

2_{∞} [Cu₂(μ₅-btb)(μ-OH)(μ-H₂O)]: a two-dimensional coordination polymer built from ferromagnetically coupled Cu₂ units (btb = benzene-1,2,3-tricarboxylate)[†]

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Hydrothermal reaction of Cu(NO₃)₂·3H₂O, Cd(OH)₂ or Zn(OH)₂ with benzene-1,2,3-tricarboxylic acid (H₃btb, hemimellitic acid) produced the 2D coordination polymer (MOF)

2_{∞} [Cu₂(μ₅-btb)(μ-OH)(μ-H₂O)] (1) and the 2D hydrogen-bonded complexes [Cd(H₂btb)₂(H₂O)₄]·2H₂O (2) and [Zn(H₂O)₆](H₂btb)₂·4H₂O (3) which are characterized by single-crystal X-ray diffraction, X-ray powder diffraction and thermoanalysis. Magnetic susceptibility measurements between 1.9–300 K for 1 revealed three magnetic active exchange pathways that link the copper(II) ions through a long μ-aqua bridge, an *anti-syn* carboxylate bridge [*j*₂ = 0.161(1) cm⁻¹], and through a mixed μ-hydroxo + *syn-syn* carboxylate bridge [*J* = 83(1) cm⁻¹]. At temperatures higher than 30 K the system behaves as isolated Cu₂ units with strong ferromagnetic Cu–Cu coupling through the μ-hydroxo and *syn-syn* carboxylate bridge. The strong ferromagnetic coupling is explained with Hoffmann's approach by means of the concept of counter-complementarity introduced by Nishida *et al.* [Chem. Lett., 1983, 1815–1818]

Introduction

Metal–organic frameworks (MOFs) or coordination polymers attract much attention because of topology and potential applications in catalysis, adsorption (gas storage), luminescence, magnetism *etc.*^{1–3} Multi-carboxylate ligands with suitable spacers, especially benzene-multicarboxylate ligands are frequent choices for metal–organic networks.^{1,2,4} Benzene-1,3,5-tricarboxylic acid (H₃btc, trimesic acid) has been extensively used in the form of its three benzene-1,3,5-tricarboxylate anions H_{*n*}btc^{(3–*n*)–} (*n* = 0, 1, 2) as a bridging ligand in the synthesis of multidimensional MOFs. Recent examples (metals as cations and ligand-bridging mode in parentheses) are for H₂btc[–] (Mn–μ₂)⁵, for Hbtc^{2–} (Mn–μ₂,⁶ Mn–μ₃,^{6,7} Co–μ₂,⁸ Co–μ₃,^{9,10} Ni–μ₃,⁹ Cu–μ₂,¹⁰ Zn–μ₂,^{9,10,11} Zn–μ₃ and Zn–μ₄,¹⁰ Cd–μ₃,¹²) and for btc^{3–}, (Fe–μ_{2,3},¹³ Co–μ₂,¹⁴ Co–μ₃,¹⁵ Ni–μ₂,^{16,17} Ni–μ₃,^{17,18} Cu–μ_{2,3},¹⁹ Cu–μ₃,²⁰ Zn–μ₃,^{18,21} Ag–μ₃,²² Ag–μ_{5,6},²³ In–μ₃,²⁴ Y–μ₂,²⁵). In comparison, there are only a handful of structurally authenticated molecular complexes^{26,27} and coordination networks^{28–31} with the anions of benzene-1,2,3-tricarboxylic acid (H₃btb, hemimellitic acid).³² The btb^{3–} ligand possesses polar and non-polar regions, special orientations and strong steric hindrance of its three carboxylate groups to form frameworks which cannot be achieved by other symmetric benzene carboxylates, such as benzene-1,4-dicarboxylate,³³ benzene-1,3,5-tricarboxylate

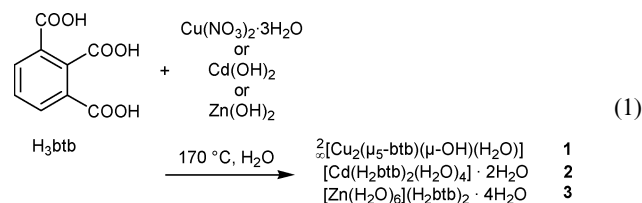
and benzene-1,2,4,5-tetracarboxylate.³⁴ Assembling polynuclear copper complexes with the aid of polydentate ligands is of great interest, including magnetic phenomena.³⁵

Herein, we report the synthesis and structure of the 2D coordination polymer [Cu₂(μ₅-btb)(μ-OH)(H₂O)] (1), which displays strong ferromagnetic interactions, and of the 2D-hydrogen-bonded molecular complexes [Cd(H₂btb)₂(H₂O)₄]·2H₂O (2) and [Zn(H₂O)₆](H₂btb)₂·4H₂O (3).

Results and discussion

Syntheses

Hydrothermal treatment of metal salts with benzene-1,2,3-tricarboxylic acid (H₃btb) yield metal complexes of the carboxylate with various composition (eqn (1)).



Metal complexes with the benzene-1,2,3-tricarboxylate ligand seem to have a propensity to crystallize in more or less thin plates. This plate-shaped crystal morphology often hampered single-crystal data collection and refinement. Only the crystal structures of compounds 1 and 2 could be solved and satisfactorily refined. A crystallographic data set was collected for compound 3 with the triclinic cell parameters *a* = 6.6584(4), *b* = 6.6632(5), *c* = 16.376(2) Å, *α* = 93.318(5), *β* = 92.635(5), *γ* = 117.580(3)^o and *V* = 640.74(8) Å³, which upon refinement in space group *P* $\bar{1}$ showed a structure of composition [Zn(H₂O)₆](H₂btb)₂·4H₂O but did not refine to satisfactory *R* values. This was presumably due to the

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plate-shaped crystal morphology (crystal size $0.410 \times 0.260 \times 0.020$ mm). Space group and cell parameters match with those of the analogous [hexaaquanickel(II)] bis(dihydrogen benzene-1,2,3-tricarboxylate) tetrahydrate compound [CSD-Refcode KIXLIM, $a = 6.671(1)$, $b = 6.683(1)$, $c = 16.357(3)$ Å, $\alpha = 93.10(2)$, $\beta = 92.85(1)$, $\gamma = 117.69(1)^\circ$].²⁶

Thermal stability

Compound **1** is thermally stable until 210 °C where the first weight loss is observed by thermogravimetric analysis (Fig. S1 in ESI†) from 210–280 °C which corresponds to the removal of the aqua ligand (obs. 5.2, calcd 4.9%). Between 300–400 °C, decomposition and loss of the carboxylate ligand takes place (obs. 48.4%, calcd for $C_9H_3O_6-O$ 51.7%) presumably to leave copper oxide, CuO, upon a further slight and gradual weight loss until 600 °C (remaining mass obs. 46.3, calcd 43.1%).

IR

The absence of the –COOH absorption band at 1700 cm^{-1} for the free H_3btb ligand in **1** is indicative of the full deprotonation to btb^{3-} . The shift to lower frequencies of $\nu_{asym}CO_2$ at 1613, 1582 and $\nu_{sym}CO_2$ at 1457, 1395 cm^{-1} in the IR spectrum of **1** compared to $\nu_{asym}CO_2$ at 1700, 1588 cm^{-1} and $\nu_{sym}CO_2$ at 1471, 1411 cm^{-1} for H_3btb indicates that all btb oxygen atoms are involved in copper coordination,³⁶ which is consistent with the X-ray structure (see below).

X-Ray crystallography

Single crystals of **1** and **2** used for the structure determination were ascertained to be representative of the bulk sample by positive comparison of the X-ray powder diffractogram from the bulk to the calculated pattern from the single-crystal structure refinement (Fig. S5 and S6 in ESI†).

Crystal structure of $[\text{Cu}_2(\mu_5\text{-btb})(\mu\text{-OH})(\mu\text{-H}_2\text{O})]$ (1**).** The asymmetric unit of **1** (Fig. 1) contains two crystallographically independent Cu(II) atoms, bridged by a hydroxo ligand and a *syn-syn*-coordinated carboxylate group ($\text{Cu}2^1 \cdots \text{Cu}2 = 3.083$ Å) or by a *syn-anti*-coordinated carboxylate group ($\text{Cu}1^2 \cdots \text{Cu}1^{4'} = 5.447$ Å). The btb bridging mode creates double strands (Fig. 2a) which are extended into a 2D network through the *syn-anti* coordination of the central carboxylate group (Fig. 2b). Cu1 can either be considered fourfold-coordinated in an approximately square-planar fashion or fivefold-coordinated (square-pyramidal, $\tau = 0.04$ ³⁷) with a fifth and apical (bridging) aqua-ligand from an adjacent Cu1 atom (*cf.* Fig. 5). The μ -aqua bridge is rather long with 2.651(2) Å for the apical Cu1–O8 contact. Cu2 displays a square-pyramidal geometry with four short bonds in the square plane, including a chelating carboxylate group and a longer apical contact of 2.289(2) Å for Cu2 \cdots O4 from the *syn-anti*-bridging carboxylate group. The hydrogen atoms of the hydroxo and the aqua bridge participate in classical O–H \cdots O bonding (Table 1).

The hydroxo- and *syn-syn*-carboxylate bridged Cu \cdots Cu distance in **1** (3.083 Å) is comparable to those found in other di-hydroxo or di-alkoxo bridged dinuclear complexes,³⁸ but is considerably shorter compared to mono-hydroxo or mono-alkoxo bridged dinuclear complexes $[\text{Cu}_2(\text{L}1)(\text{O}_2\text{P}(\text{OAr}))](\text{PF}_6)_2$

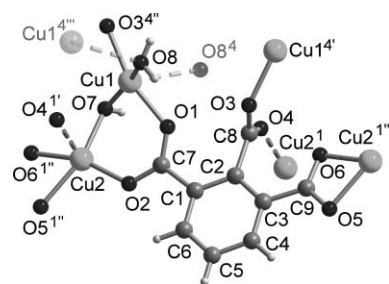


Fig. 1 Asymmetric unit, coordination environments of the copper atoms and bridging action of the btb^{3-} ligand in **1**. The long Cu1 \cdots aqua ligand contacts are depicted semi-transparent. Selected distances (Å) and angles ($^\circ$): Cu1–O1 1.960(2), Cu1–O3^{4'} 1.968(2), Cu1–O7 1.905(2), Cu1–O8 1.956(2), Cu1 \cdots O8⁴ 2.651(2), Cu2–O2 1.931(2), Cu2–O4^{1'} 2.288(2), Cu2–O5^{1''} 2.044(2), Cu2–O6^{1''} 1.978(2), O1–Cu1–O3^{4'} 163.3(1), O1–Cu1–O7 93.6(1), O1–Cu1–O8 86.2(1), O3^{4'}–Cu1–O7 98.7(1), O3^{4'}–Cu1–O8 85.9(1), O7–Cu1–O8 160.9(1), O2–Cu2–O4^{1'} 99.97(9), O2–Cu2–O5^{1''} 99.8(1), O2–Cu2–O6^{1''} 160.9(1), O2–Cu2–O7 101.1(1), O4^{1'}–Cu2–O5^{1''} 98.2(1), O4^{1'}–Cu2–O6^{1''} 94.3(1), O4^{1'}–Cu2–O7 85.71(9), O5^{1''}–Cu2–O6^{1''} 65.4(1), O5^{1''}–Cu2–O7 157.7(1), O6^{1''}–Cu2–O7 92.5(1), Cu1–O7–Cu2 107.4(1). Symmetry transformations: 1 = $x, y, 1 + z$; 1' = $x, y, -1 + z$; 1'' = $1 + x, y, -1 + z$; 1''' = $-1 + x, y, 1 + z$; 4 = $0.5 + x, 0.5 - y, 0.5 + z$; 4' = $-0.5 + x, 0.5 - y, 0.5 + z$; 4'' = $0.5 + x, 0.5 - y, -0.5 + z$; 4''' = $-0.5 + x, 0.5 - y, -0.5 + z$.

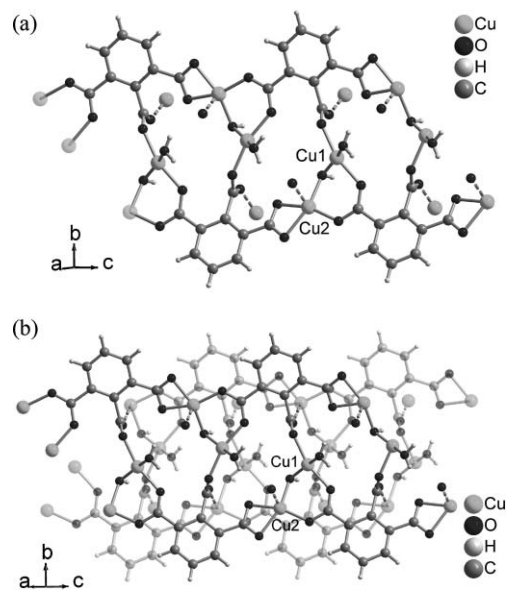


Fig. 2 (a) Double strand in the crystal structure of **1** which is extended as shown in (b) along the ac diagonal to a 2D network. A second double strand in (b), lying behind the first one, is depicted semi-transparent.

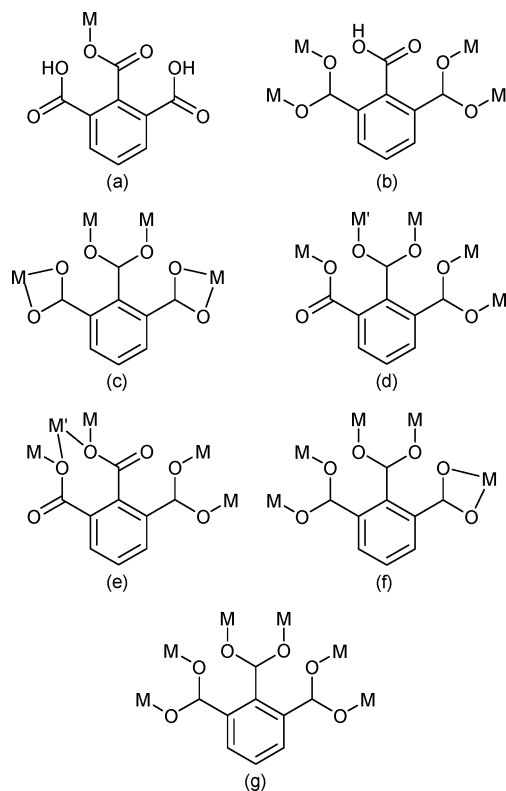
(3.773(4) Å),³⁹ $[\text{Cu}_2(\text{L}2)(\text{O}_2\text{P}(\text{OCH}_2\text{Ph}))_2](\text{ClO}_4)_2$ (3.67 Å),⁴⁰ and $[\text{Cu}_2(\text{L}3)(\text{O}_2\text{P}(\text{OAr}))](\text{ClO}_4)_2$ (3.779(1) Å)⁴¹ (HL1 = 2,6-bis[2-pyridylethyl]aminomethyl]phenol; Ar = 4-nitrophenyl; HL2 = 2,6-bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenol), HL3 = N,N,N,N -tetrakis{(6-methyl-2-pyridyl)methyl}-1,3-diaminopropan-2-ol).

Scheme 1, with the crystallographically established coordination of H_2btb^- , $Hbtb^{2-}$ and btb^{3-} in **1** and **2** and in the previously characterized metal complexes, shows that the μ_5 bridging mode in **1** is novel for btb^{3-}

Table 1 Hydrogen-bonding interactions in $[\text{Cu}_2(\mu_5\text{-btb})(\mu\text{-OH})(\mu\text{-H}_2\text{O})]$ (**1**)^a

D–H...A	D–H/Å	H...A/Å	D...A/Å	D–H...A/°
From aqua ligand				
O8–H8A...O4 ^{4m}	0.80(4)	2.19(4)	2.881(4)	145(4)
O8–H8B...O7 ^{1m}	0.76(5)	1.91(5)	2.645(3)	161(5)
From hydroxo ligand				
O7–H7...O3 ^{1v}	0.76(3)	1.89(3)	2.636(3)	171(5)

^a D = donor, A = acceptor. For found and refined atoms the standard deviations are given. Symmetry relations: 1^m = $-1 + x, y, z$; 1^v = $1 + x, y, z$; 4^m = $-0.5 + x, 0.5 - y, -0.5 + z$.



Scheme 1 Modes of coordination of $\text{H}_n\text{btb}^{(3-n)-}$ ($n = 0, 1, 2$) ligands: (a) ref. 27 and **2** in this work; (b) ref. 28; (c) ref. 29; (d) and (e) ref. 30; (f) **1** in this work; (g) ref. 31.

Compound **2** is a molecular complex with the cadmium atom coordinated by four aqua ligands in the equatorial plane and two carboxylate oxygen atoms from two *trans* H_2btb^- ligands (Fig. 3). The cadmium atom sits on a special position (Wyckoff notation 4e, at $\{0\ y\ 0.25\}$) along the 2-fold rotation axis. The crystal packing of **2** is dictated by hydrogen bonding without any π interactions (Fig. S4 and Table S1 in ESI†).⁴²

Magnetic Properties of **1**

The thermal dependence of $\chi_M T$ (χ_M being the magnetic susceptibility per mol of Cu_2) for compound **1** in the temperature range 1.9–300 K is shown in Fig. 4. The value of $\chi_M T$ at room temperature, $0.98\text{ cm}^3\text{ mol}^{-1}\text{ K}$, is higher than expected for two non-interacting copper(II) ions ($\chi_M T = 0.90\text{ cm}^3\text{ mol}^{-1}\text{ K}$ for a Landé factor $g = 2.2$).⁴³ On cooling, the $\chi_M T$ value continuously

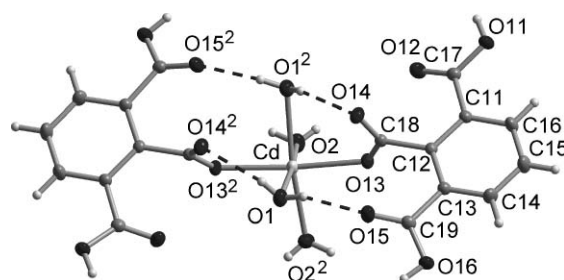


Fig. 3 Ellipsoid representation (50% probability) of the molecular structure of **2** with the intramolecular hydrogen bonds as dashes (see Table S1 for details†). Selected distances [Å] and angles [°]: Cd–O1 2.3687(15), Cd–O2 2.2862(15), Cd–O13 2.2339(12), O1–Cd–O1² 96.29(8), O1–Cd–O2 173.02(5), O1–Cd–O2² 87.92(6), O1–Cd–O13 88.03(5), O1–Cd–O13² 85.97(5), O2–Cd–O2² 88.46(8), O2–Cd–O13 97.85(5), O2–Cd–O13² 88.61(5), O13–Cd–O13² 171.01(6). Symmetry transformation: $2 = -x, y, 0.5 - z$.

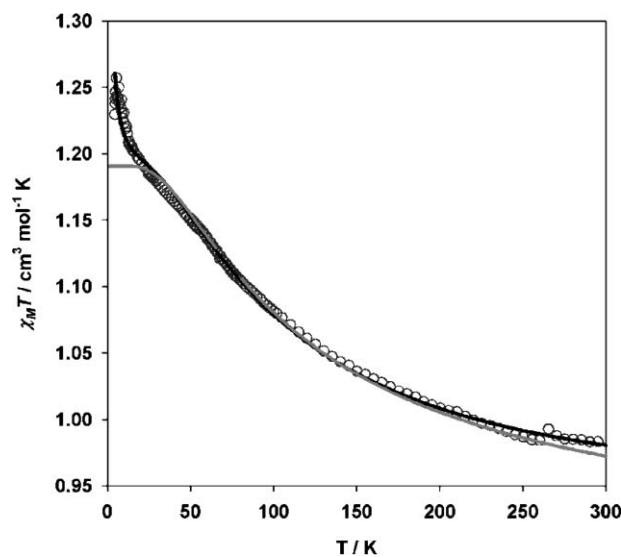


Fig. 4 $\chi_M T$ vs. T plot for compound **1**. The grey solid line corresponds to best fit through eqn (2), the black one corresponds to the best-fit trough eqn (4), see text.

increases, seems to tend to a plateau around 30 K, and afterwards continues increasing to reach a maximum at $T = 5\text{ K}$ and then decreases at lower temperatures. The plateau points towards a $\chi_M T$ value of $1.20\text{ cm}^3\text{ mol}^{-1}\text{ K}$ that corresponds to an $S = 1$ spin state and the maximum value reached, $1.25\text{ cm}^3\text{ mol}^{-1}\text{ K}$, exceeds the expected one for an isolated fully coupled copper(II) dinuclear complex. The shape of the curve and the values of $\chi_M T$ are neither typical for dinuclear complexes nor for copper(II) chains; in fact, **1** is a mix between both situations. In order to explain the $\chi_M T$ curve in a first approximation it can be said that compound **1** has some ferromagnetic interaction that exceeds the dinuclear topology and also some weak antiferromagnetic coupling that becomes noticeable at very low temperatures.

The double strands in the crystal structure of **1**, from which one is depicted in Fig. 2a, involve two different carboxylate groups of the *btb* ligand and the magnetic coupling is not propagated in this direction. However, the magnetic coupling propagates through the $\text{Cu}_2\text{-O}_4$ apical contact from the *syn-anti*-bridging carboxylate group, the contact which extends the

double strands into a two-dimensional network (Fig. 2b). Under the point of view of the transmission of the magnetic interaction, the arrangement of the copper(II) ions and the bridging groups in compound **1** is better seen as single chains of scalene Cu1–Cu2–Cu1' triangles that share two vertices (at Cu1 and Cu1') (Fig. 5, Scheme 2). This arrangement is very similar to that of compound [$\{\text{Cu}(\text{dmen})\}_2(\mu\text{-OMe})\{\mu\text{-}[\text{O}_2\text{C}(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\}(\text{ClO}_4)_2$ (dmen = *N,N*-dimethylethylenediamine) studied by López and coworkers (Scheme 2a),⁴⁴ albeit in the case of **1** the ferromagnetic coupling is the dominant one.

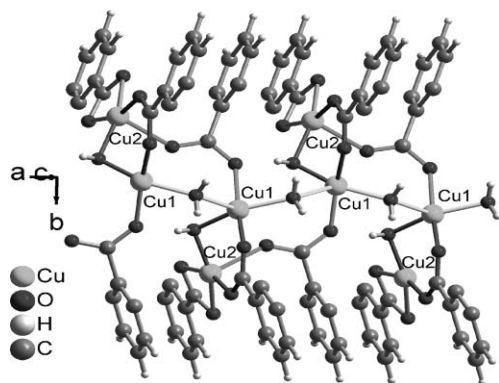
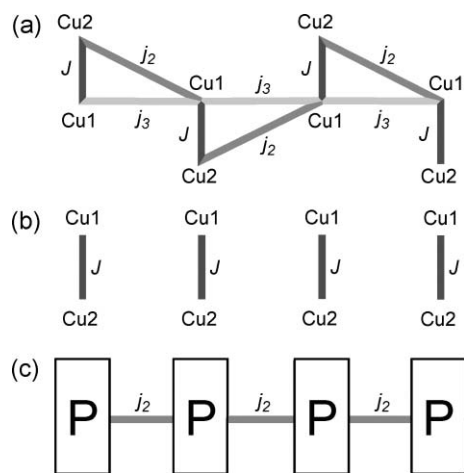


Fig. 5 Magnetic exchange pathways in compound **1**. The carboxylate groups that do not form links within the chain have been omitted for clarity. Symmetry relations are not given.



Scheme 2 Magnetic exchange pathways in compound **1**.

Compound **1** has three different active magnetic exchange pathways that lead to a rather complex situation for which no numerical expression for the magnetic susceptibility has been developed. The three active exchange pathways link the copper(II) ions through a long μ -aqua (j_3), an *anti-syn* carboxylate bridge (j_2), and through a mixed μ -hydroxo + *syn-syn* carboxylate bridge (J) [J , j_2 and j_3 correspond to the magnetic-exchange coupling constant through the respective exchange pathway] (Fig. 5 and Scheme 2). Efforts performed by other authors to solve this system were not satisfactory.⁴⁴ Hence, analyzing the potential activity of the different exchange pathways, we decomposed the system into smaller parts and analyzed them by intervals of temperature

in order to extract as much information as possible from the magnetic study. In a first approximation and in agreement with previous studies, the Cu1–Cu2 coupling through the mixed μ -hydroxo and *syn-syn* carboxylate bridges (labeled with coupling constant J in Scheme 2) is considered to be more intense than the other two. Thus, at high temperatures the system is considered as isolated Cu^{II}_2 units and the magnetic data are analyzed by means of the Bleaney–Bowers equation,^{43,45} eqn (2), where J is the intramolecular-exchange coupling constant, g the Landé factor, β the Bohr magneton and k the Boltzmann constant (Scheme 2b).

$$\chi_M = \frac{N\beta^2 g^2}{3kT} \left[\frac{6}{3 + \exp(-J/kT)} \right] \quad (2)$$

The fit is satisfactory for temperatures higher than 30 K and gives $J = +82.2(9) \text{ cm}^{-1}$, $g = 2.182(1)$ and $R = 0.9980$. Thus, at temperatures higher than 30 K the system behaves as isolated Cu_2 units with strong ferromagnetic coupling through the mixed μ -hydroxo + *syn-syn* carboxylate bridge. At lower temperatures $\chi_M T$ continues to increase and overcomes the expected value for a $S = 1$ spin state. This implies that another ferromagnetic exchange pathway must be active. Looking at the two possibilities we consider the Cu1–Cu2 exchange pathway through the *anti-syn* carboxylate bridge to be responsible (labeled with coupling constant j_2 in Scheme 2).⁴⁶ Under that approach the system would behave as chains of ferromagnetically coupled Cu_2 units and could be described with a model of 1D chains of dinuclear units, denoted P, which are ferromagnetically coupled through the *anti-syn* carboxylate group (Scheme 2c). The value of the spin of the P units, S_P , is a function of J and T ; being given by eqn (3).^{47,48}

$$S_P(S_P + 1) = \{6/[3 + \exp(-J/kT)]\} \quad (3)$$

At low temperatures S_P is high enough to be considered as a classical spin and the magnetic data of compound **1** can be analyzed by means of the Fisher equation for a chain of classical spins S_P ,⁴³ eqn (4), where u is given by eqn (5), g_P stands for the Landé factor of the P dinuclear unit and j_2 for the effective coupling constant among the P units.

$$\chi_M = \frac{N\beta^2 g_P^2}{3kT} S_P(S_P + 1) \left[\frac{1+u}{1-u} \right] \quad (4)$$

$$u = \coth[j_2 S_P(S_P + 1)/kT] - [kT/j_2 S_P(S_P + 1)] \quad (5)$$

Least-square fitting of the data leads to $g = 2.170(2)$, $J = +83(1) \text{ cm}^{-1}$, $j_2 = 0.161(1) \text{ cm}^{-1}$ and $R = 0.9999$. The calculated curve reproduces the magnetic susceptibility data down to 5 K. The values obtained for J are very similar for both models and the value obtained for j_2 is very small, which validates the applicability of the model.⁴⁸ The further decrease of $\chi_M T$ below 5 K must be due to weak Cu1 \cdots Cu1' antiferromagnetic interactions through the μ -aqua bridge (labeled with coupling constant j_3 in Scheme 2), we are not able to determine its absolute value (j_3), but it must be lower than j_2 .

The magneto-structural correlations in dinuclear copper(II) complexes bridged by carboxylate and μ -hydroxo groups have recently been revised.⁴⁴ A ferromagnetic exchange interaction is observed in **1** and in other compounds exhibiting mixed μ -hydroxo and *syn-syn* carboxylate bridges. However, it is known that antiferromagnetic coupling should be expected for copper(II) dinuclear complexes with *syn-syn* carboxylate bridges and μ -oxo

bridges with angles larger than 97° [Cu1–O(H)–Cu2 107.5(1) $^\circ$ in **1**].^{43,46,49} This apparent inconsistency can be explained by means of a phenomenon called orbital counter-complementarity which has been studied by several authors and takes place when more than one bridge occurs simultaneously.⁵⁰ In that situation the effect of the different bridges can be added or counterbalanced and the expected antiferromagnetic coupling can be turned to ferromagnetic. The ferromagnetic nature of the coupling is explained with Hoffmann's approach, in which the magnetic coupling constant for a dinuclear copper(II) complex is expressed as the sum of two contributions: a positive term (J_F , ferromagnetic) and a negative term (J_{AF} , antiferromagnetic), with the magnetic coupling constant as the sum of both, that is $J = J_F + J_{AF}$. J_{AF} is proportional to the square of the energy gap (Δ) between the two simply occupied molecular orbitals (SOMOs).⁵¹ Accurate molecular orbital calculations performed for compounds with similar structural parameters to those of **1** have shown that Δ is very small and the ferromagnetic term is the dominant one.^{44,52} In those studies the magnetic coupling constant is related to the Cu(II)–Cu(II) distance, the Cu–O–Cu angle, the angle between the coordination planes of the two Cu(II) ions and the out-of-plane shift of the hydrogen atom of the hydroxo group. Small Cu(II)–Cu(II) distances, small Cu–O–Cu angles, intermediate angles between the coordination planes and large out-of-plane shifts of the hydrogen atom lead to moderate–strong ferromagnetic couplings. The value obtained for the coupling constant of **1** falls in the expected range in agreement with previous studies for similar compounds as can be seen in Table 2. In the same way, the value obtained for j_2 is as expected, since it is well known that copper(II) ions bridged by *anti-syn* carboxylate groups exhibit either weak ferro- or weak antiferromagnetic interactions.⁴⁶

Conclusions

The 2D coordination network $[\text{Cu}_2(\mu_5\text{-btb})(\mu\text{-OH})(\mu\text{-H}_2\text{O})]$ represents an interesting magnetic case study. The carboxylate groups of the benzene-1,2,3-tricarboxylate (btb) ligand do not propagate the magnetic coupling in the three directions of the space but lead to carboxylate-bridged copper chains with complex topology and three different magnetic exchange pathways. The strong ferromagnetic coupling found through the mixed μ -hydroxo + *syn-syn* carboxylate bridge can be explained by means of the counter-complementarity of both bridging groups. The other two

exchange-path ways that involve *anti-syn* carboxylate groups and μ -aqua groups are much weaker.

Experimental

Commercially available benzene-1,2,3-tricarboxylic acid (H_3btb), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cd}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ were used without further purification. Elemental analyses were performed on a VarioEL from Elementaranalysensysteme GmbH. Infrared spectra were recorded in the range 400–4000 cm^{-1} on a Bruker Optik IFS 25 spectrophotometer using KBr pellets. Thermogravimetric analysis was carried out in a simultaneous thermoanalysis apparatus STA 409C from Netzsch under nitrogen with a heating rate of 10 $^\circ\text{C min}^{-1}$ in the range 50 to 600 $^\circ\text{C}$. Powder X-ray diffraction patterns were measured at ambient temperature using a STOE STADI-P with Debye–Scherrer geometry, Mo-K α radiation ($\lambda = 0.7093 \text{ \AA}$), a Ge(111) monochromator and the samples in glass capillaries on a rotating probe head. Simulated powder patterns were based on single-crystal data and calculated using the STOE WinXPOW software package.⁵⁷ Magnetic susceptibility measurements on polycrystalline samples were carried out in the temperature range 1.9–300 K by means of a Quantum Design SQUID magnetometer operating at 1000 Oe ($T < 15 \text{ K}$) and 10 000 Oe ($T > 15 \text{ K}$). Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per Cu(II)] and the magnetization of the sample holder.

Syntheses

catena-[Aqua(μ_5 -benzene-1,2,3-tricarboxylato- $\kappa\text{O}':\kappa\text{O}''':\kappa\text{O}''''':\kappa\text{O}''''''$)(μ -hydroxo)dicopper(II)], $[\text{Cu}_2(\mu_5\text{-btb})(\mu\text{-OH})(\mu\text{-H}_2\text{O})]$ (1**). A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (241 mg, 1.00 mmol), H_3btb (123 mg, 0.50 mmol) and water (15 mL) was stirred for 30 min at room temperature, transferred to a Teflon-lined stainless-steel autoclave and heated at 170 $^\circ\text{C}$ for 50 h. Then the autoclave was cooled to room temperature at a rate of 10 $^\circ\text{C h}^{-1}$. A green crystalline product was filtered off, washed with distilled water and dried in air (yield 120 mg, 65%). IR (KBr): $\tilde{\nu} = 3419 \text{ m} (\nu\text{OH})$, 3145 m, 3050 w (aromatic CH), 2956 and 2856 w (νCH), 1613 s ($\nu\text{CO}_{2,\text{asym}}$), 1582 s ($\nu\text{CO}_{2,\text{asym}}$), 1516 m, 1479 s, 1457 m ($\nu\text{CO}_{2,\text{sym}}$), 1417 m, 1395 s ($\nu\text{CO}_{2,\text{sym}}$), 1376 w, 1253 m ($\delta\text{OH} \cdots \text{O}$),**

Table 2 Values of the coupling constant, J ; Cu(II)–Cu(II) distance, average of the Cu–O bond lengths; Cu–O–Cu bonding angle a ; angle between the coordination planes of the two Cu(II) ions δ ; out-of-plane shift of the hydrogen atom of the hydroxo group γ

Compound ^a	J/cm^{-1}	Cu–Cu/ Å	Cu–O/ Å	$a/^\circ$	$\delta/^\circ$	$\gamma/^\circ$	Ref.
$[\text{Cu}(\text{L}^6)(\text{OH})(\text{O}_2\text{CMe})] \cdot 1.5\text{THF} \cdot \text{MeOH}$	3	3.156(3)	1.934(5)	109.3(4)	117.5	N.R.	53
$[\text{Cu}_2(\text{tmen})_2(\text{OH})(\text{O}_2\text{CFc})](\text{ClO}_4)_2$	29	3.363(1)	1.906(10)	123.9(3)	156.2	53.3	44
$[\text{Cu}_2(\text{L}^3)(\text{O}_2\text{CMe})]$	38	3.237(1)	1.927(4)	114.3(2)	119.2	50.9	54
Compound 1	83	3.083(1)	1.907(2)	107.4(1)	123.0	35	This work
$[\text{Cu}_3(\text{H}_3\text{tea})(\text{Htea})-(\text{CH}_2\text{COO})_2](\text{ClO}_4)_4$	84	3.043(3)	1.906(8)	107.2(4)	N.R.	N.R.	55
$[\text{Cu}_2(\text{phen})_2(\text{OH})(\text{O}_2\text{CEt})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	109	3.015(2)	1.929(15)	103.6(2)	122.7	N.R.	56
$[\text{Cu}_2(\text{phen})_2(\text{OH})(\text{O}_2\text{CMe})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	111	3.017(2)	1.928(8)	103.4(2)	122.8	46.3	56

^a L^6 and L^3 are described in their publications, tmen = *N,N,N,N*-tetramethylethylenediamine, Fc = ferrocenyl, H_3tea = triethanolamine, N.R. = not reported.

1167 w and 1071 m (νCO), 946 m ($\delta\text{OH}\cdots\text{O}$), 854 w, 835 m and 770 s (aromatic CH), 719 s, 699 w, 617 m, 523 w, 479 m, 434 w cm^{-1} . $\text{C}_9\text{H}_6\text{O}_8\text{Cu}_2$ (369.22): calcd C 29.28, H 1.64; found C 29.00, H 1.64%.

[Tetraaqua-bis(dihydrogen benzene-1,2,3-tricarboxylato- $\kappa\text{O}''$)-cadmium(II)] dihydrate, $[\text{Cd}(\text{H}_3\text{btb})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ (2**).** A mixture of $\text{Cd}(\text{OH})_2$ (73 mg, 0.50 mmol), H_3btb (123 mg, 0.50 mmol) and water (15 mL) was stirred for 30 min at room temperature, transferred to a Teflon-lined stainless-steel autoclave and heated at 170 °C for 3 d. Then the autoclave was cooled to room temperature at a rate of 8 °C h^{-1} . A colorless crystalline product was filtered off, washed with distilled water and dried in air (yield 95 mg, 60% based on H_3btb). IR (KBr): $\tilde{\nu} = 3441$ m, (νOH), 3041 w (aromatic CH), 2933 and 2870 w (νCH), 1738 s (free $-\text{CO}_2\text{H}$), 1580 s ($\nu\text{CO}_{2,\text{asym}}$), 1459 m ($\nu\text{CO}_{2,\text{sym}}$), 1378 s ($\nu\text{CO}_{2,\text{sym}}$), 1306 m, 1238 s ($\delta\text{OH}\cdots\text{O}$), 1208 w, 1147 and 1072 w (νCO), 999 m ($\delta\text{OH}\cdots\text{O}$), 993 w, 979 w, 770 s (aromatic CH), 703 w, 689 w, 664 m, 581 w, 541 cm^{-1} . $\text{C}_{18}\text{H}_{22}\text{O}_{18}\text{Cd}$ (638.76): calcd C 33.85, H 3.47; found C 33.58, H 3.41%.

[Hexaquaquazinc(II)-bis(dihydrogen benzene-1,2,3-tricarboxylate) tetrahydrate, $[\text{Zn}(\text{H}_2\text{O})_6(\text{H}_3\text{btb})_2]\cdot 4\text{H}_2\text{O}$ (3**).** A mixture of $\text{Zn}(\text{OH})_2$ (49 mg, 0.50 mmol), H_3btb (123 mg, 0.50 mmol) and water (15 mL) was stirred for 30 min at room temperature, transferred to a Teflon-lined stainless-steel autoclave and heated at 170 °C for 3 d. Then the autoclave was cooled to room temperature at a rate of 8 °C h^{-1} . A colorless crystalline product was filtered off, washed with distilled water and dried in air (yield 80 mg, 54% based on H_3btb). IR (KBr) $\tilde{\nu} = 3442$ m, (νOH), 3030 w (aromatic C–H), 2882 w (νCH), 2768 w, 2604 w, 1703 s (free $-\text{CO}_2\text{H}$), 1613 m, 1578 s ($\nu\text{CO}_{2,\text{asym}}$), 1461 s ($\nu\text{CO}_{2,\text{sym}}$), 1376 s ($\nu\text{CO}_{2,\text{sym}}$), 1307 m, 1228 m ($\delta\text{OH}\cdots\text{O}$), 1206 w, 1155 and 1071 m (νCO), 995 m ($\delta\text{OH}\cdots\text{O}$), 975 w, 897 m, 850 m, 767 s (aromatic CH), 685 w, 661 s, 581 m, 533 m, 560 cm^{-1} . $\text{C}_{18}\text{H}_{22}\text{O}_{18}\text{Zn}$ (no crystal water, 591.75; with crystal water 663.81) calcd for no crystal water C 36.54, H 3.75; found C 36.28, H 3.72%.

X-Ray crystallography†

Suitable single crystals were carefully selected under a polarizing microscope.

Data collection: Bruker AXS with APEXII CCD area-detector, temperature 203(2) K, Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, ω -scans, data collection with APEX2,⁵⁸ cell refinement and data reduction with SAINT,⁵⁸ experimental absorption correction with SADABS.⁵⁹

Structure analysis and refinement: the structure was solved by direct methods (SHELXS-97);⁶⁰ refinement was done by full-matrix least-squares on F^2 using the SHELXL-97 program suite.⁶⁰ All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms for aromatic CH were positioned geometrically (C–H = 0.94 Å) and refined using a riding model (AFIX 43) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Hydrogen atoms on the aqua ligands, the crystal water and the protonated carboxylate groups (in **2**) were found and refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Details of the X-ray structure determinations and refinements are provided in Table 3. Graphics were drawn with DIAMOND.⁶¹ CCDC-680410 for **1** and CCDC-680411 for **2** contain the crystallographic data for this paper.†

Table 3 Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_9\text{H}_6\text{Cu}_2\text{O}_8$	$\text{C}_{18}\text{H}_{22}\text{CdO}_{18}$
$M/g\text{ mol}^{-1}$	369.22	638.76
Crystal size/mm	$0.13 \times 0.12 \times 0.01$	$0.36 \times 0.24 \times 0.14$
2θ range/ $^\circ$	3.00–52.70	5.52–59.70
$h; k; l$ range	$\pm 7; -30, +33; \pm 8$	$\pm 41; -9, +8; \pm 16$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
$a/\text{Å}$	5.6820(1)	29.6359(6)
$b/\text{Å}$	27.2143(6)	6.5873(1)
$c/\text{Å}$	6.7260(2)	11.7026(2)
$\alpha/^\circ$	90	90
$\beta/^\circ$	107.618(1)	95.654(2)
$\gamma/^\circ$	90	90
$V/\text{Å}^3$	991.27(4)	2273.47(7)
Z	4	4
$D_{\text{calc}}/g\text{ cm}^{-3}$	2.474	1.866
$F(000)$	728	1288
μ/mm^{-1}	4.329	1.053
Max./min. transmission	0.9499/0.5947	0.8666/0.7030
Reflections collected (R_{int})	7609 (0.0452)	24112 (0.0288)
Independent reflections	2015	3265
Observed reflections [$I > 2\sigma(I)$]	1706	3001
Parameters refined	176	192
Max./min. $\Delta\rho/e\text{ Å}^{-3a}$	0.546/−0.518	1.223/−0.389
$R1/wR2$ [$I > 2\sigma(I)$] ^b	0.0286/0.0647	0.0246/0.0620
$R1/wR2$ (all reflect.) ^b	0.0391/0.0682	0.0282/0.0636
Goodness-of-fit on F^2c	1.061	1.101
Weight scheme $w; a/b^d$	0.0323/0.5993	0.0338/2.6779

^a Largest difference peak and hole. ^b $R_1 = [\Sigma(|F_o| - |F_c|)]/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. ^c Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. ^d $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 - F_c^2) + 2F_c^2)/3$.

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