cantarero, J. M. Amigó, J. Faus, M. Julve and T. Debaerdemaeker, *J. Chem. Soc., Dalton Trans.*, 1988, 2033.
- 6 J. Faus, M. Julve, J. M. Amigó and T. Debaerdemaeker, *J. Chem. Soc., Dalton Trans.*, 1989, 1681.
- 7 I. Castro, J. Faus, M. Julve, J. M. Amigó, J. Sletten and T. Debaerdemaeker, *J. Chem. Soc., Dalton Trans.*, 1990, 891.
- 8 D. C. de Castro Gomes, H. O. Stumpf, F. Lloret, M. Julve, V. González, H. Adams and J. A. Thomas, *Inorg. Chim. Acta*, 2005, 358, 1113.
- 9 (a) I. Castro, J. Faus, M. Julve, M. Mollar, A. Monge and E. Gutiérrez-Puebla, Inorg. Chim. Acta, 1989, 161, 97; (b) I. Castro, J. Faus, M. Julve, Y. Journaux and J. Sletten, J. Chem. Soc., Dalton Trans., 1991, 2533; (c) I. Castro, J. Sletten, J. Faus, M. Julve, Y. Journaux, F. Lloret and S. Alvarez, Inorg. Chem., 1992, 31, 1889; (d) I. Castro, M. L. Calatayud, J. Sletten, F. Lloret, J. Cano, M. Julve, G. Seitz and K. Mann, Inorg. Chem., 1999, 38, 4680; (e) M. L. Calatayud, I. Castro, J. Sletten, F. Lloret and M. Julve, Inorg. Chim. Acta, 2000, 300-302, 846; (f) B. Vangdal, J. Carranza, F. Lloret, M. Julve and J. Sletten, J. Chem. Soc., Dalton Trans., 2002, 566; (g) R. Lescouëzec, G. Marinescu, J. Vaissermann, F. Lloret, J. Faus, M. Andruh and M. Julve, Inorg. Chim. Acta, 2003, 350, 131; (h) D. Cangussu, H. O. Stumpf, H. Adams, J. A. Thomas, F. Lloret and M. Julve, Inorg. Chim. Acta, 2005, 358, 2292; (i) D. Cangussu, L. M. Toma, H. O. Stumpf, H. Adams, J. A. Thomas, F. Lloret and M. Julve, Polyhedron, 2008, 27, 559; (j) I. Carlucci, G. Ciani, S. Maggini, D. M. Proserpio, R. Sessoli and F. Totti, Inorg. Chim. Acta, 2011, 376, 538; (k) W. Wu, W.-J. Pan and Y.-Q. Zheng, J. Coord. Chem., 2013, 66, 4415; (l) W. X. C. Oliveira, C. B. Pinheiro, M. M. da Costa, A. P. S. Fontes, W. C. Nunes, F. Lloret, M. Julve and C. L. M. Pereira, Cryst. Growth Des., 2016, 16, 4094.
- (a) J. Sletten, M. Julve, F. Lloret, I. Castro, G. Seitz and K. Mann, *Inorg. Chim. Acta*, 1996, 250, 219; (b) T. R. G. Simões, R. V. Mambrini, D. O. Reis, M. V. Marinho, M. A. Ribeiro, C. B. Pinheiro, J. Ferrando-Soria, M. Déniz, C. Ruiz-Pérez, D. Cangussu, H. O. Stumpf, F. Lloret and M. Julve, *Dalton Trans.*, 2013, 42, 5778.
- L. M. Toma, R. Lescouëzec, D. Cangussu, R. Llusar, J. Mata, S. Spey, J. A. Thomas, F. Lloret and M. Julve, *Inorg. Chem. Commun.*, 2005, 8, 382.
- W. X. C. Oliveira, M. A. Ribeiro, C. B. Pinheiro, M. M. da Costa, A. P. S. Fontes, W. C. Nunes, D. Cangussu, M. Julve, H. O. Stumpf and C. L. M. Pereira, *Cryst. Growth Des.*, 2015, 15, 1325.
- (a) J. V. Folgado, E. Coronado, D. Beltrán-Porter, R. Burriel, A. Fuertes and C. Miratvilles, J. Chem. Soc., Dalton Trans., 1988, 3041; (b) H. Casellas, F. Costantino, A. Mandonnet, A. Caneschi and D. Gatteschi, Inorg. Chim. Acta, 2005, 358, 177; (c) C. Yuste, D. Cangussu, H. Adams, J. A. Thomas, F. Lloret and M. Julve, Polyhedron, 2008, 27, 2577; (d) P. Halder, E. Zangrando and T. K. Paine, Polyhedron, 2010, 29, 434; (e) K. Abdi, H. Hadadzadeh, M. Weil and H. A. Rudbari, Polyhedron, 2014, 416, 109.

- 14 (a) M. Graf, B. Greaves and H. Stoeckli-Evans, Inorg. Chim. Acta, 1993, 204, 239; (b) M. Graf, H. Stoeckli-Evans, A. Escuer and R. Vicente, Inorg. Chim. Acta, 1997, 257, 89; (c) J. Carranza, C. Brennan, J. Sletten, J. M. Clemente-Juan, F. Lloret and M. Julve, Inorg. Chem., 2003, 42, 8716; (d) J. Carranza, J. Sletten, C. Brennan, F. Lloret, J. Cano and M. Julve, Dalton Trans., 2004, 3997; (e) H. Hadadzadeh, A. R. Rezvani, G. P. A. Yap and R. J. Crutchley, Inorg. Chim. Acta, 2005, 358, 1289; (f) G.-Y. Hsu, C.-W. Chen, S.-C. Cheng, S.-H. Lin, H.-H. Wei and C.-J. Lee, Polyhedron, 2005, 24, 487; (g) C. Yuste, D. Armentano, N. Marino, L. Cañadillas-Delgado, F. S. Delgado, C. Ruiz-Pérez, D. P. Rillema, F. Lloret and M. Julve, Dalton Trans., 2008, 1583; (h) C. Yuste, L. Cañadillas-Delgado, C. Ruiz-Pérez, F. Lloret and M. Julve, Dalton Trans., 2010, 39, 167; (i) B. Machura, A. Switlicka, J. Palion and R. Kruszynski, Struct. Chem., 2013, 24, 89.
- 15 (a) C. S. Campos-Fernández, B. W. Smucker, R. Clérac and K. R. Dunbar, Isr. J. Chem., 2001, 41, 207; (b) J. Yuasa and S. Fukuzumi, J. Am. Chem. Soc., 2006, 128, 15976; (c) L. M. Toma, D. Armentano, G. De Munno, J. Sletten, F. Lloret and M. Julve, Polyhedron, 2007, 26, 5263; (d) J. Yuasa and S. Fukuzumi, J. Am. Chem. Soc., 2008, 130, 566; (e) M. Trivedi, D. S. Pandey and N. P. Rath, Inorg. Chim. Acta, 2009, 362, 284; (f) L. M. Callejo, G. Madariaga, L. Lezama, L. Fidalgo, N. De la Pinta and R. Cortés, Inorg. Chem., 2010, 49, 5355; (g) J. Luo, L. Qiu, B. Liu, X. Zhang, F. Yang and L. Cui, Chin. I. Chem., 2012, 30, 522; (h) F. H. Haghighi, H. Hadadzadeh, F. Darabi, Z. Jannesari, M. Ebrahimi, T. Khayamian, M. Salimi and H. A. Rudbari, Polyhedron, 2013, 65, 16; (i) B. Machura, J. Palion, J. Mrozinski, B. Kalinska, M. Amini, M. M. Najafpour and R. Kruszynski, Polyhedron, 2013, 53, 132; (*j*) J. Palion-Gazda, A. Switlicka-Olszewska, B. Machura, T. Grancha, E. Pardo, F. Lloret and M. Julve, Inorg. Chem., 2014, 53, 10009; (k) S. Demir, M. Nippe, M. I. González and J. R. Long, Chem. Sci., 2014, 5, 4701; (1) R. Davidson, J.-H. Liang, D. C. Milan, B.-W. Mao, R. J. Nichols, S. J. Higgings, D. S. Yufit, A. Beeby and P. J. Low, Inorg. Chem., 2015, 54, 5487.
- (a) Y.-B. Dong, M. D. Smith, R. C. Layland and H. C. zur Loye, *Inorg. Chem.*, 1999, 38, 5027; (b) M. V. Marinho, M. I. Yoshida, K. J. Guedes, K. Kambrock, A. J. Bortoluzzi, M. Hörner, F. C. Machado and W. M. Teles, *Inorg. Chem.*, 2004, 43, 1539; (c) X.-Q. Wang, K.-K. Cheng, Y.-H. Wen, J. Zhang, Z.-J. Li and Y.-G. Yao, *Inorg. Chem. Commun.*, 2005, 8, 897; (d) C. C. Corrêa, R. Diniz, L. H. Chagas, B. L. Rodrigues, M. I. Yoshida, W. M. Teles, F. C. Machado and L. F. C. de Oliveira, *Polyhedron*, 2007, 26, 989; (e) G. Marinescu, G. Marin, A. M. Madalan, A. Vezeanu, C. Tiseanu and M. Andruh, *Cryst. Growth Des.*, 2010, 10, 2096; (f) C. C. Corrêa, R. Diniz, J. Janczak, M. I. Yoshida, L. F. C. de Oliveira and F. C. Machado, *Polyhedron*, 2010, 29, 3125; (g) G.-G. Luo, H.-B. Xiong and J.-C. Dai, *Cryst. Growth Des.*,

2011, 11, 507; (h) E. E. B. de Paula, L. C. Visentin, M. I. Yoshida, F. F. C. De Oliveira and F. C. Machado, Polyhedron, 2011, 30, 213; (i) A. Kondo, T. Satomi, K. Azuma, R. Takeda and K. Maeda, Dalton Trans., 2015, 44, 12717; (j) T.-T. Fan, J.-J. Li, X.-L. Qu, H.-L. Han and X. Li, CrystEngComm, 2015, 17, 9443; (k) A. J. Hernádez-Maldonado, R. R. Arrieta-Pérez, J. N. Primera-Pedrozo and J. Exley, Cryst. Growth Des., 2015, 15, 4123; (l) M. V. Marinho, L. F. Marques, D. S. Maia, N. L. Speziali, M. I. Yoshida, J. Janczak, M. Hörner, C. C. Corrêa, R. Diniz and F. C. Machado, Z. Anorg. Allg. Chem., 2015, 641, 2333; (m) N. R. de Campos, M. A. Ribeiro, W. X. C. Oliveira, D. O. Reis, H. O. Stumpf, A. C. Doriguetto, F. C. Machado, C. B. Pinheiro, F. lloret, J. Cano and M. V. Marinho, Dalton Trans., 2016, 45, 172; (n) A. Halder, B. Bhattacharya, R. Dey, D. K. Maity and D. Ghoshal, Cryst. Growth Des., 2016, 16, 4783; (o) E. Melnic, E. B. Coropceanu, A. Forni, E. Cariati, O. V. Kulikova, A. V. Siminel, V. Ch. Kravtsov and M. S. Fonari, Cryst. Growth Des., 2016, 16, 6275.

- 17 H. A. Godwin and F. Lions, J. Am. Chem. Soc., 1959, 81, 6415.
- 18 A. Earnshaw, *Magnetochemistry*, Academic Press, London and New York, 1968.
- 19 Xcalibur CCD system, Agilent Technologies: CrysAlisPro Software system, version 1.171.35.15, Agilent Technologies UK Ltd, Oxford, 2011.
- 20 G. M. Sheldrick, *SADABS, Version 2012/1*, Bruker AXS Inc., 2012.
- 21 (a) Sheldrick, XPREP Version 2013/3, Bruker AXS Inc.; (b)
 G. M. Sheldrick, XS Version 2013/1, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112; (c) G. M. Sheldrick, XL
 Version 2013/3, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 22 G. M. L. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv., 2015, 71, 3-8.
- 23 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 24 (a) M. Nardelli, J. Appl. Crystallogr., 1999, 32, 563; (b) C. K. Johnson, Crystallographic Computing, ed. F. R. Ahmed, S. R. Hall and C. P. Huber, Munksgaard, Copenhagen, 1970, p. 207.
- 25 F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van der Streek, *J. Appl. Crystallogr.*, 2006, 39, 453.
- 26 M. R. Rosenthal, J. Chem. Educ., 1973, 50, 331.
- 27 A. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
- 28 I. Krossing and I. Raabe, Angew. Chem., Int. Ed., 2004, 43, 2066.
- 29 B. Bleaney and K. D. Bowers, Proc. R. Soc. London, Ser. A, 1952, 214, 451.
- 30 O. Kahn, *Molecular Magnetism*, VCH Publishers, Weinheim, 1993, p. 159.