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Solid-State Anion–Guest Encapsulation by Metallosupramolecular Capsules Made from Two Tetranuclear Copper(II) Complexes

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A new cationic tetranuclear copper(II) complex self-assembles from one 1,3-phenylenebis(oxamato) (mpba) bridging ligand and four Cu^{II} ions partially blocked with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen) terminal ligands. In the solid state, two of these tetracopper(II) oxamato complexes of bowl-like shape and helical conformation then serve as a building block for the generation of either hetero- (*MP*) or homochiral (*MM*/*PP*) dimeric capsules depending on the nature of the encapsulated anion guest, perchlorate or hexafluorophosphate. The overall magnetic behaviour of these metallosupramolecular capsules does not depend on the nature of the encapsulated anion guest, but it is consistent with the dimer-of-dimer structure of the tetracopper(II) cation host, where the interdimer magnetic coupling through the *meta*-phenylenediamidate bridge is negligibly small relative to the reasonably strong intradimer one across the oxamato bridge.

Introduction

Coordination chemistry offers many possibilities for the construction of a seemingly limitless range of metallosupramolecular species based on metal–ligand coordinative interactions.[1] These include a great variety of metal cages formed by the self-assembly of rigid organic ligands and transition metal ions.[2–10] Some of them are formed with the use of templates and counterions, either cations[3] or anions,[4–7] that are hosted within the confined space of the charged metal cage and held through ionic interactions and/or weak coordination bonds. Others are even able to reversibly bind or stabilise neutral guest molecules through hydrophobic interactions and/or hydrogen bonds.[8] In contrast to their purely organic analogues prepared from covalent synthesis[9] and/or hydrogen-bond-directed self-assembly,[10] these metallosupramolecular capsules may possess other interesting properties ligated to the presence of the transition metal ions. Thus, the combination of the encapsulation ability with other metal-based electronic properties (redox, optical or magnetic) would render these assemblies suitable for applications as molecular sensors or switches.

In the search for self-assembling metallosupramolecular complexes with aromatic dioxamato ligands,[11a] we recently prepared double- and triple-stranded binuclear copper(II) complexes of the metallacyclophane- and metallacryptand-type from the self-assembly of two Cu^{II} ions and either two or three 1,3-phenylenebis(oxamato) (mpba) ligands, respectively, which then served as building blocks for discrete hexa- and octanuclear copper(II) complexes.[11b–11d] In this communication, we report the syntheses, X-ray crystal structures and magnetic properties of two new tetranuclear oxamato copper(II) complexes of formula $[Cu_4(mpba)(tmen)_4(H_2O)_4](ClO_4)_4\cdot 3H_2O$ (**1a**) and $[Cu_4(mpba)(tmen)_4(H_2O)_4](PF_6)_4\cdot 2H_2O$ (**1b**) (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), which constitute unique examples of anion guest encapsulation in the solid state.

Results and Discussion

Complexes **1a** and **1b** were synthesised in one step by a stoichiometric reaction (1:4) in water of the diethyl ester derivative of 1,3-phenylenebis(oxamic acid)-(H_2Et_2mpba),[11a] previously treated with 4 equiv. of NaOH

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that serve to deprotonate and hydrolyse the amide and ester groups, respectively, and the perchlorate or nitrate salts of the cationic mononuclear copper(II) complex [Cu(tmen)]$^{2+}$, which were prepared in situ from a mixture of either Cu(ClO_4)$_2$·$6H_2O$ or Cu(NO_3)$_2$·$3H_2O$ and tmen in a 1:1 relation. They were isolated as either the perchlorate (**1a**) or the hexafluorophosphate (**1b**) salts by addition of KPF_6 at the end of the reaction in the latter case.

The structures of **1a** and **1b** consist of tetranuclear copper(II) cations, [Cu_4(mpba)(tmen)$_4$(H_2O)$_4$]$^{4+}$ (Figure 1), crystallisation water molecules and either perchlorate or hexafluorophosphate anions, respectively. The tetracopper(II) cations are formed by four [Cu(tmen)(H_2O)]$^{2+}$ subunits connected by the tetrakis(bidentate) mpba ligand, which adopts a helical conformation with the two oxamato bridging groups tilted up and down with respect to the plane of the *m*-phenylene spacer. The values of the torsion angle around the N(amide)–C(phenylene) bonds (ϕ) are 91.0(3) and 108.8(4)° for **1a** and 90.7(5) and 112.7(6)° for **1b**, values which are greater than that of H_2Et_2mpba [ϕ = 32.6(5)°].[11a] This gives rise to chiral bisbinuclear entities of pseudo-twofold symmetry, either *M* or *P* helical conformers, which are made up of two oxamato-bridged Cu^{II}_2 units connected through a *meta*-phenylenediamidate bridge between one of the two copper atoms of each binuclear unit (Figure 1, left). The intramolecular distances between the copper atoms through the oxamato bridge average 5.190(2) (**1a**) and 5.224(2) Å (**1b**), whereas those through the *meta*-phenylenediamidate bridge are 7.762(2) (**1a**) and 7.571(2) Å (**1b**).

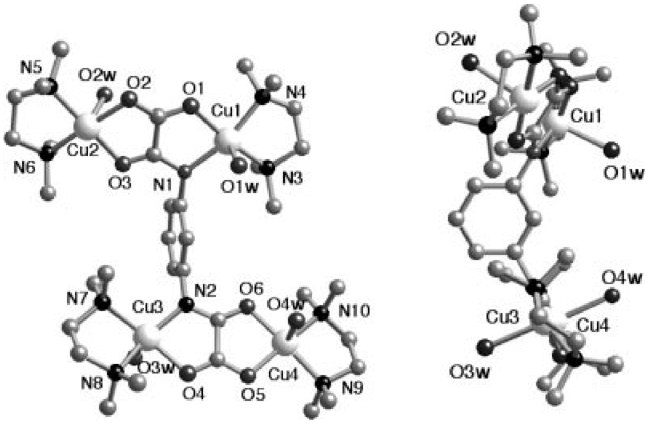

Figure 1. Front and side views of the cationic tetracopper unit of **1a** with the atom numbering scheme for the metal coordination environments (hydrogen atoms are omitted for clarity). Selected intermetallic distances [Å] with standard deviations in parentheses: Cu1–Cu2 5.199(2), Cu1–Cu3 7.762(2), Cu1–Cu4 7.989(2), Cu2–Cu3 7.796(2), Cu2–Cu4 10.844(2) and Cu3–Cu4 5.180(2) for **1a**; Cu1–Cu2 5.229(2), Cu1–Cu3 7.571(2), Cu1–Cu4 8.122(2), Cu2–Cu3 7.654(2), Cu2–Cu4 10.934(2) and Cu3–Cu4 5.218(2) for **1b**.

The four crystallographically independent copper atoms of **1a** and **1b** exhibit five-coordinate square pyramidal geometries, CuN_3O_2 for Cu1 and Cu3 and CuN_2O_3 for Cu2 and Cu4, with axially coordinated water molecules [Cu–Ow 2.283(8)–2.521(9) for **1a** and 2.365(7)–2.460(6) Å for **1b**], which are arranged in a *trans* position within each binuclear unit (Figure 1, right). The values of the geometric τ parameter are in the range 0.02–0.20 (for **1a**) and 0.01–0.12 (for **1b**) (τ = 0 and 1 for ideal square pyramidal and trigonal bipyramidal geometries, respectively).[11d] The two oxamato groups of the mpba ligand coordinate through the amidate nitrogen and carboxylate oxygen atoms to the Cu1 and Cu3 atoms [Cu–N 1.997(6)–2.012(7) (**1a**) and 2.002(6)–2.004(6) Å (**1b**); Cu–O 1.979(5)–2.004(7) (**1a**) and 1.984(5)–2.003(6) Å (**1b**)] and through the carbonyl oxygen atoms to the Cu2 and Cu4 atoms [Cu–O 1.948(5)–1.965(9) (**1a**) and 1.951(5)–1.996(5)(**1b**)], whereas the remaining positions of the equatorial plane are occupied by two amine nitrogen atoms from the tmen ligands [Cu–N 1.994(7)–2.048(7) (**1a**) and 2.000(7)–2.036(8) Å (**1b**)]. The copper basal planes and the oxamato plane of each binuclear unit are quite coplanar [dihedral angles in the range 3.8(2)–17.7(2) (**1a**) and 6.7(2)–11.2(2)° (**1b**)], whereas they are almost perpendicular to the phenylene plane [dihedral angles in the range 70.4(3)–89.3(2) (**1a**) and 75.4(2)–84.1(2)° (**1b**)]. Because of the *meta* topology of the ligand spacer, the two mean planes of the two oxamato bridging groups form a dihedral "bite" angle of 54.5(2) (**1a**) and 53.9(1)° (**1b**), which thus confers a global bowl-like shape to the tetracopper(II) cations (Figure 1, right).

Interestingly, two symmetry-related, bowl-shaped tetranuclear copper(II) cations of opposite (**1a**) or identical (**1b**) chirality encapsulate two perchlorate and three hexafluorophosphate anions, respectively, to yield either a centrosymmetric heterochiral (*MP* mesomer) or a racemic mixture of twofold homochiral (*MM* and *PP* enantiomers) dimeric capsules (Figure 2a and Figure 2b, respectively). The diastereoisomer differentiation that occurs in these 2:2 and 2:3 host–guest complexes, {2(ClO_4)Ì*meso*-(*MP*)-[Cu_4(mpba)(tmen)$_4$(H_2O)$_4$]$_2$}$^{6+}$ and {3(PF_6)Ì*rac*-(*MM*/*PP*)-[Cu_4(mpba)(tmen)$_4$(H_2O)$_4$]$_2$}$^{5+}$, respectively, would be likely related to the different size and geometry of the tetrahedral perchlorate and octahedral hexafluorophosphate anions. The intermolecular distances between the equivalent copper atoms from each tetranuclear cation are in the range 9.988(2)–14.626(2) (**1a**) and 7.031(2)–14.135(2) Å (**1b**), values which can be taken as the approximate dimensions of these nanometre-sized metallosupramolecular capsules.

The encapsulated ClO_4^- and PF_6^- anions establish weak dative interactions with the coordinatively unsaturated copper atoms [Cu–O 2.894(2) Å (**1a**) and Cu–F 3.044(8)–3.221(8) Å (**1b**)], together with hydrogen bonds with the axially coordinated water molecules pointing toward the inner side of the capsule [Ow–O 2.977(9) Å (**1a**) and Ow–F 2.858(8)–2.933(8) Å (**1b**)]. These coordinative and hydrogen-bonding interactions between the cationic hosts and the anionic guests contribute to stabilise the resulting noncovalent capsules, together with the host–guest Coulombic attractions. The two encapsulated ClO_4^- anions in **1a** occupy equivalent positions within the confined space of the capsule [Cl3–Cl3^I 5.247(4) Å] (Figure 2a), whereas the three encapsulated PF_6^- anions in **1b** are disposed in a triangular

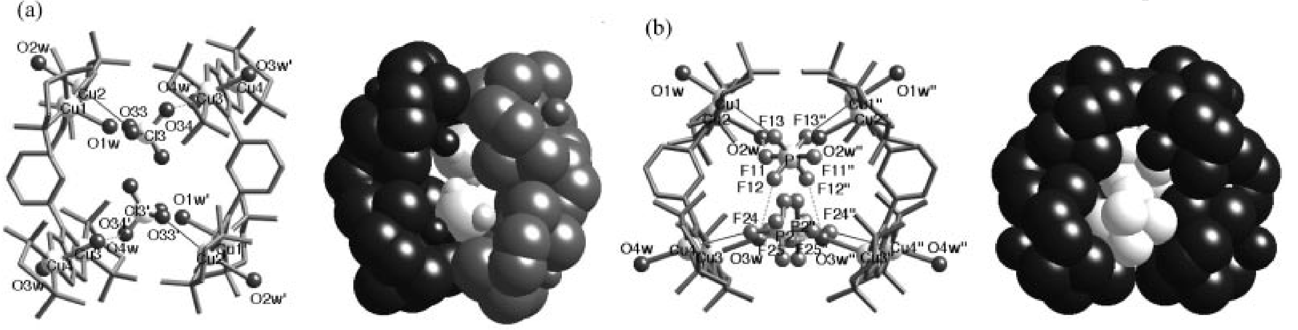

Figure 2. Perspective views of the dimeric capsule of **1a** (a) and **1b** (b) with two and three encapsulated perchlorate and hexafluorophosphate anions, respectively (hydrogen atoms are omitted for clarity). Coordinative and hydrogen bonds with the encapsulated anions are drawn as solid and dashed lines, respectively, in the ball-and-stick model (left). Atoms from each tetracopper helical unit are represented by black (*M* conformer) and grey (*P* conformer) spheres, whereas those of the encapsulated perchlorate and hexafluorophosphate anions are white in the space-filling model (right). Selected intermetallic distances [Å] with standard deviations in parentheses: Cu1–Cu1^{I} 9.988(2), Cu2–Cu2^{I} 14.626(2), Cu3–Cu3^{I} 10.718(2) and Cu4–Cu4^{I} 11.674(2) for **1a**; Cu1–Cu1^{II} 7.031(2), Cu2–Cu2^{II} 10.094(2), Cu3–Cu3^{II} 7.485(2) and Cu4–Cu4^{II} 14.135(2) for **1b** (I = $-x$, $-y$, $-z$; II = $-x$, y, $1/2 - z$).

arrangement [P1–P2 5.632(6) Å and P2–P2^{II} 8.898(7) Å] (Figure 2b).

In the crystal lattice, some of the unencapsulated ClO_4^- and PF_6^- anions also establish weak coordinative bonds with the copper atoms [Cu–O 2.874(8) Å (**1a**) and Cu–F 3.411(8) Å (**1b**)] and hydrogen bonds with the axially coordinated water molecules pointing toward the outer side of the capsule [Ow–O 2.563(8)–2.918(8) Å (**1a**) and Ow–F 2.951(8)–2.959(8) Å (**1b**)]. This situation gives rise to a rather close packing of the spherical-shaped capsules for **1a** and **1b** (Figure 3a and Figure 3b, respectively). Certainly, these intermolecular interactions can play a nonnegligible role in the different metallosupramolecular structural motifs of **1a** and **1b**.

The magnetic properties of **1a** and **1b** in the form of both χ_M and $\chi_M T$ versus T plots (χ_M being the magnetic susceptibility per Cu_4 unit and T the temperature) indicate an overall antiferromagnetic interaction with a singlet spin ($S = 0$) ground state (Figure 4). At 315 K, $\chi_M T$ is 0.82 (**1a**) and 0.88 $cm^3\,K\,mol^{-1}$ (**1b**), values which are well below that expected for four magnetically isolated Cu^{II} ions ($\chi_M T = 1.65\,cm^3\,mol^{-1}\,K$ with $g = 2.1$). Upon cooling, $\chi_M T$ decreases continuously and vanishes around 60 (**1a**) and 50 K (**1b**), whereas χ_M shows a rounded maximum at 310 (**1a**) and 295 K (**1b**).

The temperature dependence of the magnetic susceptibility data of **1a** and **1b** were fitted according to the spin Hamiltonian for a "dimer-of-dimers" model, $\mathbf{H} = -J(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_3\cdot\mathbf{S}_4) - J'(\mathbf{S}_1\cdot\mathbf{S}_3) + g\beta(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4)\cdot B$ [Equation (1), with $S_1 = S_2 = S_3 = S_4 = S_{Cu} = 1/2$], where J ($J = J_{12} = J_{34}$) and J' ($J' = J_{13}$) are the intra- and interdimer coupling constants, respectively, and g is the Zeeman factor of the Cu^{II} ions.[12] In this model, the interdimer interactions given by J'' ($J'' = J_{14} = J_{23}$) and J''' ($J''' = J_{24}$) were ignored because they involve longer exchange pathways. The quality of the fit according to this model does not depend on the sign and magnitude of the J' value, which can be varied from zero to a few tens of cm^{-1}, either positive or negative, with a relatively small variation in the J value.[13]

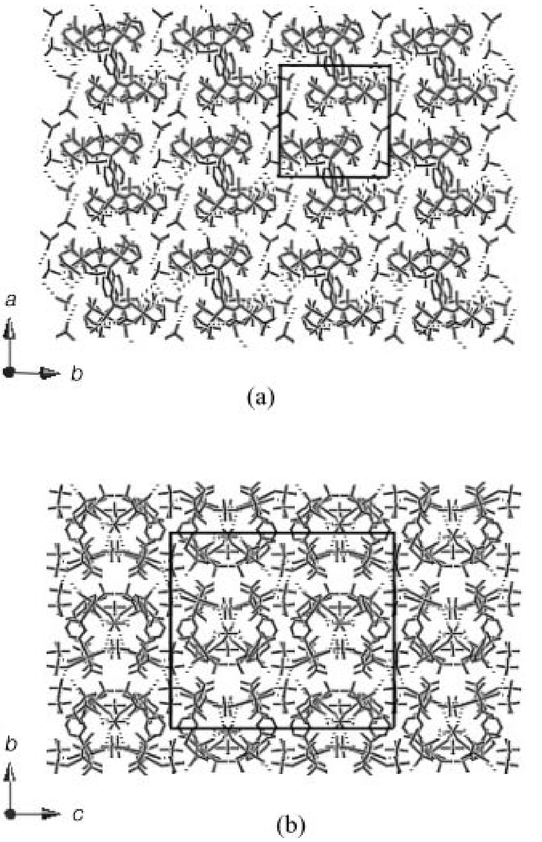

Figure 3. View of the crystal packing of the dimeric capsules of **1a** (a) and **1b** (b) with both encapsulated and unencapsulated perchlorate and hexafluorophosphate anions, respectively, and crystallisation water molecules (hydrogen atoms are omitted for clarity). Coordinative and hydrogen bonds with the anions are drawn as solid and dashed lines, respectively.

This fact suggests that the interdimer magnetic coupling through the *meta*-phenylenediamidate bridge is negligible relative to the intradimer one across the oxamato bridge. Least-squares fit of the experimental data through the Bleaney–Bowers equation for a dimer model ($J' = 0$) gave

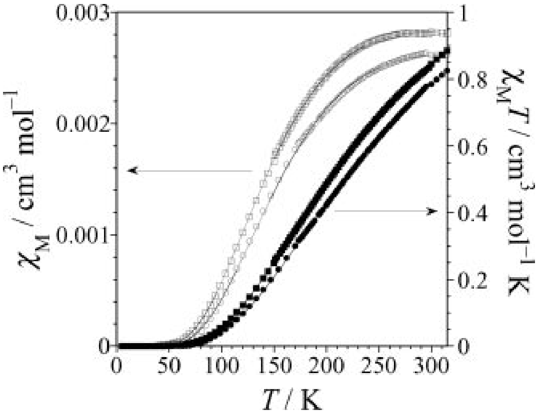

Figure 4. Temperature dependence of χ_M and $\chi_M T$ for **1a** (○,●) and **1b** (□,■). The solid lines are the best fit curves (see text).

$J = -350\ \text{cm}^{-1}$, $g = 2.09$ and $R = 3.4 \times 10^{-8}$ for **1a**, and $J = -330\ \text{cm}^{-1}$, $g = 2.10$ and $R = 3.0 \times 10^{-8}$ for **1b** {R is the agreement factor defined as $R = \Sigma[(\chi_M T)_{\text{exp}} - (\chi_M T)_{\text{calcd}}]^2/\Sigma[(\chi_M T)_{\text{exp}}]^2$}. The theoretical curves reproduce very well the experimental data over the whole temperature range (solid lines in Figure 4). The calculated $-J$ values for **1a** and **1b** agree with those reported for related strong antiferromagnetically coupled oxamato-bridged dicopper(II) complexes ($-J = 366$–$425\ \text{cm}^{-1}$).[14]

Conclusions

Discrete cationic tetranuclear copper(II) complexes possessing a helical conformation and a bowl-like shape were self-assembled through metal–ligand coordinative interactions from a *m*-phenylenedioxamato acting as a tetrakis(bidentate) bridging ligand toward four Cu^{II} ions with a diamine as a blocking ligand. Importantly, two of these tetracopper(II) cations further self-assemble in the solid state through noncovalent host–guest interactions (Coulombic attractions, weak coordination and hydrogen bonds) with anions of different size and geometry to yield unusual examples of homo- and heterochiral metallosupramolecular capsules. Current efforts are devoted to analyse the influence of the nature of the ligand spacer (size, rigidity and substitution pattern) of related tetranuclear copper(II) oxamato complexes on their anion encapsulation ability in the solid state.

Experimental Section

Preparation of the Complexes: A solution of H_2Et_2mpba (0.077 g, 0.25 mmol) in water (10 mL) and NaOH (0.040 g, 1.0 mmol) was added dropwise to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.0 mmol) and tmen (0.150 mL, 1.0 mmol) in water (10 mL). The obtained deep-green solution was filtered and allowed to evaporate in air at room temperature. X-ray quality green prisms of **1a** were obtained after several days on standing. Yield: 0.36 g (75%). IR (KBr): $\tilde{\nu}$ = 3419 (OH), 2986 and 2909 (CH), 1636 (CO), 1144, 1113, and 1089 (ClO) cm^{-1}. $C_{34}H_{82}Cl_4Cu_4N_{10}O_{29}$ (1491.06): calcd. C 27.36, H 5.50, N 9.39; found C 27.06, H 5.45, N 9.45.

Complex **1b** was prepared in a similar way as described for **1a**, but with the use of $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g, 1.0 mmol), and solid KPF_6 (0.19 g, 1.0 mmol) was added at the end of the reaction. X-ray quality green prisms of **1b** were obtained by slow evaporation at room temperature of the deep-green filtered solution after 1 d. Yield: 0.31 g (80%). IR (KBr): $\tilde{\nu}$ = 3428 (OH), 2991 and 2930 (CH), 1633 (CO), 841 (PF) cm^{-1}. $C_{34}H_{80}Cu_4F_{24}N_{10}O_{12}P_4$ (1655.12): calcd. C 24.65, H 4.83, N 8.46; found C 24.34, H 4.72, N, 8.68.

X-ray Crystallographic Data: $C_{34}H_{82}Cl_4Cu_4N_{10}O_{29}$ (**1a**), M = 1491.06, triclinic, space group $P\bar{1}$, a = 14.3494(9) Å, b = 14.8957(15) Å, c = 15.1787(19) Å, α = 70.862(8)°, β = 86.966(6)°, γ = 88.797(6)°, V = 3060.7(5) Å^3, T = 100(2) K, Z = 2, $\rho_{\text{calcd.}}$ = 1.618 g cm^{-3}, μ(Mo-K_α) = 1.634 mm^{-1}. $C_{34}H_{80}Cu_4F_{24}N_{10}O_{12}P_4$ (**1b**), M = 1655.12, monoclinic, space group $C2/c$, a = 16.045(2) Å, b = 26.659(2) Å, c = 30.758(3) Å, β = 96.187(10)°, V = 13080(3) Å^3, T = 293(2) K, Z = 8, $\rho_{\text{calcd.}}$ = 1.681 g cm^{-3}, μ(Mo-K_α) = 1.506 mm^{-1}. 13164 (**1a**) and 14223 (**1b**) unique reflections, and 11057 (**1a**) and 6115 (**1b**) observed with $I > 2\sigma(I)$. All the measured independent reflections were used in the analysis. The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 by using the SHELXS-97 and SHELXL-97 programs. The hydrogen atoms from the organic ligands were calculated and refined with isotropic thermal parameters, whereas those from the water molecules were neither found nor calculated. Refinement of 730 (**1a**) and 790 (**1b**) variables with anisotropic thermal parameters for all non-hydrogen atoms gave R = 0.0743 (**1a**) and 0.0854 (**1b**), and R_w = 0.1920 (**1a**) and 0.1379 (**1b**), with S = 1.058 (**1a**) and 1.013 (**1b**) (observed data).

CCDC-650175 (**1a**) and -650176 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements: Variable-temperature (2.0–315 K) magnetic susceptibility measurements were carried out on powdered samples of **1a** and **1b** with a Quantum Design SQUID magnetometer. The magnetic data were corrected for diamagnetism of the sample holder and the constituent atoms and for the temperature-independent paramagnetism of the copper atoms (60×10^{-6} cm^3 per Cu^{II} ion) as well.

Acknowledgments

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[13] Least-squares fit of the magnetic susceptibility data of **1a** and **1b** by full-matrix diagonalisation of the appropriate spin Hamiltonian for a tetranuclear model, $\mathbf{H} = -J(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_3\cdot\mathbf{S}_4) - J'(\mathbf{S}_1\cdot\mathbf{S}_3) - J''(\mathbf{S}_1\cdot\mathbf{S}_4 + \mathbf{S}_2\cdot\mathbf{S}_3) - J'''(\mathbf{S}_2\cdot\mathbf{S}_4) + g\beta(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4)\cdot B$ [Equation (2), with $S_1 = S_2 = S_3 = S_4 = S_{\mathrm{Cu}} = 1/2$], leads to the same conclusions than those derived from the dimer-of-dimers model.

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