



Cite this: *CrystEngComm*, 2016, 18, 437

## Self-assembly, binding ability and magnetic properties of dicopper(II) pyrazolenophanes†

Wdeson P. Barros,<sup>ac</sup> M. Luisa Calatayud,<sup>a</sup> Francesc Lloret,<sup>a</sup> Miguel Julve,<sup>a</sup> Nadia Marino,<sup>\*ef</sup> Giovanni De Munno,<sup>e</sup> Humberto O. Stumpf,<sup>d</sup> Rafael Ruiz-García<sup>ab</sup> and Isabel Castro<sup>\*a</sup>

A novel series of dinuclear copper(II) pyrazolenophanes of the formula  $[\text{Cu}_2(\mu\text{-}4\text{-Mepz})_2(\mu\text{-ClO}_4)(\text{ClO}_4)(\text{bpm})_2]$  (**1**),  $[\text{Cu}_2(\mu\text{-pz})_2(\mu\text{-H}_2\text{O})(\text{ClO}_4)(4,7\text{-Me}_2\text{phen})_2]\text{ClO}_4\cdot\text{H}_2\text{O}\cdot\text{CH}_3\text{CN}$  (**2**),  $[\text{Cu}_2(\mu\text{-pz})_2(\mu\text{-H}_2\text{O})(\text{ClO}_4)_{3/2}(\text{H}_2\text{O})_{1/2}(\text{phen})_2]_2[\text{Cu}_2(\mu\text{-pz})_2(\mu\text{-ClO}_4)(\text{ClO}_4)_2(\text{phen})_2]\cdot 8\text{H}_2\text{O}$  (**3**), and  $[\text{Cu}_2(\mu\text{-pz})_2(\text{CH}_3\text{CN})_2(3,4,7,8\text{-Me}_4\text{phen})_2](\text{ClO}_4)_2$  (**4**) (Hpz = pyrazole, H-4-Mepz = 4-methylpyrazole, bpm = 2,2'-bipyrimidine, phen = 1,10-phenanthroline, 4,7-Me<sub>2</sub>phen = 4,7-dimethyl-1,10-phenanthroline, and 3,4,7,8-Me<sub>4</sub>phen = 3,4,7,8-tetramethyl-1,10-phenanthroline) have been synthesized and magneto-structurally investigated. The crystal structures of **1–4** contain bis(pyrazolate)(perchlorate)- (**1** and **3**), bis(pyrazolate)(aqua)- (**2** and **3**), or bis(pyrazolate)-bridged (**4**) dicopper(II) entities of the metallacyclophane-type with bpm (**1**), 4,7-Me<sub>2</sub>phen (**2**), phen (**3**), and 3,4,7,8-Me<sub>4</sub>phen (**4**) as blocking bidentate ligands. All of them exhibit a saddle conformation with an overall not planar but bent, six-membered Cu-(N-N)<sub>2</sub>-Cu metallacyclic core with relatively short intermetallic distances across the bis(pyrazolate)(perchlorate) [ $r = 3.3076(5)$  (**1**) and  $3.382(1)$  Å (**3**)], bis(pyrazolate)(aqua) [ $r = 3.383(1)$  (**2**) and  $3.357(1)$  Å (**3**)], and bis(pyrazolate) bridges [ $r = 3.098(1)$  Å (**4**)]. The analyses of the variable-temperature magnetic susceptibility of **1–4** reveal the occurrence of a moderately strong antiferromagnetic coupling across the bis(pyrazolate)(perchlorate) [ $-J = 228$  (**1**) and  $193$  cm<sup>-1</sup> (**3**)], bis(pyrazolate)(aqua) [ $-J = 189$  (**2**) and  $221$  cm<sup>-1</sup> (**3**)], and bis(pyrazolate) bridges [ $-J = 197$  cm<sup>-1</sup> (**4**)] (the spin Hamiltonian being defined as  $H = -JS_1\cdot S_2$  with  $S_1 = S_2 = S_{\text{Cu}} = \frac{1}{2}$ ).

Received 21st October 2015,  
Accepted 27th November 2015

DOI: 10.1039/c5ce02058a

[www.rsc.org/crystengcomm](http://www.rsc.org/crystengcomm)

## Introduction

Metallacyclophanes have been thoroughly investigated as model systems for the study of metal-directed self-assembly processes in the field of supramolecular coordination chemistry (so-called metallosupramolecular chemistry).<sup>1–7</sup> They are prepared by the stereospecific self-assembly of a variety of transition metal ions and suitably designed bridging ligands possessing multiple metal binding sites which are separated by more or less rigid aromatic spacers.<sup>8–14</sup> Besides their

unique self-assembly and structural features which allow one to understand the role of weak intramolecular  $\pi\text{-}\pi$  and  $\pi\text{-}$ anion interactions in metallosupramolecular aggregation processes,<sup>8</sup> the binding abilities of metallacyclophanes toward neutral molecules and charged cationic or anionic species are investigated,<sup>9</sup> as well as their catalytic,<sup>10</sup> redox,<sup>11</sup> photochemical,<sup>12</sup> optical (luminescence),<sup>13</sup> and magnetic<sup>14</sup> properties, which could be exploited in related supramolecular fields of metal-organic framework (MOF) chemistry,<sup>15</sup> host-guest chemistry and catalysis,<sup>16</sup> electro-,<sup>17</sup> photo-,<sup>18</sup> and magnetochemistry.<sup>19,20</sup>

This type of metallacyclic complexes includes the large class of dicopper(II) pyrazolenophanes, where two simple pyrazolate ligands or their substituted derivatives act as *N,N'*-bis(monodentate) bridges between the two metal centers to give an overall six-membered Cu-(N-N)<sub>2</sub>-Cu metallacyclic entity.<sup>21</sup> In this case, the use of different blocking ligands, either bi-<sup>21a,c,d</sup> or tridentate<sup>21h,i</sup> acyclic ligands or bis(bidentate) macrocyclic ones,<sup>21b</sup> leads to the stereospecific self-assembly of heteroleptic bis(pyrazolate)-bridged dicopper(II) complexes of the metallacyclophane-type with a saddle-type molecular conformation, preventing thus the formation of the undesired homoleptic bis(pyrazolate)-bridged copper(II) chains.<sup>22</sup>

<sup>a</sup> Instituto de Ciencia Molecular (ICMol), Universitat de València, c/José Beltrán 2, E-46980 Paterna, València, Spain. E-mail: isabel.castro@uv.es

<sup>b</sup> Fundació General de la Universitat de València (FGUV), Valencia, Spain

<sup>c</sup> Instituto de Química, Universidade Estadual de Campinas, Campinas, Brazil

<sup>d</sup> Departamento de Química - ICEx, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, 31270-901, Belo Horizonte, Brazil

<sup>e</sup> Dipartimento di Chimica e Tecnologia Chimiche (CTC), Università della Calabria, I-87036, Rende, Cosenza, Italy. E-mail: nadia.marino@unical.it

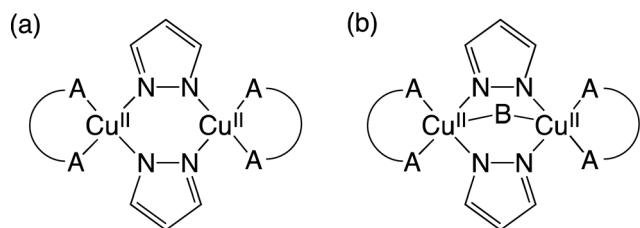
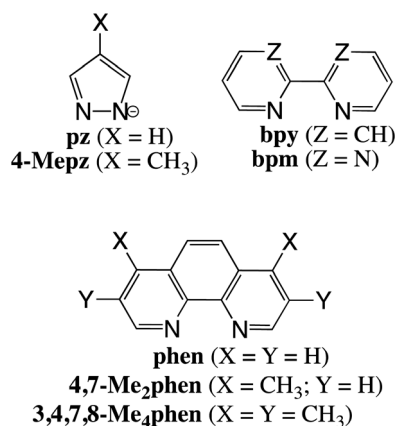
<sup>f</sup> Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100, USA

† Electronic supplementary information (ESI) available: Selected bond distances and angles and metal-metal separations for **1–4** (Tables S1–S4). CCDC 1047962–1047965. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/10.1039/c5ce02058a

The nature of both the pyrazolate bridging ligand and the blocking ligand determines the folding of the resulting dicopper(II) pyrazolenophanes in the solid state, so that they are able to interact with exogenous anions and neutral solvent molecules through either inward (“endo”) or outward (“exo”) coordination.<sup>21</sup> On the one hand, the endo binding ability opens up an interesting host–guest chemistry and sets up the principle of templating effects for the self-assembly of dicopper(II) pyrazolenophanes.<sup>16</sup> On the other hand, the exo binding capacity would allow obtaining of extended coordination polymers from dicopper(II) pyrazolenophanes, which constitutes a major challenge in the field of MOF chemistry and crystal engineering.<sup>15</sup>

So, for instance, the use of the well known 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen)<sup>21c,d</sup> ligands as blocking bidentate ligands led to the exclusive formation of dicopper(II) pyrazolenophanes with double bis(pyrazolate) bridges, while some unique examples of dicopper(II) pyrazolenophanes with triple bis(pyrazolate)(chloride) bridges were obtained when dihydrobis(1-pyrazolyl)borate (H<sub>2</sub>Bpz<sub>2</sub>)<sup>21a</sup> or bis(2-pyridyl)amine (dpa)<sup>21d</sup> was used instead, as illustrated in Scheme 1.

Herein we report the synthesis and general physical, structural, and magnetic characterization of a novel series of dinuclear copper(II) complexes of the metallacyclophane-type with pyrazolate (pz) or 4-methylpyrazolate (4-Mepz) as bridging ligands, and 2,2'-bipyrimidine (bpm), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me<sub>2</sub>phen), or 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-Me<sub>4</sub>phen) as blocking ligands.



**Scheme 1** General chemical structure of the (a) doubly- and (b) triply-bridged dicopper(II) pyrazolenophanes with blocking bidentate ligands (AA) and exogenous bridging ligands (B).

Our goal is to investigate the ligand effects on the molecular and crystal structures as well as the magnetic properties of this unique family of dicopper(II) pyrazolenophanes of the formula [Cu<sub>2</sub>(μ-4-Mepz)<sub>2</sub>(μ-ClO<sub>4</sub>)(ClO<sub>4</sub>)(bpm)<sub>2</sub>] (1), [Cu<sub>2</sub>(μ-pz)<sub>2</sub>(μ-H<sub>2</sub>O)(ClO<sub>4</sub>)(4,7-Me<sub>2</sub>phen)<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O·CH<sub>3</sub>CN (2), [Cu<sub>2</sub>(μ-pz)<sub>2</sub>(μ-H<sub>2</sub>O)(ClO<sub>4</sub>)<sub>3/2</sub>(H<sub>2</sub>O)<sub>1/2</sub>(phen)<sub>2</sub>]<sub>2</sub>[Cu<sub>2</sub>(μ-pz)<sub>2</sub>(μ-ClO<sub>4</sub>)(ClO<sub>4</sub>)<sub>2</sub>(phen)<sub>2</sub>]·8H<sub>2</sub>O (3), and [Cu<sub>2</sub>(μ-pz)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>(3,4,7,8-Me<sub>4</sub>phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (4). By varying the ligand substituents on the parent dicopper(II) pyrazolenophanes with bpy and phen as blocking ligands,<sup>21c,d</sup> it would be possible to perform a systematic analysis on how electronic and steric factors influence their self-assembling, hosting and binding abilities in the solid state.

## Experimental

### Materials and methods

Hpz, H-4-Mepz, bpm, phen, 4,7-Me<sub>2</sub>phen, 3,4,7,8-Me<sub>4</sub>phen, triethylamine, and copper(II) perchlorate hexahydrate were purchased from commercial sources and used as received. Elemental (C, H, N) analyses were performed by the Servicio Interdepartamental de la Universidad de Valencia. Infrared spectra were recorded on a Bruker IF555 spectrometer as KBr pellets.

**Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. We worked at the mmol scale and the starting perchlorate salt was an aqua complex. The diluted solutions were handled with care and evaporated slowly at room temperature in an open hood.

### Synthetic procedures

[Cu<sub>2</sub>(μ-4-Mepz)<sub>2</sub>(μ-ClO<sub>4</sub>)(ClO<sub>4</sub>)(bpm)<sub>2</sub>] (1). An aqueous solution (20 mL) of bpm (79 mg, 1/2 mmol) was slowly added to an aqueous solution (15 mL) of copper(II) perchlorate hexahydrate (183 mg, 1/2 mmol) under continuous stirring. The addition of an aqueous solution (80 mL) of H-4-Mepz (42 mg, 1/2 mmol) and triethylamine (0.1 mL, 1/2 mmol) caused a color change from green to deep blue. Dark blue crystals of **1** were grown from the filtered solution by slow evaporation at room temperature. Yield *ca.* 40%. Anal. calcd. for C<sub>24</sub>H<sub>22</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>12</sub>O<sub>8</sub> (1): C, 35.83; H, 2.76; N, 20.89. Found: C, 35.53; H, 2.76; N, 20.68%. IR (KBr/cm<sup>-1</sup>): 1593s (C=N, 2,2'-bipyrimidine), 1500m (C=N, methyl-substituted pyrazolate), and 1084vs (Cl–O, perchlorate).

[Cu<sub>2</sub>(μ-pz)<sub>2</sub>(μ-H<sub>2</sub>O)(ClO<sub>4</sub>)(4,7-Me<sub>2</sub>phen)<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O·CH<sub>3</sub>CN (2), [Cu<sub>2</sub>(μ-pz)<sub>2</sub>(μ-H<sub>2</sub>O)(ClO<sub>4</sub>)<sub>3/2</sub>(H<sub>2</sub>O)<sub>1/2</sub>(phen)<sub>2</sub>]<sub>2</sub>[Cu<sub>2</sub>(μ-pz)<sub>2</sub>(μ-ClO<sub>4</sub>)(ClO<sub>4</sub>)<sub>2</sub>(phen)<sub>2</sub>]·8H<sub>2</sub>O (3), and [Cu<sub>2</sub>(μ-pz)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>(3,4,7,8-Me<sub>4</sub>phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (4). A similar procedure was used for the preparation of all three complexes. An acetonitrile solution (20 mL) of either 4,7-Me<sub>2</sub>phen (2) (104 mg, 1/2 mmol), phen (3) (90 mg, 1/2 mmol), or 3,4,7,8-Me<sub>4</sub>phen (4) (118 mg, 1/2 mmol) was slowly poured into an aqueous solution (10 mL) of copper(II) perchlorate hexahydrate (183 mg, 1/2 mmol) under continuous stirring. An aqueous solution (10 mL) of Hpz (34 mg, 1/2 mmol) and triethylamine (0.1 mL, 1/2 mmol) was then added leading to a deep blue solution.

Dark blue crystals of 2–4 were grown from the filtered solution by slow evaporation at room temperature. Yield *ca.* 36 (2), 50 (3), and 26% (4). Anal. calcd. for  $C_{36}H_{37}Cl_2Cu_2N_9O_{10}$  (2): C, 45.34; H, 3.91; N, 13.22. Found: C, 45.26; H, 3.77; N, 13.07%. Anal. calcd. for  $C_{90}H_{88}Cl_6Cu_6N_{24}O_{35}$  (3): C, 41.64; H, 3.34; N, 12.94. Found: C, 41.41; H, 3.21; N, 13.00%. Anal. calcd. for  $C_{42}H_{44}Cl_2Cu_2N_{10}O_8$  (4): C, 49.71; H, 4.37; N, 13.80. Found: C, 49.54; H, 4.22; N, 13.59%. IR (KBr/cm<sup>-1</sup>) for 2: 3435s (O–H, water), 2265w (C≡N, acetonitrile), 1625s, 1610s (C=N, dimethyl-substituted phenanthroline), 1527m (C=N, pyrazolate), and 1089vs (Cl–O, perchlorate). IR (KBr/cm<sup>-1</sup>) for 3: 3447s (O–H, water), 1636s, 1578s (C–N, phenanthroline), 1520m (C=N, pyrazolate), and 1090vs (Cl–O, perchlorate). IR (KBr/cm<sup>-1</sup>) for 4: 2265w (C≡N, acetonitrile), 1618s, 1600s (C=N, tetramethyl-substituted phenanthroline), 1530m (C=N, pyrazolate), and 1095vs (Cl–O, perchlorate).

### Magnetic measurements

Variable-temperature (2.0–300 K) magnetic susceptibility measurements on crushed crystals of 1–4 were carried out with a SQUID magnetometer under an applied dc field of 500 G. Diamagnetic corrections for the constituent atoms were estimated by using Pascal's constants. The experimental data were also corrected for the temperature-independent paramagnetism of the metal center ( $120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  per two Cu<sup>II</sup> ions) and the sample holder (a plastic bag).

### Crystallography

X-ray diffraction data for single crystals of 1–4 were collected at room temperature with a Bruker-Nonius X8-APEXII CCD area detector system by using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were processed through the SAINT<sup>23</sup> reduction and SADABS<sup>24</sup> absorption software. The structures were solved by direct methods and subsequently completed by Fourier recycling using the SHELXTL-2013 software package,<sup>25</sup> then refined by full-matrix least-squares refinements based on  $F^2$  with all observed reflections, using established methods.<sup>26</sup> Non-hydrogen atoms were refined anisotropically, unless otherwise specified. The hydrogen atoms of the blocking bpm (1), 4,7-Me<sub>2</sub>phen (2), phen (3), and 3,4,7,8-Me<sub>4</sub>phen (4) and the bridging 4-Mepz (1) and pz (2–4) ligands, as well as those of the crystallization and coordinated acetonitrile molecules (2 and 4) were included at geometrically calculated positions and refined using a riding model. The hydrogen atoms of the bridging and crystallization water molecules in 2 as well as those of the bridging water molecule in 3 were located from the Fourier difference map and refined with restraints on O–H and H $\cdots$ H distances. The hydrogen atoms of the weakly coordinated water molecule [O(2w)] (*vide infra*) and those of the disordered crystallization water molecules [O(3w)–O(7w)] in 3 were not located and the corresponding oxygen atoms were refined isotropically. Because of disorder, only half occupancy was assigned to the water molecules [O(2w), O(6w), and O(7w)] in 3 giving a total of 4.5 water molecules

per asymmetric unit, *i.e.*, 3 water molecules per dicopper(II) unit. The perchlorate anions in 1–4 were found to be more or less severely disordered. The coordinated perchlorate [Cl(2)] in 1, the uncoordinated perchlorate [Cl(2)] in 2, the coordinated and bridging perchlorate groups [Cl(2) and Cl(4)] in 3, and the uncoordinated perchlorate [Cl(2)] in 4 were partially or fully modeled over two positions, as appropriate. In each case, the relative occupancies of the two different atomic sets were refined freely within SHELXL, while constraining their sum to unity.<sup>26</sup> These disorders were generally refined with the aid of similarity restraints on 1,2- and 1,3 distances as well as rigid-bond restraints.<sup>26</sup> Of such list, the coordinated perchlorate [Cl(2)] in 3 was refined isotropically (both atomic sets). This specific perchlorate group was found to be involved in further statistical disorder, as it appeared to compete 50:50 with a water molecule [O(2w)] for the coordination to the metal center [Cu(2)] in 3. The coordinating perchlorate in 2 [Cl(1)] was found engaged in a different case of statistical disorder. In fact, to satisfy charge balance requirements and considering the otherwise unusually large ADPs, half occupancy had to be crystallographically imposed on this perchlorate group, which appears to coordinate to only one of the two metal centers at the time (or on average), unfulfilling the overall  $C_m$  molecular symmetry of the bis(pyrazolate)(aqua)-bridged dicopper(II) unit in 2. The final geometrical calculations and graphical manipulations were performed using the XP utility within SHELXTL;<sup>25</sup> graphical manipulations were also performed with the Diamond software.<sup>27</sup> A summary of the crystallographic data and structure refinement for 1–4 is given in Table 1. Selected bond distances and interbond angles for 1–4 are given in Tables S1–S4,† respectively. CCDC reference numbers are 1047962 (1), 1047964 (2), 1047963 (3), and 1047965 (4).

## Results and discussion

### Description of the structures of 1–4

The crystal structures of 1 and 2 comprise neutral bis(pyrazolate)(perchlorate)- and cationic bis(pyrazolate)-(aqua)-bridged dicopper(II) units,  $[Cu^{II}_2(\mu\text{-}4\text{-Mepz})_2(\mu\text{-ClO}_4)(\text{ClO}_4)(\text{bpm})_2]$  and  $[Cu^{II}_2(\mu\text{-pz})_2(\mu\text{-H}_2\text{O})(\text{ClO}_4)(4,7\text{-Me}_2\text{phen})_2]^+$ , of  $C_1$  (1) and pseudo- $C_m$  (2) molecular symmetries, respectively (Fig. 1 and 2). The lack of perfect  $C_m$  molecular symmetry in 2 is due to the partial axial coordination of a perchlorate group to the metal centers, with only one coordinating perchlorate ion per dicopper(II) unit, on average. The charge balance in 2 is ensured by perchlorate counteranions, while additional water and acetonitrile molecules of crystallization are also present.

Both types of bis(pyrazolate)(perchlorate)- and bis(pyrazolate)(aqua)-bridged dicopper(II) entities occur, instead, in 3 (Fig. 3). In this case, however, only the coordination sphere of the metal center of the bis(pyrazolate)(perchlorate)-bridged dicopper(II) entity is crystallographically uniquely defined, producing the anionic  $C_m$ -symmetric  $[Cu^{II}_2(\mu\text{-pz})_2(\mu\text{-ClO}_4)(\text{ClO}_4)_2(\text{phen})_2]^-$  unit [Fig. 3(a)]. In fact, a water molecule

Table 1 Summary of crystallographic data for 1–4

	1	2	3	4
Formula	C <sub>24</sub> H <sub>22</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>12</sub> O <sub>8</sub>	C <sub>36</sub> H <sub>37</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>9</sub> O <sub>10</sub>	C <sub>90</sub> H <sub>88</sub> Cl <sub>6</sub> Cu <sub>6</sub> N <sub>24</sub> O <sub>35</sub>	C <sub>42</sub> H <sub>44</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>10</sub> O <sub>8</sub>
FW	804.51	953.72	2659.78	1014.85
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>Pbcm</i>	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> /Å	13.1874(8)	8.497(2)	12.6355(4)	13.8410(13)
<i>b</i> /Å	11.9065(8)	25.544(7)	41.3258(13)	8.0261(8)
<i>c</i> /Å	19.8014(13)	18.675(5)	20.8981(7)	39.946(3)
$\beta$ /°	100.142(2)			96.565(4)
<i>V</i> /Å <sup>3</sup>	3060.5(3)	4053.3(17)	10912.4(6)	4408.5(7)
<i>Z</i>	4	4	4	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.746	1.563	1.586	1.529
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	1.634	1.249	1.376	1.151
<i>T</i> /K	296(2)	296(2)	296(2)	296(2)
<i>F</i> (000)	1624	1952	5048	2088
$\theta$ range/°	1.569–27.102	1.594–27.134	1.771–24.108	1.026–26.404
Refl. collected	25 127	49 742	137 264	79 919
Refl. indep. [ <i>R<sub>int</sub></i> ]	6750 [0.0268]	4604 [0.0434]	8781 [0.0525]	8979 [0.0901]
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.035	1.098	1.027	1.122
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] (all)	0.0408 (0.0523)	0.0632 (0.0874)	0.0670 (0.0982)	0.0825 (0.1523)
<i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] (all)	0.1053 (0.1138)	0.1933 (0.2132)	0.1971 (0.2268)	0.2243 (0.2595)
$\Delta\rho_{\max,\min}$ /e Å <sup>-3</sup>	0.936, -1.216	0.760, -0.595	1.047, -0.783	0.965, -0.923

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^{2/3}] \}^{1/2}$  and  $w = 1 / [\sigma^2(F_o^2) + (mP)^2 + nP]$  with  $P = (F_o^2 + 2F_c^2) / 3$ ,  $m = 0.0552$  (1), 0.1228 (2), 0.1328 (3) and 0.0922 (4), and  $n = 3.6221$  (1), 3.1892 (2), 29.5123 (3) and 27.9269 (4).

and a perchlorate group compete 50:50 to complete the coordination sphere of one metal center of the bis(pyrazolate)(aqua)-bridged dicopper(II) unit, producing either the neutral pseudo-*C<sub>m</sub>*-symmetric [Cu<sup>II</sup><sub>2</sub>( $\mu$ -pz)<sub>2</sub>( $\mu$ -H<sub>2</sub>O)(ClO<sub>4</sub>)<sub>2</sub>(phen)<sub>2</sub>] or the cationic acentric [Cu<sup>II</sup><sub>2</sub>( $\mu$ -pz)<sub>2</sub>( $\mu$ -H<sub>2</sub>O)(ClO<sub>4</sub>)(H<sub>2</sub>O)(phen)<sub>2</sub>]<sup>+</sup> units [Fig. 3(b)].

Finally, 4 is made up of cationic bis(pyrazolate)-bridged dicopper(II) units, [Cu<sup>II</sup><sub>2</sub>( $\mu$ -pz)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>(3,4,7,8-Me<sub>4</sub>phen)<sub>2</sub>]<sup>2+</sup>, of approximately *C<sub>2</sub>* molecular symmetry (Fig. 4), together with perchlorate counteranions.

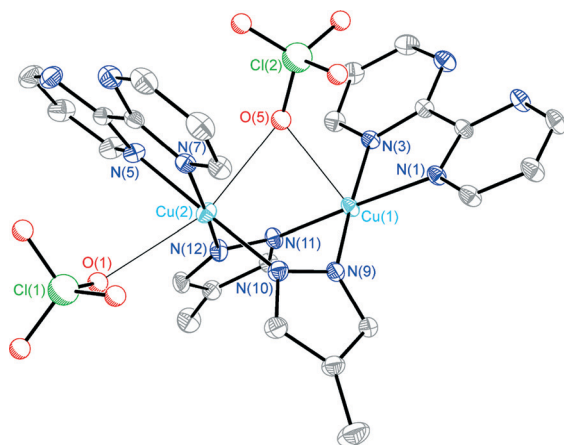


Fig. 1 Perspective view of the neutral bis(pyrazolate)(perchlorate)-bridged dicopper(II) unit of 1 with the atom-numbering scheme of selected atoms. Hydrogen atoms on the 4-Mepz and bpm ligands are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. The perchlorate anions are depicted using a ball-and-stick model. Only one atomic set for the disordered perchlorate anion [Cl(2)] is shown for clarity.

While 1 comprises neutral dicopper(II) molecules, 2 and 4 have in common the presence of cationic dicopper(II) units counterbalanced by uncoordinated perchlorate anions. Complex 3 represents, on the other hand, a nice example of a molecular salt, where both the cation and the anion are dicopper(II) units, and whose structure is further stabilized by the presence of an additional neutral dicopper(II) molecule (Fig. 5). The anionic bis(pyrazolate)(perchlorate)- plus the cationic and neutral bis(pyrazolate)(aqua)-bridged dicopper(II) units in 3 form altogether a neutral “trimer-of-dimers” supra-molecular motif, with the aid of hydrogen bonds involving the coordinated and bridging perchlorate groups and the coordinated [O(2w)] and crystallization [O(6w) and O(7w)] water molecules [Ow...Ow = 2.79(3)–2.81(3) Å and Ow...OClO<sub>3</sub> =

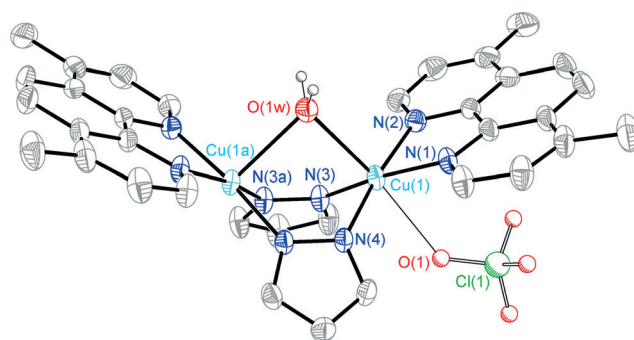
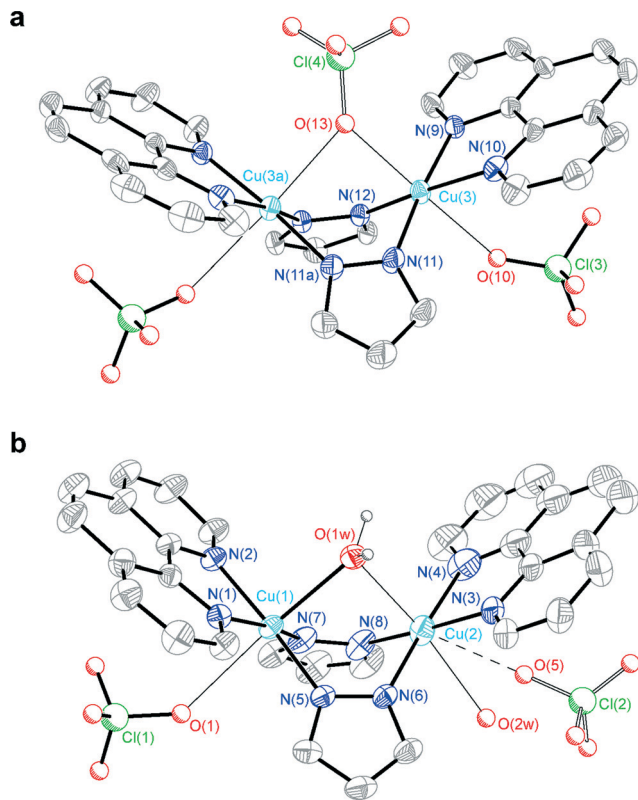
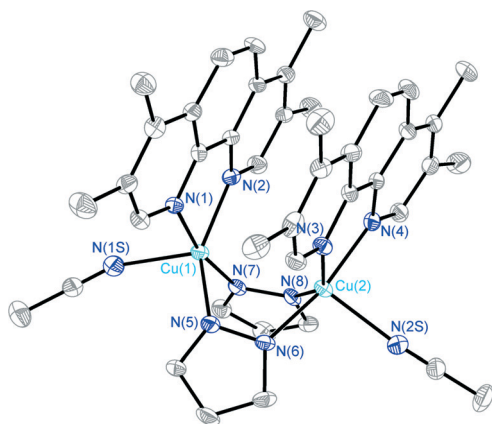


Fig. 2 Perspective view of the cationic bis(pyrazolate)(aqua)-bridged dicopper(II) unit of 2 with the atom-numbering scheme of selected atoms [symmetry code: (a) = *x*, *y*, -*z* + 1/2]. Hydrogen atoms on the pz and 4,7-Me<sub>2</sub>phen ligands are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. The perchlorate anion is depicted using a ball-and-stick model; note that it does not fulfill the *C<sub>m</sub>* molecular symmetry.

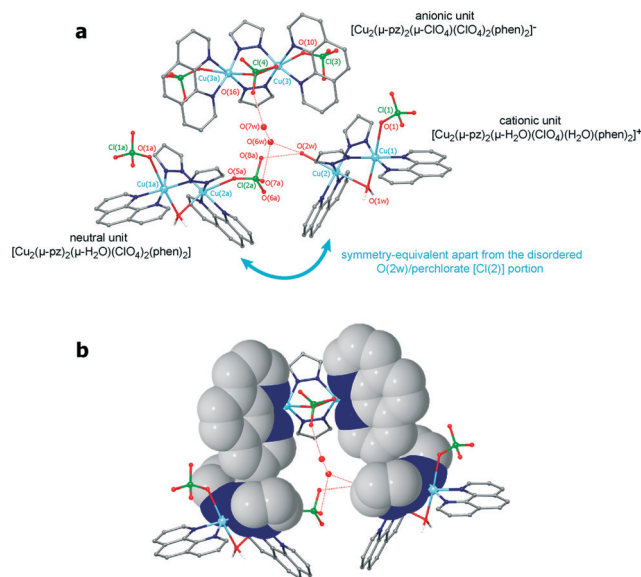


**Fig. 3** Perspective views of (a) the anionic bis(pyrazolate)(perchlorate)- and (b) the cationic or neutral bis(pyrazolate)(aqua)-bridged dicopper(II) units of **3** with the atom-numbering scheme of selected atoms [symmetry code: (a) =  $x, -y + 1/2, z$ ]. The water molecule [O(2w)] and the perchlorate anion [Cl(2)] in (b) coordinate to the copper(II) ion [Cu(2)] alternately (either one or the other is present at a time). Hydrogen atoms on the phen and pz ligands are omitted for clarity; those on O(2w) were not located from the diffraction data. Thermal ellipsoids are drawn at the 30% probability level. The perchlorate anions are depicted using a ball-and-stick model; only one atomic set for the disordered perchlorate anions [Cl(2)], [Cl(3)] and [Cl(4)] is shown for clarity.

2.55(3)–2.93(3) Å [Fig. 5(a)], as well as hydrophobic interactions between the pyrazolate bridging ligands and the



**Fig. 4** Perspective view of the cationic bis(pyrazolate)-bridged dicopper(II) unit of **4** with the atom-numbering scheme of selected atoms. Thermal ellipsoids are drawn at the 30% probability level.



**Fig. 5** (a) and (b) Views of the neutral “trimer-of-dimers” supramolecular motif in **3** with the atom-numbering scheme of selected atoms showing plausible hydrogen bonds (dotted lines in the ball-and-stick model representation) and hydrophobic interactions (close contacts in the space-filling model representation), respectively [symmetry code: (a) =  $x, -y + 1/2, z$ ]. Hydrogen atoms on the phen and pz ligands are omitted for clarity, whereas those on the coordinated [O(2w)] and crystallization [O(6w) and O(7w)] water molecules were not located from the diffraction data.

pyridine rings of the blocking phen ligands from adjacent dicopper(II) units [Fig. 5(b)].

**Coordination environments.** In both **1** and **2**, the two metal ions of the corresponding bis(pyrazolate)(perchlorate)- and bis(pyrazolate)(aqua)-bridged dicopper(II) units are five- and six-coordinate, in apically elongated  $\text{CuN}_4\text{O}$  square pyramidal and axially elongated  $\text{CuN}_4\text{O}_2$  octahedral geometries, respectively (Fig. 1 and 2). The two metal ions of both bis(pyrazolate)(aqua)- and bis(pyrazolate)(perchlorate)-bridged dicopper(II) units in **3** are six-coordinate with axially elongated  $\text{CuN}_4\text{O}_2$  octahedral geometries (Fig. 3), whereas those of the bis(pyrazolate)-bridged dicopper(II) units in **4** are both five-coordinate in a trigonally distorted  $\text{CuN}_5$  square pyramidal geometry (Fig. 4).

The average values of the equatorial/basal Cu–N distances from the pyrazolate bridges are somewhat shorter than those from the blocking  $\alpha$ -diimine ligands (Table 2), as previously found in related dicopper(II) pyrazolenophanes with triple bis(pyrazolate)(chloride) and double bis(pyrazolate) bridges.<sup>21a,c,d</sup> On the other hand, the average values of the apical Cu–N distances from the terminally coordinated acetonitrile molecule in **4** are much shorter than those of the axial Cu–O distance from the weakly coordinated perchlorate anions and water molecules in **1**–**3** (Table 2). Only slight differences can be found instead in the values of the axial/apical Cu–O distances from either the perchlorate (**1** and **3**) or the aqua (**2** and **3**) bridges (Table 2).

A relatively large trigonal distortion of the five-coordinate square pyramidal copper(II) ions is observed in **4** when

**Table 2** Selected structural data for 1–4<sup>a</sup>

	1	2	3 <sup>b</sup>	4
Cu–N <sub>pz</sub> <sup>c</sup> /Å	1.959(2)	1.977(4)	1.965(5)/1.974(6)	1.978(7)
Cu–N <sub>im</sub> <sup>d</sup> /Å	2.019(2)	2.024(4)	2.025(5)/2.038(6)	2.038(6)
Cu–N <sub>ac</sub> <sup>e</sup> /Å				2.211(9)
Cu–O <sub>per</sub> <sup>f</sup> /Å	2.705(3)	2.740(9)	2.704(8)/2.730(14)	
Cu–O <sub>w</sub> <sup>g</sup> /Å			2.66(1)	
Cu–O <sub>per</sub> <sup>h</sup> /Å	2.488(7)		2.478(2)	
Cu–O <sub>w</sub> <sup>i</sup> /Å		2.404(3)	2.425(5)	
Cu–O <sub>per</sub> –Cu <sup>j/o</sup>	83.4(1)		86.3(2)	
Cu–O <sub>w</sub> –Cu <sup>k/o</sup>		89.5(2)	87.6(2)	
$\tau^l$	0.013	0.092		0.337
$\delta^m/o$	3.5	10.9	8.0/5.8	33.1
$h_M^n/\text{Å}$	0.022(1)	0.131(2)	0.095(3)/0.064(3)	0.371(4)
$\theta^p/o$	89.4(1)	89.1(3)	92.9(3)/98.9(3)	78.6(3)
$\psi^q/o$	89.4(1)	103.7(1)	101.6(1)/97.6(1)	45.9(2)
$\varphi^r/o$	119.6(1)	121.7(5)	124.3(7)/124.8(3)	104.6(3)
$\phi^s/o$	168.6(1)	168.3(5)	171.0(7)/174.2(3)	169.0(3)
$\rho^t/o$	87.6(1)	134.7(1)	128.6(1)/110.5(1)	0.9(1)
$r^u/\text{Å}$	3.3076(5)	3.383(1)	3.382(1)/3.357(1)	3.098(1)

<sup>a</sup> The estimated standard deviations are given in parentheses.

<sup>b</sup> Structural data for the two crystallographically independent, bis( $\mu$ -pyrazolate)( $\mu$ -perchlorate)/bis( $\mu$ -pyrazolate)( $\mu$ -aqua)dicopper(II) units [see Fig. 3(a) and (b), respectively]. <sup>c</sup> Average values of the equatorial/basal Cu–N distances from the pyrazolate bridges. <sup>d</sup> Average values of the equatorial/basal Cu–N distances from the blocking  $\alpha$ -diimine ligands. <sup>e</sup> Average values of the axial/apical Cu–N distances from the acetonitrile molecules. <sup>f</sup> Average values of the axial/apical Cu–O distances from the weakly coordinated perchlorate anions. <sup>g</sup> Average values of the axial/apical Cu–O distances from the weakly coordinated water molecules. <sup>h</sup> Average values of the axial/apical Cu–O distances from the perchlorate bridge. <sup>i</sup> Average values of the axial/apical Cu–O distances from the aqua bridge. <sup>j</sup> Value of the Cu–O–Cu angle at the perchlorate bridge. <sup>k</sup> Value of the Cu–O–Cu angle at the aqua bridge. <sup>l</sup> Average trigonality parameter of the metal atoms. <sup>m</sup> Average values of the dihedral angle between the two CuN<sub>2</sub> planes from the pyrazolate bridges and the blocking  $\alpha$ -diimine ligands. <sup>n</sup> Average value of the metal displacement from the mean equatorial/basal planes. <sup>o</sup> Value of the dihedral angle between the pyrazolate mean planes. <sup>p</sup> Value of the dihedral angle between the metal equatorial/basal planes. <sup>q</sup> Average value of the dihedral angle between the metal equatorial/basal planes and the pyrazolate mean planes. <sup>r</sup> Average value of the Cu–N–N–C torsion angle between the metal atoms and the pyrazolate rings. <sup>s</sup> Value of the dihedral angle between the mean planes of the two blocking  $\alpha$ -diimine ligands. <sup>t</sup> Value of the intramolecular Cu–Cu distance.

compared to 1 and 2, as expressed by the average values of the trigonality parameter ( $\tau$ ) in Table 2 ( $\tau = 0$  and 1 for ideal square pyramid and trigonal bipyramid, respectively).<sup>28</sup> The average value of  $\tau$  for 4 is, however, within the range of those found in related bis(pyrazolate)-bridged dicopper(II) complexes with the parent phen as the blocking ligand and no additional bridging ligands ( $\tau = 0.14$ – $0.63$ ).<sup>21c,d</sup> On the other hand, a larger tetrahedral distortion of the basal plane of the five-coordinate square pyramidal copper(II) ions occurs in 4 when compared to that of the basal/equatorial planes of the five-coordinate square pyramidal and six-coordinate octahedral copper(II) ions in 1–3. This is reflected by the average values of the dihedral angle between the two CuN<sub>2</sub> planes ( $\delta$ ) in Table 2, the two nitrogen atoms belonging to the blocking  $\alpha$ -diimine ligands in one plane and to the pyrazolate bridging

ligands in the other one. This tetrahedral distortion is accompanied by greater mean values of the metal displacements from the mean equatorial/basal planes ( $h_M$ ) toward the terminally coordinated acetonitrile molecules in 4 when compared to those observed in 1–3 toward either the perchlorate (1 and 3) or the aqua (2 and 3) bridges (Table 2). The average values of  $\delta$  and  $h_M$  for 4 are even greater than those found in related five-coordinate square pyramidal bis(pyrazolate)-bridged dicopper(II) complexes with the parent bpy and phen as the blocking ligands and no additional bridging ligands ( $\delta = 16.7$ – $21.3^\circ$ ;  $h_M = 0.204$ – $0.256$ ).<sup>21c</sup>

**Molecular conformations.** Each dicopper(II) metallacyclophane entity in 1–4 shows a saddle molecular conformation with an alternately up and down disposition of the two metal equatorial/basal planes and the two pyrazolate rings, respectively, as previously found in related doubly- and triply-bridged dicopper(II) pyrazolenophanes.<sup>21a,c,d</sup> This is expressed by the values of the dihedral angle between the pyrazolate mean planes ( $\theta$ ) and those between the metal equatorial/basal planes ( $\psi$ ) in Table 2, which show rather large deviations from the coplanar molecular conformation ( $\theta = \psi = 180^\circ$ ). This is more likely due to the steric constraints between the pyrazolate bridges and the blocking ligands at each metal ion. As a matter of fact, 1–4 adopt an almost perpendicular disposition of both the pyrazolate mean planes and the metal equatorial/basal mean planes ( $\theta = \psi = 90^\circ$ ). This situation is also reflected by the average values of the dihedral angles between the metal equatorial/basal planes and the mean pyrazolate planes ( $\varphi$ ) in 1–4, which are more or less close to orthogonality (Table 2).

The geometrical parameters for the bis(pyrazolate)-(perchlorate)- and/or bis(pyrazolate)(aqua)-bridged dicopper(II) units in 1–3 are similar to those found in the bis(pyrazolate)(chloride)-bridged dicopper(II) complexes of formulas  $\text{Ph}_4\text{P}[\text{Cu}_2(\mu\text{-pz})_2(\mu\text{-Cl})(\text{H}_2\text{Bpz}_2)_2] \cdot 0.5\text{Me}_2\text{CO}$  and  $[\text{Cu}_2(\mu\text{-pz})_2(\mu\text{-Cl})(\text{H}_2\text{O})(\text{dpa})]\text{Cl} \cdot \text{H}_2\text{O}$  ( $\theta = 92.2$ – $98.1^\circ$ ,  $\psi = 104.6$ – $104.7^\circ$ , and  $\varphi = 124.8$ – $126.1^\circ$ ),<sup>21a,d</sup> while the corresponding ones for the bis(pyrazolate)-bridged dicopper(II) unit in 4 are somewhat smaller than those found in the series of bis(pyrazolate)-bridged dicopper(II) complexes of the general formula  $[\text{Cu}_2(\mu\text{-4-Rpz})_2\text{L}_2]\text{X}_2 \cdot n\text{H}_2\text{O}$  [R = H (pz), Me (4-Mepz), Cl (4-Clpz), and Br (4-Brpz); L = bpy and phen; X =  $\text{NO}_3^-$  and Cl] ( $\theta = 88.3$ – $124.3^\circ$ ,  $\psi = 48.1$ – $71.3^\circ$ , and  $\varphi = 110.0$ – $114.8^\circ$ ).<sup>21c,d</sup> In 1–3, the values of the Cu–O–Cu angle from both the perchlorate and aqua bridges (see Table 2) are, however, somewhat greater compared to those of the Cu–Cl–Cu angle in  $\text{Ph}_4\text{P}[\text{Cu}_2(\mu\text{-pz})_2(\mu\text{-Cl})(\text{H}_2\text{Bpz}_2)_2] \cdot 0.5\text{Me}_2\text{CO}$  and  $[\text{Cu}_2(\mu\text{-pz})_2(\mu\text{-Cl})(\text{H}_2\text{O})(\text{dpa})]\text{Cl} \cdot \text{H}_2\text{O}$  ( $79.7$ – $82.6^\circ$ ).<sup>21a,d</sup>

Hence, the exogenous bridging ligand does not appear to play a key role in the achievement of the saddle conformation in 1–4 (see Fig. 1–4). Actually, the bis(pyrazolate)-bridged dicopper(II) unit in 4 exhibits a greater folding of the saddle conformation compared to that of the bis(pyrazolate)-(perchlorate)- and/or bis(pyrazolate)(aqua)-bridged dicopper(II) units in 1–3, because of the presence of relatively strong  $\pi$ – $\pi$  stacking intramolecular interactions between the blocking

3,4,7,8-Me<sub>4</sub>phen ligands (the value of the centroid-centroid distance between the central benzene rings being *ca.* 3.7 Å and that of the average off-set angle between the centroid-centroid vector and the normal to their planes being 17.2°). This situation occurs in spite of the steric hindrance among their methyl substituents and it is likely explained by the electron donating nature of the methyl group, which would maximize the inter-ring  $\pi$ - $\pi$  stacking interactions. Accordingly, the intermetallic separation through the bis(pyrazolate) bridge in **4** is shorter than those in **1-3** across the bis(pyrazolate)(perchlorate) (**1** and **3**) and bis(pyrazolate)(aqua) (**2** and **3**) bridges, which are in turn within the range of those reported for related bis(pyrazolate)- and bis(pyrazolate)(chloride)-bridged dicopper(II) complexes ( $r = 3.225$ – $3.874$  Å).<sup>21a-e,g-i</sup>

Due to their saddle conformation, the dicopper(II) pyrazolenophanes in **1-4** exhibit a global “butterfly-like” geometry, wherein the two blocking  $\alpha$ -diimine ligands would act as “wings” (Fig. 6). They appear more or less folded, as reflected by the aforementioned  $\psi$  values of the dihedral angle between the mean metal equatorial/basal planes, or, alternatively, by the values of the dihedral angle ( $\rho$ ) between the mean planes of the two blocking  $\alpha$ -diimine ligands (Table 2). The folding in **4**, where no additional bridge is present, appears maximized by the possibility of  $\pi$ -stacking, as mentioned above. Although there is no apparent relationship between the amount of inner space and the nature or size of the hosted water molecule or perchlorate anion in **1-3**, a progressive molecular folding is observed that follows the trend 4,7-Me<sub>2</sub>phen (**2**) < phen (**3**) < bpm (**1**). The side-by-side views of the five core geometries of the bis(pyrazolate)(aqua)-, bis(pyrazolate)(perchlorate)-, and bis(pyrazolate)-bridged dicopper(II) units of **1-4** look like a “butterfly ballet”, the butterfly wings being wide-opened in **2** and closed in **4** (Fig. 6).

The saddle conformation in **1-4** leads to a bent six-membered Cu–(N–N)<sub>2</sub>–Cu metallacyclic ring with small but not negligible differences in the values of the atomic deviations ( $h'_x$ ) from the least-squares plane of the central four-membered N<sub>4</sub> core, which reflect the presence of additional perchlorate and/or water supporting bridges (Fig. 7). The average value of the Cu–N–N–C torsion angle for the bis(pyrazolate)-bridged dicopper(II) entity is intermediate between those for the bis(pyrazolate)(perchlorate)- and

bis(pyrazolate)(aqua)-bridged dicopper(II) units (Table 2), all of them being within the range of those reported for related bis(pyrazolate)- and bis(pyrazolate)(chloride)-bridged dicopper(II) complexes ( $\phi = 160.3$ – $177.9^\circ$ ).<sup>21a-e,g-i</sup>

**Crystal packing.** Compounds **1-4** show rather different supramolecular organizations of the dicopper(II) metallacyclopentane entities within the crystal lattice, but with some elements in common like the occurrence of intermolecular  $\pi$ - $\pi$  stacking and/or anion- $\pi$  interactions and, where applicable, hydrogen-bonding interactions to stabilize the structures (Fig. 8–11).

In particular, 1D supramolecular motifs are observed in **1** and **2** [Fig. 8(a) and 9(a), respectively]. In **1**, the terminal perchlorate ion coordinated to Cu(2) interacts very weakly with the five-coordinate Cu(1) atom of an adjacent dicopper(II) unit [Cl(1)–O(4)···Cu(1a) = 3.078(5) Å; symmetry code: (a) =  $x$ ,  $1.5 - y$ ,  $-0.5 + z$ ], concurrently being trapped between two bpm molecules each belonging to one of the two adjacent units, thus developing chains along the crystallographic  $c$  axis [Fig. 8(b) and (c)]. Hydrogen bonds involving the bridging water molecule, the crystallization water molecule, and the uncoordinated perchlorate ion [O(1w)···O(2w) = 2.691(8) Å, O(1w)···O(6) = 2.98(2) Å, and O(2w)···O(8b) = 2.73(2) Å; symmetry code: (a) =  $x - 1$ ,  $y$ ,  $z$ ] generate chains that run along the crystallographic  $a$  axis in **2** [Fig. 9(b)]. In order to accommodate the uncoordinated perchlorate counteranions and the crystallization acetonitrile molecules, these 1D supramolecular motifs in **2** are less closely packed than those observed in **1** [Fig. 8(a) and 9(a)]. So, adjacent supramolecular chains in **2** are arranged along the crystallographic  $c$  axis by means of off-set  $\pi$ - $\pi$  stacking between 4,7-Me<sub>2</sub>phen molecules (interplanar centroid-centroid distance of *ca.* 3.5 Å) and, alternately, weak anion- $\pi$  interactions involving the coordinated perchlorate group (O<sub>perchlorate</sub>-centroid distance in the range of *ca.* 3.2–3.3 Å) [Fig. 9(c)]. Such chain disposition leads to channels along the crystallographic  $a$  axis, where the H-bonded crystallization solvent (both the water and the acetonitrile molecules) and the uncoordinated perchlorate counteranion are hosted [Fig. 9(a)].

In addition, the occurrence of several intermolecular interactions in **3** generates pseudo-channels running along the crystallographic  $a$  axis, where the coordinated perchlorate anions are hosted [Fig. 10(a) and (b)]. These include both

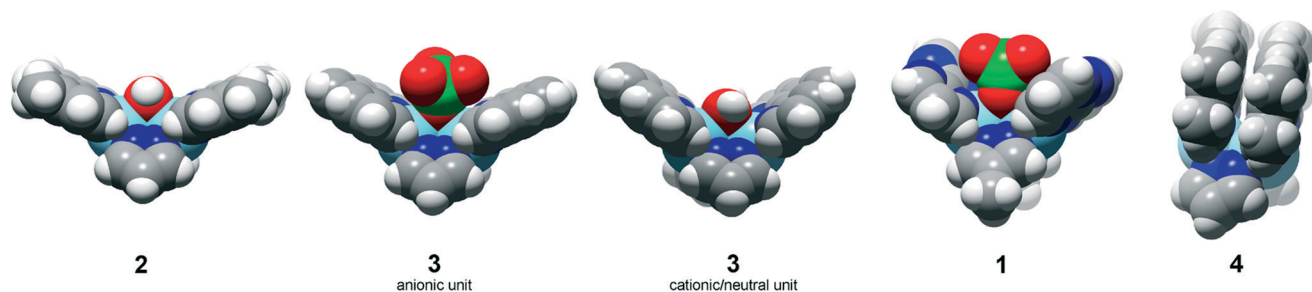


Fig. 6 Space-filling representation of the bis(pyrazolate)(aqua)-, bis(pyrazolate)(perchlorate)-, and bis(pyrazolate)-bridged dicopper(II) units of **1-4**, arranged according to their progressive folding.

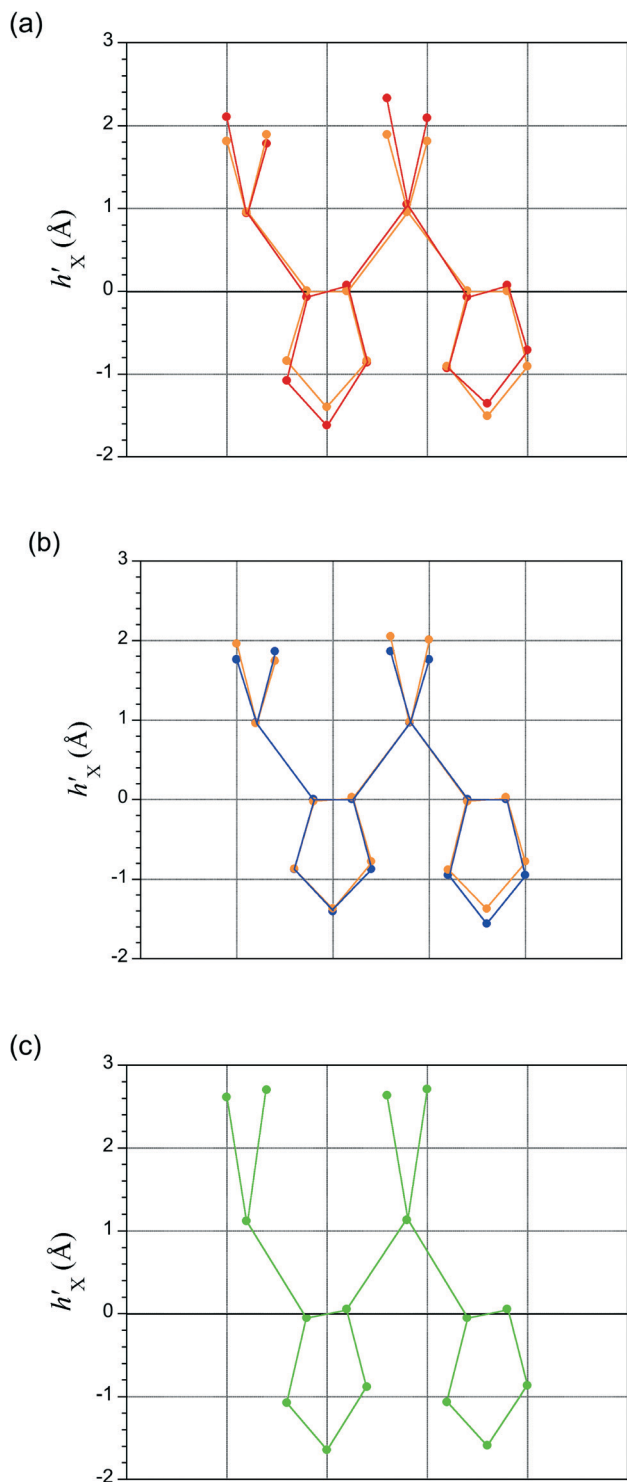


Fig. 7 Plot of the atomic deviations ( $h'_x$ ) of the (a) bis(pyrazolate)perchlorate-, (b) bis(pyrazolate)aqua-, and (c) bis(pyrazolate)-bridged dicopper(II) units from the least-squares plane of the central four-membered  $N_4$  pyrazolenophane core for 1 (red circles), 2 (blue circles), 3 (orange circles), and 4 (green circles).

classical  $\pi$ - $\pi$  stacking of phen moieties (interplanar distances ranging from 3.6 to 4.0 Å) and pz-phen hydrophobic interactions, each phen ligand of the anionic dicopper(II) unit being pinched by the pz double-bridge of either the cationic or

neutral dicopper(II) unit within the supramolecular “trimer-of-dimers” motif in 3 [see Fig. 5(b)]. Columnar stacks of dicopper(II) units along the crystallographic  $b$  axis are found in 4 instead, with alternate intra/inter-molecular  $\pi$ - $\pi$  stacking of 3,4,7,8-Me<sub>4</sub>phen molecules (interplanar distances of *ca.* 3.5 and 3.7 Å, respectively) [Fig. 11(b)]. Adjacent columns are in this case well-separated from each other because of the presence of perchlorate counteranions and coordinated acetonitrile molecules being located within the inter-column space [Fig. 11(a)].

#### Magnetic properties of 1–4

The magnetic properties of 1–4 in the form of the  $\chi_M$  and  $\chi_M T$  vs.  $T$  plots [ $\chi_M$  being the molar magnetic susceptibility per dicopper(II) unit and  $T$  the absolute temperature] are typical of antiferromagnetically coupled  $Cu^{II}_2$  pairs (Fig. 12). At room temperature, the  $\chi_M T$  values in the range of 0.55–0.61  $cm^3 mol^{-1} K$  are lower than that expected for two magnetically isolated  $Cu^{II}$  ions [ $\chi_M T = (2N\beta^2 g^2 / 3k_B) S_{Cu}(S_{Cu} + 1) = 0.83 cm^3 mol^{-1} K$  with  $S_{Cu} = \frac{1}{2}$  and  $g = 2.10$ ]. Upon cooling,  $\chi_M T$  decreases continuously from room temperature while  $\chi_M$

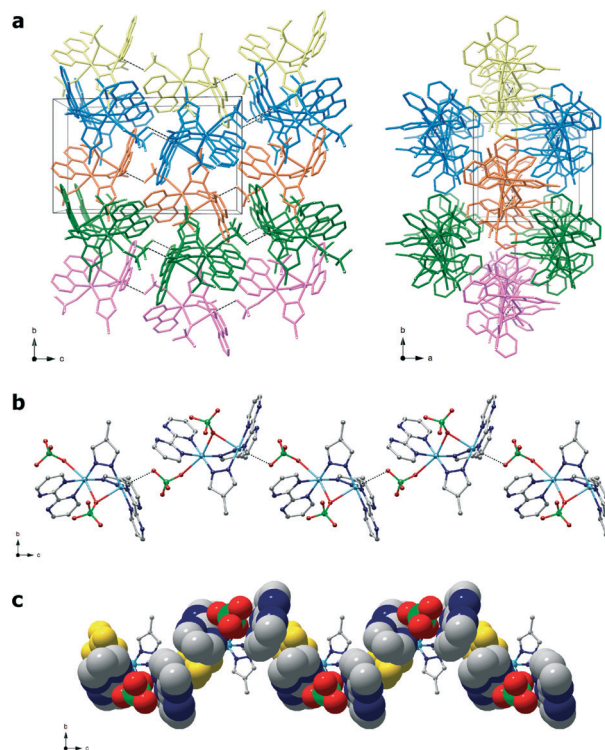
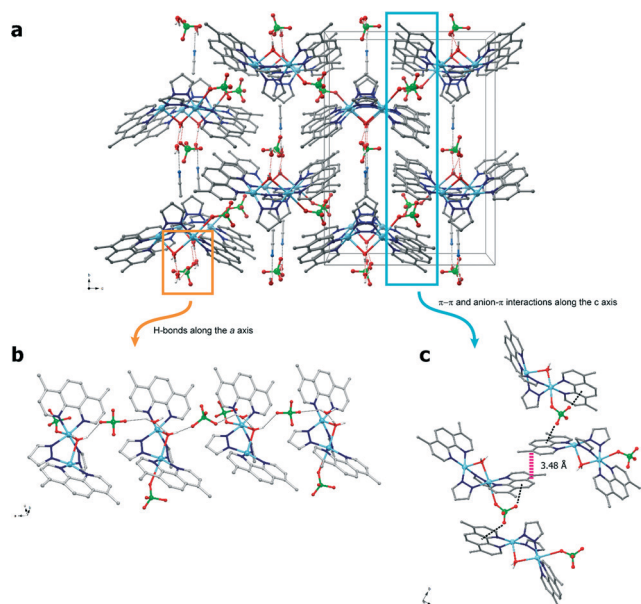
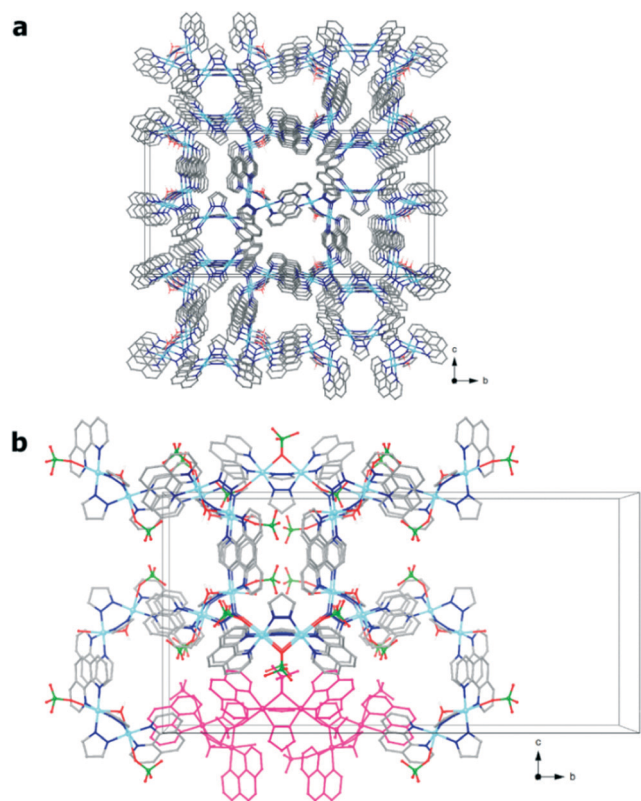


Fig. 8 (a) Views of a portion of the crystal packing of 1 along the  $a$  (left) or the  $c$  (right) crystallographic axis. Neighboring chains are shown in different colors for clarity. (b) and (c) Views of the 1D supramolecular motif generated by adjacent neutral dicopper(II) units in 1 through very weak  $Cu-O_{perchlorate}$  contacts [dashed lines in (b)] and anion- $\pi$  interactions [see the space-filling model representation in (c)], respectively. The terminal perchlorate anion in (c), trapped between the blocking bpm ligands of two adjacent units, is depicted in yellow for clarity. Hydrogen atoms on the 4-Mepz and bpm ligands are omitted for clarity.

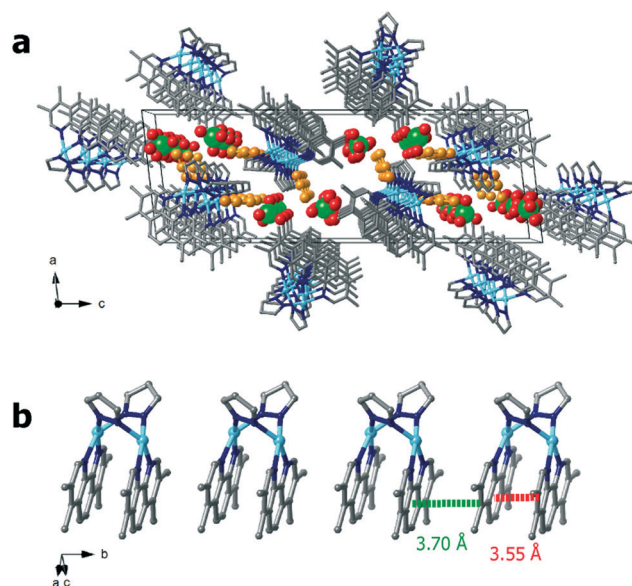




**Fig. 9** (a) Perspective view of a portion of the crystal packing of **2** along the crystallographic *a* axis. Main packing forces are evidenced in (b) and (c). Hydrogen atoms on the pz and 4,7-Me<sub>2</sub>phen ligands are omitted for clarity.



**Fig. 10** (a) and (b) Perspective view of a portion of the crystal packing of **3** along the crystallographic *a* axis, with and without the perchlorate ions, respectively. The supramolecular “trimer-of-dimers” motif is evidenced in (b) with a pink color. Hydrogen atoms on the pz and phen ligands are omitted for clarity.



**Fig. 11** (a) Perspective view of a portion of the crystal packing of **4** along the crystallographic *b* axis. The uncoordinated perchlorate counteranions and the coordinated acetonitrile molecules are represented by a *pseudo* space-filling model, with the acetonitrile molecules colored in orange for clarity. (b) View of a columnar stack of cationic dicopper(II) units in **4** along the crystallographic *b* axis showing the two distinct intra- and intermolecular  $\pi$ - $\pi$  stacking interactions (thick dashed lines). Hydrogen atoms on the pz and 3,4,7,8-Me<sub>4</sub>phen ligands are omitted for clarity, as well as the coordinated acetonitrile molecules.

exhibits a rounded maximum at *ca.* 200 (1), 165 (2), 180 (3), and 170 K (4), which unambiguously demonstrates the occurrence of a singlet ( $S = 0$ ) ground state resulting from the moderate antiferromagnetic coupling between the unpaired electrons of the two Cu<sup>II</sup> ions.

The magnetic properties of **1–4** were analyzed through a spin Hamiltonian for a simple dinuclear model [eqn (1) with  $S_1 = S_2 = S_{\text{Cu}} = \frac{1}{2}$ ], where  $J$  is the magnetic coupling parameter and  $g$  is the average Landé factor of the Cu<sup>II</sup> ions. Satisfactory least-squares fits of the magnetic susceptibility data were obtained through the well-known Bleaney–Bowers expression [eqn (2)] (Table 3).<sup>29</sup> In fact, the theoretical curves closely match the experimental data and, particularly, they reproduce very well the rounded  $\chi_M$  maximum observed experimentally (solid lines in Fig. 12).

$$H = -JS_1 \cdot S_2 + g\beta H(S_1 + S_2) \quad (1)$$

$$\chi_M = (2N\beta^2 g^2 / k_B T) / [3 + \exp(-J/k_B T)] \quad (2)$$

In order to take into account its actual crystal structure, the magnetic properties of **3** were alternatively analyzed through a spin Hamiltonian for a “trimer-of-dimers” model which considers a 2 : 1 stoichiometric ratio of the two distinct bis( $\mu$ -pyrazolate)( $\mu$ -aqua)- and bis( $\mu$ -pyrazolate)( $\mu$ -perchlorate)-dicopper(II) entities [eqn (3) with  $S_1 = S_2 = S_3 = S_4 = S_5 = S_6 = S_{\text{Cu}} = \frac{1}{2}$ ], where  $J$  and  $J'$  are the magnetic coupling parameters

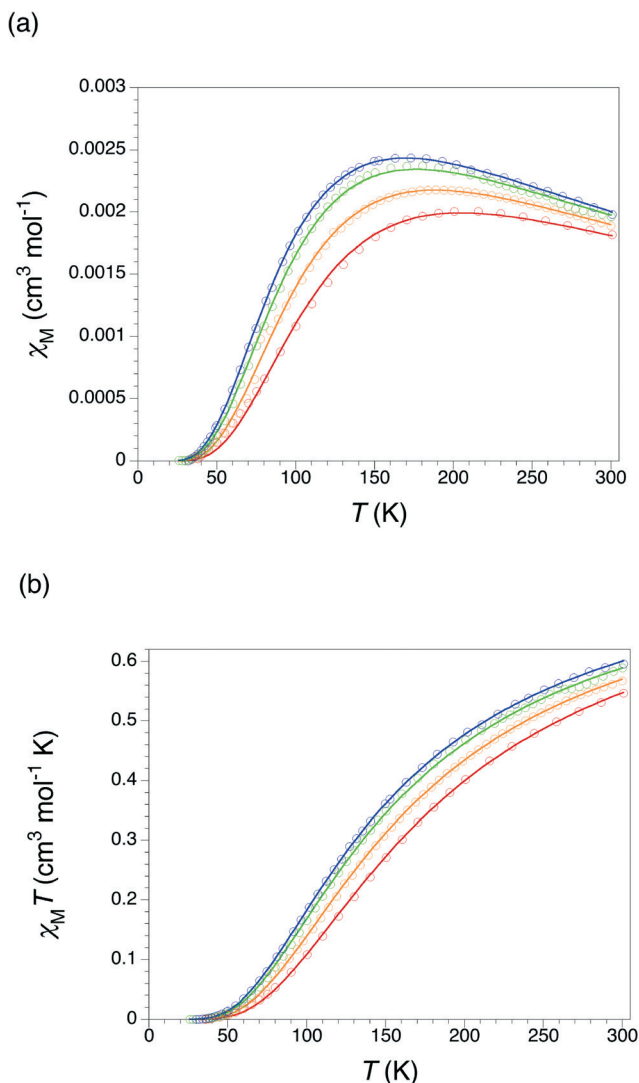


Fig. 12 Temperature dependence of  $\chi_M$  (a) and  $\chi_M T$  (b) for 1 (red circles), 2 (blue circles), 3 (orange circles), and 4 (green circles). The solid lines are the best-fit curves (see text).

for each type of dicopper(II) entity, respectively, and  $g$  is the average Landé factor of the  $\text{Cu}^{\text{II}}$  ions. A satisfactory least-squares fit of the magnetic susceptibility data was obtained through a modified Bleaney–Bowers expression [eqn (4)].

Table 3 Least-squares best-fit magnetic parameters for 1–4

Compound	$J^a/\text{cm}^{-1}$	$J'^a/\text{cm}^{-1}$	$g^b$	$F^c (\times 10^5)$
1	-228(1)		2.082(9)	0.4
2	-189(1)		2.095(1)	0.1
3	-210(1) [-221(1)]	[-193(1)]	2.087(4) [2.093(7)]	0.5 [0.5]
4	-197(1)		2.097(3)	0.2

<sup>a</sup> Values of the magnetic coupling parameters obtained through eqn (1) and (3). The values in square brackets correspond to those obtained through eqn (3). <sup>b</sup> Values of the Landé factor obtained through eqn (1) and (3). The values in square brackets correspond to those obtained through eqn (1). <sup>c</sup> Values of the agreement factor defined as  $F = \sum[(\chi_M T)_{\text{exp}} - (\chi_M T)_{\text{calcd}}]^2 / \sum[(\chi_M T)_{\text{exp}}]^2$ . The values in square brackets correspond to those obtained through eqn (3).

Because of the different weights of each dicopper(II) entity, a unique set of  $J$  and  $J'$  values were univocally obtained for 3, values which would be otherwise undetermined and correlated with each other (Table 3).

$$H = -J(S_1 \cdot S_2 + S_3 \cdot S_4) - J'S_5 \cdot S_6 + g\beta H(S_1 + S_2 + S_3 + S_4 + S_5 + S_6) \quad (3)$$

$$\chi_M = (2N\beta^2 g^2 / k_B T) \{ (2/3) / [3 + \exp(-J/k_B T)] + (1/3) / [3 + \exp(-J'/k_B T)] \} \quad (4)$$

The moderate antiferromagnetic couplings found in 1–4 agree with those previously reported for the aforementioned structurally characterized dicopper(II) pyrazolenophanes with triple bis(pyrazolate)(chloride) and double bis(pyrazolate) bridges ( $-J = 143$ – $268 \text{ cm}^{-1}$ ).<sup>21a,c,d</sup> The values of  $-J$  (and  $-J'$ ) in 1–4 suggest that the additional perchlorate or water bridges are not directly responsible for the small variation of the antiferromagnetic coupling found along this series of dicopper(II) pyrazolenophanes with bis(pyrazolate)(perchlorate) [ $228 \text{ cm}^{-1}$  (1) and  $193 \text{ cm}^{-1}$  (3)], bis(pyrazolate)(aqua) [ $189$  (2) and  $221 \text{ cm}^{-1}$  (3)], and bis(pyrazolate) bridges [ $197 \text{ cm}^{-1}$  (4)]. So, the  $-J$  value of the bis( $\mu$ -pyrazolate)( $\mu$ -perchlorate)dicopper(II) entity in 1 is greater than that of the bis( $\mu$ -pyrazolate)( $\mu$ -aqua)dicopper(II) entity in 2. On the contrary, the  $-J'$  value of the bis( $\mu$ -pyrazolate)( $\mu$ -perchlorate)dicopper(II) entity is smaller than the corresponding  $-J$  value of the bis( $\mu$ -pyrazolate)( $\mu$ -aqua)dicopper(II) entities in 3. Moreover, the bis( $\mu$ -pyrazolate)dicopper(II) entity in 4 has a  $-J$  value which is intermediate between those of the bis( $\mu$ -pyrazolate)( $\mu$ -perchlorate)- and bis( $\mu$ -pyrazolate)( $\mu$ -aqua)dicopper(II) entities in 1–3.

Overall, these features indicate that the strength of the antiferromagnetic coupling in 1–4 is independent of the presence and the nature of the axial supporting bridging ligand, being only governed by the electron exchange interactions between the  $\text{Cu}^{\text{II}}$  ions through the two pyrazolate bridges. Finally, we would like to outline that although several attempts have been performed in order to find appropriate relationships between the strength of the antiferromagnetic coupling and some structural factors, such as the bending of the pyrazolate rings relative to the Cu–N–N–Cu bridging units<sup>21c</sup> or the trigonal distortion of the metal atoms,<sup>21c,d</sup> no general trends were observed along this series of dicopper(II) pyrazolenophanes.

## Conclusions

In this work, we provide a comparative study on the self-assembling, hosting and binding abilities, as well as magnetic properties of a unique series of heteroleptic bis( $\mu$ -pyrazolato)-, bis( $\mu$ -pyrazolate)( $\mu$ -perchlorate)-, and bis( $\mu$ -pyrazolate)( $\mu$ -aqua)-dicopper(II) complexes with polymethyl-substituted aromatic  $\alpha$ -diimines as blocking bidentate ligands. A stereospecific self-assembly of metallacyclophanes with a saddle-type molecular conformation, so-called dicopper(II) pyrazolenophanes, occurs in all these cases, regardless of the nature of the pyrazolate

bridging ligand and/or the blocking  $\alpha$ -diimine ligand. Yet it appears that the nature of the blocking  $\alpha$ -diimine ligand controls the folding of the resulting dicopper(II) pyrazolenophanes in the solid state along this series, so that they interact with exogenous perchlorate anions and neutral water or acetonitrile solvent molecules through either endo or exo coordination. Hence, 1–3 provide novel examples of triply-bridged dicopper(II) pyrazolenophanes with endo coordinated perchlorate anions and/or water molecules as guests, while 4 constitutes a classical example of doubly-bridged dicopper(II) pyrazolenophane with exo coordinated acetonitrile molecules. On the other hand, the weakly exo coordinated perchlorate anions in 1 act as additional bridging ligands between the dicopper(II) pyrazolenophanes to give alternating zigzag chains in the solid state. Concerning their magnetic properties, a moderate antiferromagnetic coupling is found in 1–4, regardless of the nature of the blocking and exogenous bridging ligands. Current efforts are devoted to obtaining general magneto-structural correlations for the vast family of dicopper(II) metallacyclophanes reported in the literature, which might provide additional insights into the orbital mechanism of through-ligand electron exchange coupling in these simple metallacyclic model systems.

## Acknowledgements

This work was supported by the Ministerio Español de Economía y Competitividad (Project CTQ2013-44844P and Unidad de Excelencia MDM-2015-0538) and the Generalitat Valenciana (PROMETEOII/2014/070). We also acknowledge the financial support from Brazilian agency of Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), the Programa Hispano-Brasileño PHB2014-00024 for a stage grant (W. P. B.), and the European Commission (FSE, Fondo Sociale Europeo) and the Calabria Region for a fellowship grant (N. M.). Thanks are also extended to Julia Vallejo (Universitat de València) for the assistance in the magnetic measurements.

## References

- (a) *Transition Metals in Supramolecular Chemistry*, ed. J. P. Sauvage, Wiley, New York, USA, 1999, vol. 5; (b) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; (c) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; (d) P. J. Steel, *Acc. Chem. Res.*, 2005, **38**, 243; (e) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810; (f) H. T. Chifotides and K. R. Dunbar, *Acc. Chem. Res.*, 2013, **46**, 894; (g) T. R. Cook and P. J. Stang, *Chem. Rev.*, 2015, **115**, 7001.
- (a) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; (b) S. Lenninger, B. Olenyuk and J. Stang, *Chem. Rev.*, 2000, **100**, 853; (c) S. R. Seidel and P. J. Stang, *Acc. Chem. Res.*, 2002, **35**, 972.
- (a) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (b) M. Fujita, *Acc. Chem. Res.*, 1999, **32**, 53; (c) M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369.
- (a) M. Albrecht, *Chem. Soc. Rev.*, 1998, **27**, 281; (b) C. A. Schalley, A. Lützen and M. Albrecht, *Chem. – Eur. J.*, 2004, **10**, 1072; (c) M. Albrecht, I. Janser and R. Fröhlich, *Chem. Commun.*, 2005, 157.
- (a) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975; (b) D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185.
- (a) L. K. Thompson, *Coord. Chem. Rev.*, 2002, 233–234, 193; (b) L. N. Dawe, T. S. M. Abedin and L. K. Thompson, *Dalton Trans.*, 2008, 1661.
- (a) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J. M. Lehn, *Angew. Chem., Int. Ed.*, 2004, **43**, 3644; (b) M. Ruben, J. M. Lehn and P. Müller, *Chem. Soc. Rev.*, 2006, **35**, 1056.
- (a) C. S. Campos-Fernández, R. Clérac, J. M. Koomen, D. H. Russell and K. R. Dunbar, *J. Am. Chem. Soc.*, 2001, **123**, 773; (b) C. S. Campos-Fernández, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsá, J. M. Koomen, D. H. Russell and K. R. Dunbar, *J. Am. Chem. Soc.*, 2005, **127**, 12909.
- (a) A. Jouaiti, M. Loï, M. W. Hosseini and A. De Cian, *Chem. Commun.*, 2000, 2085; (b) S.-S. Sun, J. A. Anspach, A. J. Lees and P. Y. Zavalij, *Organometallics*, 2002, **21**, 685; (c) C. L. M. Pereira, E. F. Pedroso, H. O. Stumpf, M. A. Novak, L. Ricard, R. Ruiz-García, E. Rivière and Y. Journaux, *Angew. Chem., Int. Ed.*, 2004, **43**, 956; (d) M. A. Palacios, A. Rodríguez-Diéguez, A. Sironi, J. M. Herrera, A. J. Mota, V. Moreno, J. Cano and E. Colacio, *Eur. J. Inorg. Chem.*, 2008, **33**, 1287; (e) X. Qu, X. Song, W. Li, Y. Xu, L. Li, D. Liao and Z. Jiang, *New J. Chem.*, 2009, **33**, 1901; (f) J. Ferrando-Soria, J. Pasán, C. Ruiz-Pérez, Y. Journaux, M. Julve, F. Lloret, J. Cano and E. Pardo, *Inorg. Chem.*, 2011, **50**, 8694; (g) J. Ferrando-Soria, T. Grancha, J. Pasán, C. Ruiz-Pérez, L. Cañadillas-Delgado, Y. Journaux, M. Julve, J. Cano, F. Lloret and E. Pardo, *Inorg. Chem.*, 2012, **51**, 7019; (h) J. Ferrando-Soria, H. Khajavi, P. Serra-Crespo, J. Gascon, F. Kapteijn, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux and E. Pardo, *Adv. Mater.*, 2012, **24**, 5625; (i) J. Ferrando-Soria, R. Ruiz-García, J. Cano, S.-E. Stiriba, J. Vallejo, I. Castro, M. Julve, F. Lloret, P. Amorós, J. Pasán, C. Ruiz-Pérez, Y. Journaux and E. Pardo, *Chem. – Eur. J.*, 2012, **18**, 1608; (j) J. Ferrando-Soria, P. Serra-Crespo, M. De Lange, J. Gascon, F. Kapteijn, M. Julve, J. Cano, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux and E. Pardo, *J. Am. Chem. Soc.*, 2012, **134**, 15301; (k) T. Grancha, C. Tourbillon, J. Ferrando-Soria, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, O. Fabelo and E. Pardo, *CrystEngComm*, 2013, **15**, 9312; (l) R. A. A. Cassaro, S. Ciattini, S. Soriano, H. S. Amorim, N. L. Speziali, M. Andruh and M. G. F. Vaz, *Cryst. Growth Des.*, 2013, **13**, 2711; (m) H. Lee, T. H. Noh and O.-S. Jung, *Angew. Chem., Int. Ed.*, 2013, **52**, 11790.
- (a) S. J. Lee, A. Hu and W. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 12948; (b) H. Jiang, A. Hu and W. Lin, *Chem. Commun.*, 2003, 96; (c) J. Hua and W. Lin, *Org. Lett.*, 2004, **6**, 861; (d) W. D. Do Pim, W. X. C. Oliveira, M. A. Ribeiro, E. N. De Faria, I. F. Teixeira, H. O. Stumpf, R. M. Lago, C. L. M. Pereira, C. B. Pinheiro, J. C. D. Figueiredo-Júnior, W. C. Nunes, P. P. De Souza, E. F. Pedroso, M. Castellano, J. Cano and M. Julve, *Chem. Commun.*, 2013, **49**, 10778.

- 11 (a) J. Ferrando-Soria, M. Castellano, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, L. Cañadillas-Delgado, Y. Li, Y. Journaux and E. Pardo, *Chem. Commun.*, 2012, **48**, 8401; (b) J. Ferrando-Soria, M. Castellano, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, C. Ruiz-Pérez, J. Pasán, L. Cañadillas-Delgado, D. Armentano, Y. Journaux and E. Pardo, *Chem. – Eur. J.*, 2013, **19**, 12124; (c) M. Castellano, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, Y. Journaux, G. De Munno and D. Armentano, *Chem. Commun.*, 2013, **49**, 3534; (d) M. Castellano, W. P. Barros, A. Acosta, M. Julve, F. Lloret, Y. Li, Y. Journaux, G. De Munno, D. Armentano, R. Ruiz-García and J. Cano, *Chem. – Eur. J.*, 2014, **20**, 13965.
- 12 M. Castellano, J. Ferrando-Soria, E. Pardo, M. Julve, F. Lloret, C. Mathonière, J. Pasán, C. Ruiz-Pérez, L. Cañadillas-Delgado, R. Ruiz-García and J. Cano, *Chem. Commun.*, 2011, **47**, 11035.
- 13 (a) R. Lin, J. H. K. Yip, K. Zhang, L. L. Koh, K.-Y. Wong and K. P. Ho, *J. Am. Chem. Soc.*, 2004, **126**, 15852; (b) M. Sathiyendiran, R.-T. Liao, P. Thanasekaran, T.-T. Luo, N. S. Venkataramanan, G.-H. Lee, S.-M. Peng and K.-L. Lu, *Inorg. Chem.*, 2006, **45**, 10052; (c) P. Thanasekaran, R.-T. Liao, B. Manimaran, Y.-H. Liu, P.-T. Chou, S. Rajagopal and K.-L. Lu, *J. Phys. Chem. A*, 2006, **110**, 10683; (d) J. Hu, M.-H. Nguyen and J. H. K. Yip, *Inorg. Chem.*, 2011, **50**, 7429.
- 14 (a) I. Fernández, R. Ruiz, J. Faus, M. Julve, F. Lloret, J. Cano, X. Ottenwaelder, Y. Journaux and M. C. Muñoz, *Angew. Chem., Int. Ed.*, 2001, **40**, 3039; (b) E. Pardo, J. Faus, M. Julve, F. Lloret, M. C. Muñoz, J. Cano, X. Ottenwaelder, Y. Journaux, R. Carrasco, G. Blay, I. Fernández and R. Ruiz-García, *J. Am. Chem. Soc.*, 2003, **125**, 10770; (c) M. Du, X.-H. Bu, Z. Huang, S.-T. Chen, Y.-M. Guo, C. Díaz and J. Ribas, *Inorg. Chem.*, 2003, **42**, 552; (d) A. R. Paital, T. Mitra, D. Ray, W. T. Wong, J. Ribas-Ariño, J. J. Novoa, J. Ribas and G. Aromí, *Chem. Commun.*, 2005, 5172; (e) A. R. Paital, A. Q. Wu, G. G. Guo, G. Aromí, J. Ribas-Ariño and D. Ray, *Inorg. Chem.*, 2007, **46**, 2947; (f) E. Pardo, R. Carrasco, R. Ruiz-García, M. Julve, F. Lloret, M. C. Muñoz, Y. Journaux, E. Ruiz and J. Cano, *J. Am. Chem. Soc.*, 2008, **130**, 576; (g) M.-C. Dul, X. Ottenwaelder, E. Pardo, R. Lescouëzec, Y. Journaux, L.-M. Chamoreau, R. Ruiz-García, J. Cano, M. Julve and F. Lloret, *Inorg. Chem.*, 2009, **48**, 5244; (h) M. A. Palacios, A. Rodríguez-Diéguez, A. Sironi, J. M. Herrera, A. J. Mota, J. Cano and E. Colacio, *Dalton Trans.*, 2009, 8538; (i) M. Castellano, F. R. Fortea-Pérez, S.-E. Stiriba, M. Julve, F. Lloret, D. Armentano, G. De Munno, R. Ruiz-García and J. Cano, *Inorg. Chem.*, 2011, **50**, 11279; (j) M. Castellano, F. R. Fortea-Pérez, A. Bentama, S.-E. Stiriba, M. Julve, F. Lloret, G. De Munno, D. Armentano, Y. Li, R. Ruiz-García and J. Cano, *Inorg. Chem.*, 2013, **52**, 7645.
- 15 (a) O. M. Yaghi, M. O'Keeffe, M. Eddaoudi, H. K. Chae, J. Kim and N. W. Ockwig, *Nature*, 2003, **423**, 705; (b) C. Janiak, *Dalton Trans.*, 2003, 2781; (c) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (d) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109; (e) D. MasPOCH, D. Ruiz-Molina and J. Veciana, *Chem. Soc. Rev.*, 2007, **36**, 770; (f) E. Pardo, R. Ruiz-García, J. Cano, X. Ottenwaelder, R. Lescouëzec, Y. Journaux, F. Lloret and M. Julve, *Dalton Trans.*, 2008, 2780; (g) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191; (h) G. Férey and C. Serre, *Chem. Soc. Rev.*, 2009, **38**, 130; (i) J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213; (j) V. A. Blatov, M. O'Keeffe and D. M. Proserpio, *CrystEngComm*, 2010, **12**, 44; (k) M.-C. Dul, E. Pardo, R. Lescouëzec, Y. Journaux, J. Ferrando-Soria, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, D. Cangussu, C. L. M. Pereira, H. O. Stumpf, J. Pasán and C. Ruiz-Pérez, *Coord. Chem. Rev.*, 2010, **254**, 2281; (l) T. Grancha, J. Ferrando-Soria, M. Castellano, M. Julve, J. Pasán, D. Armentano and E. Pardo, *Chem. Commun.*, 2014, **50**, 7569.
- 16 (a) D. Fiedler, D. H. Leung, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2005, **38**, 351; (b) M. D. Pluth and K. N. Raymond, *Chem. Soc. Rev.*, 2007, **36**, 161; (c) *Supramolecular Catalysis*, ed. P. W. N. M. van Leeuwen, VCH, Weinheim, Germany, 2008.
- 17 (a) V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759; (b) P. L. Bualas, M. Gómez-Kaifer and L. Echegoyen, *Angew. Chem., Int. Ed.*, 1998, **37**, 216; (c) *Supramolecular Electrochemistry*, ed. A. E. Kaifer and M. Gómez-Kaifer, VCH, Weinheim, Germany, 2000.
- 18 (a) N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Sausalito, California, USA, 1991; (b) L. R. MacGillivray, G. S. Papaefstathiou, T. Friscic, T. D. Hamilton, D. K. Buar, Q. Chu, D. B. Varshney and I. G. Georgiev, *Acc. Chem. Res.*, 2008, **41**, 280; (c) *Supramolecular Photochemistry: Controlling Photochemical Processes*, ed. V. Ramamurthy and Y. Inoue, VCH, Weinheim, Germany, 2011.
- 19 (a) O. Kahn, *Molecular Magnetism*, VCH, New York, USA, 1993; (b) *Magnetism: A Supramolecular Function*, ed. O. Kahn, NATO ASI Series C, Kluwer, Dordrecht, 1996, vol. 484.
- 20 (a) M. Castellano, R. Ruiz-García, J. Cano, J. Ferrando-Soria, E. Pardo, F. Fortea-Pérez, S.-E. Stiriba, M. Julve and F. Lloret, *Acc. Chem. Res.*, 2015, **48**, 510; (b) M. Castellano, R. Ruiz-García, J. Cano, J. Ferrando-Soria, E. Pardo, F. R. Fortea-Pérez, S. Eddine-Stiriba, W. P. Barros, H. O. Stumpf, L. Cañadillas-Delgado, J. Pasán, C. Ruiz-Pérez, G. De Munno, D. Armentano, Y. Journaux, F. Lloret and M. Julve, *Coord. Chem. Rev.*, 2015, **303**, 110.
- 21 (a) D. Ajò, A. Bencini and F. Mani, *Inorg. Chem.*, 1988, **27**, 2437; (b) M. G. B. Drew, P. C. Yates, F. S. Esho, J. Trocha-Grimshaw, A. Lavery, K. P. McKillop, S. M. Nelson and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1988, 2995; (c) H. Matsushima, H. Hamada, K. Watanabe, M. Koikawa and T. J. Tokii, *J. Chem. Soc., Dalton Trans.*, 1999, 971; (d) E. Spodine, A. M. Atria, J. Valenzuela, J. Jalocha, J. Manzur, A. M. Garcís, M. T. Garland, O. Pena and J.-Y. Saillard, *J. Chem. Soc., Dalton Trans.*, 1999, 3029; (e) X. Liu, J. A. McAllister, M. P. De Miranda, E. J. L. McInnes, C. A. Kilner and M. A. Halcrow, *Chem. – Eur. J.*, 2004, **10**, 1827; (f) G. Mezei and R. G. Raptis, *Inorg. Chim. Acta*, 2004, **357**, 3279; (g) T. O. Denisova, E. V. Amelchenkova, I. V. Pruss, Z. V. Dobrokhotova, O. P. Fiaikovskii and S. E. Nifedov, *Russ. J. Inorg. Chem.*, 2006, **51**, 1098; (h) Y. H. Xing, X. J. Zhang, Z.

- Sun, J. Han, Y. H. Zhang, B. L. Zhang, M. F. Ge and S. Y. Niu, *Spectrochim. Acta, Part A*, 2007, **68**, 1256; (i) C. Di Nicola, F. Marchetti, M. Monari, L. Pandolfo and C. Pettinari, *Inorg. Chem. Commun.*, 2008, **11**, 665.
- 22 (a) M. K. Ehlert, S. J. Retting, A. Storr, R. C. Thompson and J. Troter, *Can. J. Chem.*, 1989, **67**, 1970; (b) M. K. Ehlert, S. J. Retting, A. Storr, R. C. Thompson and J. Troter, *Can. J. Chem.*, 1991, **69**, 432; (c) M. K. Ehlert, S. J. Retting, A. Storr, R. C. Thompson and J. Troter, *Can. J. Chem.*, 1992, **70**, 1121.
- 23 *SAINTE*, Version 6.45, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2003.
- 24 *SADABS*, Version 2.03, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2000.
- 25 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
- 26 (a) P. Müller, *Crystallogr. Rev.*, 2009, **15**, 57; (b) P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider and M. R. Sawaya, *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*, ed. P. Müller, IUCR Texts on Crystallography, Oxford University Press, Oxford, 2006.
- 27 *DIAMOND 3.1b*, *Crystal Impact GbR*, *CRYSTAL IMPACT*, ed. K. Brandenburg and H. Putz, GBR, Bonn, Germany, 2006.
- 28 A. W. Addison, T. Nageswara, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
- 29 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.