FULL PAPER

Synthesis, structural and magnetic properties of a series of copper(II) complexes containing a monocarboxylated perchlorotriphenylmethyl radical as a coordinating open-shell ligand

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Received 16th December 2003, Accepted 24th February 2004 First published as an Advance Article on the web 8th March 2004

A series of complexes of copper(II)-containing a perchlorotriphenylmethyl radical functionalized with a carboxylic group as a new ligand is reported. The compounds $[Cu(PTMMC)_2(L)_3]$ (PTMMC = (tetradecachloro-4-carboxy-triphenyl)methyl radical; L = (1) H₂O, (2) pyrimidine and ethanol or (3) pyridine), $[Cu_2(PTMMC)_2(MeCOO)_2(H_2O)_2]$ (4) and $[Cu(HPTMMC)_2(L)_3]$ (HPTMMC = α -*H*-(tetradecachlorotriphenyl)methane-4-carboxylic acid; L = pyridine) (5) were structurally characterized. In complexes 1, 2, 3 and 5, the copper(II) ion is coordinated to two PTMMC (or HPTMMC) units in a slightly distorted square planar surrounding, while 4 shows a paddle-wheel copper(II) dimer structure, where each Cu metal ion has four O atoms of different carboxylate groups, two of them belonging to two PTMMC radicals. The copper(II)-radical exchange couplings are antiferromagnetic for complexes 1, 2 and 3. A linear three-spin model was applied to complexes 1, 2 and 3 to give $J/k_B = -24.9$, -15.0 and -20.7 K, respectively. Magnetic properties of 4 show that it is one of the scarce examples of a spin-frustrated system composed of organic radicals and metal ions. In this case, experimental data were fitted to a magnetic model based on a symmetrical butterfly arrangement to give a copper(II)-copper(II) exchange coupling of $J/k_B = -350.0$ K and a copper(II)-radical exchange to that observed for the copper(II)-radical interactions in complexes 1, 2 and 3.

Introduction

10.1039/b316458

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The design and synthesis of molecular-based magnetic materials is a major focus of molecular materials research. One of the more promising strategies is the so-called metal-radical approach that combines paramagnetic metal ions and pure organic radicals as ligating sites.1 The electronic open-shell character of such organic ligands is particularly appealing since they are expected to interact with transition metal ions enhancing the strength of magnetic interactions and increasing the magnetic dimensionality of the molecular material in comparison with systems made up from paramagnetic metal ions and diamagnetic coordinating ligands. However, even though a large number of metal-radical systems have been studied, the variety of radical-based ligands used up to know is fairly limited. Among them, one of the most extensively used families is that of nitroxide-based radicals, namely nitroxides and α -nitronyl or imino nitroxide radicals.²⁻⁵ Besides nitroxidebased radicals, other examples of open-shell ligands used up to now are: (1) derivatives of the verdazyl radical family, which turned out to be very attractive because of their abundance of donor atoms and efficiency in transmitting magnetic interactions;6 (2) o-quinone ligands that can be found in different accessible oxidation states, including the radical semiquinones,⁷ (3) TCNE and TCNQ radical anions⁸ and (4) diphenylcarbenes substituted with chemical functionalities able to coordinate with metal ions.9

Following this metal-radical approach, our group has recently initiated a scientific project focussed in the use of perchlorinated triphenylmethyl (PTM) radicals functionalized with one carboxylic group, PTMMC, as new ligating sites to build magnetic molecular materials. Among others, the main advantages of these radicals are their astonishing thermal and chemical stability and their stereochemical characteristics, with a helical (chiral) surrounding of the radical center by very bulky substituents. Up to now, it has been demonstrated that the supramolecular self-assembly of PTMMC in the solid state forms hydrogen-bonded dimeric motifs that promote the presence of ferromagnetic interactions.¹⁰ Herein, we present the controlled synthesis, crystal structure analysis, spectroscopic characterization and magnetic properties of a new family of Cu(II) complexes using the perchlorinated triphenylmethyl radical PTMMC as a new ligand.¹¹ More specifically, we report a monomeric Cu(II) complex [Cu-(PTMMC)₂(H₂O)₃]·6H₂O·2EtOH, 1, which in its magnetic properties shows a relatively strong exchange coupling constant between the metal ion and the radical ligand. This result confirms that carboxylic-based PTM radicals could act as excellent ligands for the design of new magnetic complexes following the metal-radical approach. With the simple modification of the auxiliary ligands of 1, two new monomeric complexes, [Cu(PTMMC)2(pyrimidine)2(EtOH)]·THF·4EtOH, 2, and [Cu(PTMMC)₂(py)₃]·2.5n-hexane, 3, have been synthesized. Structurally, the bulkiness of these ligands has significant implications for their microporous crystal packing. Furthermore, the simple modification of the stoichiometry of the initial reaction for obtaining 1 gives a paddle-wheel Cu(II) complex [Cu₂(PTMMC)₂(MeCOO)₂(H₂O)₂]·4EtOH, 4. Its magnetic behavior can be understood as a spin-frustrated system. Finally, the possibility to work with the non-radical analogues of PTMMC, the hydrogenated form HPTMMC, allows us to synthesize the non-radical Cu(II) complex [Cu(HPTMMC)₂(py)₃]·4THF, 5, for comparison purposes. Its condition of isostructurality with respect on 3 highlights the magnetic interactions between radical PTMMC and Cu(II) ions



Scheme 1 Schematic synthesis of PTMMC-based complexes. Reagents and conditions: (i) $PTMMC/Cu_2(O_2CMe)_4$ ·H₂O (4 : 1) in EtOH-H₂O; (ii) PTMMC/Cu_2(O_2CMe)_4·H₂O (2 : 1) in EtOH-H₂O; (iii) 1/excess of pyrimidine (pyrim) in EtOH-*n*-hexane and THF; (iv) 1/excess of pyridine (py) in EtOH-*n*-hexane and THF.



Results and discussion

A. Synthesis

Complex 1 was synthesized in an initial reaction of copper acetate monohydrate and PTMMC in a solution of ethanolwater in high yields (89%). High-quality crystals of 1 suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of the reaction solvent. Afterwards, slow diffusion of an excess of pyrimidine (or pyridine) in a solution of ethanol-n-hexane into a solution of 2 in THF allowed the preparation of complexes 2 and 3. In both complexes the auxiliary water ligands of 1 were replaced by pyrimidine and ethanol in 2 and by pyridine in 3 (Scheme 1). Crystals suitable for single crystal X-ray diffraction were isolated directly from the diffusion method. Surprisingly, the crystal structure analysis showed that 1-3 do not adopt the paddle-wheel motif with four bidentate carboxylate ligands joining two Cu(II) ions, characteristic of most of copper acetate clusters. The tendency to form mononuclear Cu(II) clusters instead of binuclear ones is attributed to the extreme steric demand of the molecules of the PTMMC radical.¹² Indeed, due to the great steric hindrance of the chlorine atoms located at the ortho positions of the carboxylate group, the rotation angles of the polychlorinated phenyl rings relative to the COO⁻ moieties in 1-3 are in the range of 79 to 89°. Such a structural arrangement is expected to disrupt the formation of a binuclear complex with a paddlewheel disposition of the four molecules of PTMMC around the two Cu(II) units, simply due to the direct confrontation of bulky chlorine atoms of neighboring (syn) radicals. This result prompted us to control the stoichiometry of the metal-radical complex by modification of the molar ratio of PTMMC in its reaction with $Cu_2(O_2CMe)_4$ ·2H₂O since this may lead to the formation of a mixed dimeric complex with PTMMC and acetate groups. Indeed, slow addition of PTMMC radical to an excess of $Cu_2(O_2CMe)_4$ ·2H₂O in EtOH-H₂O at room temperature yielded a crystalline sample of complex **4**. Finally, crystals of **5** were obtained in a similar synthetic methodology as for the monomeric PTM-based complexes. Thus, an *n*-hexane solution of pyridine was diffused into a THF solution of the solid isolated by filtration from the reaction of copper acetate monohydrate with an ethanolic solution of HPTMMC.

B. Spectroscopic properties

The IR spectra of 1-4 exhibit the typical vibrational modes attributed to PTM radicals. Indeed, in such PTM-based complexes, the benzenoic peaks appear at 1509 and 1380-1300 cm⁻¹, due to the highly chlorinated character of PTMMC units. Furthermore, the typical peak corresponding to the PTM moieties is found around 730 cm^{-1} .¹³ More information of these complexes can be extracted from the stretching peaks produced by the carboxylate groups. Thus, a detailed analysis of the IR spectra of 1-3 indicates the presence of the antisymmetric COO stretching frequency around 1600-1620 cm⁻¹, while the symmetric COO stretching frequency appears at 1410-1400 cm⁻¹. Thus, a relatively large splitting of the COO stretching frequencies (200-225 cm⁻¹) is observed, being an indication of monodentate coordination.¹⁴ By contrast, the IR spectrum of the paddle-wheel complex 4 shows a lower value of this splitting since the antisymmetric COO stretching frequency appears at 1607 cm⁻¹ and the symmetric one at 1417 cm⁻

The electronic absorption spectra recorded in the UV-visible region in pure THF also exhibits the absorptions corresponding to PTM radicals. Thus, the electronic absorption spectrum of 1–3 show the typical four bands, denoted as A, B, C and D, around 222 ($\varepsilon \sim 160000$), 290 ($\varepsilon \sim 17000$), 385 ($\varepsilon \sim 65000$) and 500 ($\varepsilon \sim 2500 \text{ M}^{-1} \text{ cm}^{-1}$) nm (Fig. 1), respectively.¹⁵ Among them, C and D bands are associated with the radical character of PTMMC ligand, while the other two are the primary and secondary (¹L_b) bands characteristic of substituted benzene units of such a ligand. No additional bands, that could be



Fig. 1 Electronic absorption spectra of the PTMMC radical (dashed line) and complex 3 (continuous line).

assigned to a radical-to-metal charge-transfer phenomenon, were observed.

As occurs in the above-described radical-based complexes, the non-radical complex 5 shows identical IR and electronic spectrum as its precursor HPTMMC. Thus, the characteristic peak of non-radical PTM derivatives appears at 804 cm⁻¹.¹⁰ The electronic spectrum shows the presence of the primary band characteristic of substituted benzenes around 223 nm $(\varepsilon \sim 265000 \text{ M}^{-1} \text{ cm}^{-1}).$

C. X-Ray crystal structures

The molecular and crystal structures of 1-5 were investigated by single crystal X-ray analysis. Crystallographic data and experimental parameters for all complexes are summarized in Table 1. Selected bond lengths and angles for metal complexes are given in Table 2. Structural disorder analysis of complexes 1–3 and 5 is described in the Experimental Section.

(i) [Cu(PTMMC)₂(H₂O)₃]·6H₂O·2EtOH, 1. Complex 1 crystallizes in the $P2_1/c$ monoclinic space group with the cell parameters reported in Table 1. An ORTEP drawing for the metal-radical cluster, formed by two PTMMC molecules and one Cu(II) ion, is shown in Fig. 2. The Cu(II) ion displays a square pyramidal coordination geometry by binding to the two oxygen atoms of two distinct PTMMC ligands and the three oxygen atoms of water molecules acting as auxiliary ligands. The Cu-O1 (carboxylate) and Cu-O3 (carboxylate) distances are 1.967(14) and 1.99(2) Å, respectively, so that the PTMMC anion is unidentate with the copper(II) ion. Due to the great steric hindrance of the chlorine atoms in ortho positions with respect the carboxylate group in PTMMC, the latter groups are twisted by angles of 87 and 89° with respect to the phenyl plane to which they are bonded. Furthermore, the O1-Cu-O3 angle is 175.4(9)°, which leads to a linear system of the three electronic open-shell units (S = 1/2) with distances of 8.43 and 8.34 Å between the copper(II) ion and the central carbon of both



Fig. 2 ORTEP drawing of metal-radical clusters of 1 at the 50% probability level.

PTMMC ligands, where most of the spin density is localized. The two central carbon atoms of PTMMC ligands are separated by 16.56 Å.

The self-assembly of metal-radical clusters in 1, probably steered by chlorine-chlorine contacts, generates large micropores along the [010] direction. Thus, each metal-radical cluster interacts through 16 different chlorine-chlorine contacts (3.60 and 3.25 Å) with its neighbouring clusters, building a three-dimensional network of such supramolecular interactions. Two facing metal-radical clusters create a rectangular synthon, which is partially divided in two nearly square micropores, which are separated by the theoretical wall formed by the water ligands O5 of both complexes (Fig. 4). The Cu-Cu distance in this configuration is 9.33 Å and the dimensions of the micropores are 8.4 and 8.1 Å, with an effective size of 5.1×4.6 Å, when van der Waals radii are considered. The cavities are filled with water and ethanol molecules, with all of them bonded through hydrogen bonds between themselves and between water ligands and the PTMMC carboxylate groups. The void volume of the cavities is 2028 Å³, which equals 28%of the unit cell volume.16

(ii) [Cu(PTMMC)₂(pyrimidine)₂(EtOH)]·THF·4EtOH, 2. In complex 2, molecules crystallize in the $P\bar{1}$ triclinic space group with the cell parameters given in Table 1. An ORTEP drawing of 2 is shown in Fig. 3. The coordination geometry of metalradical clusters around the Cu(II) ion is distorted square pyramidal in which the Cu(II) is coordinated to the two oxygen atoms of two PTMMC, two nitrogen atoms of pyrimidine molecules and one oxygen atom of an ethanol molecule. As occurs in 1, two molecules of PTMMC are coordinated to one Cu(II) ion through one oxygen atom of their carboxylate group, which are twisted by angles of 80 and 81° with respect to the phenyl plane to which they are bonded. The distances Cu-O1 (carboxylate) and Cu-O3 (carboxylate) are 2.068(8) and 1.926(6) Å and the O1-Cu-O3 angle is 169.7(3)°. Moreover, the distances between the Cu(II) ion and the central carbon of PTMMC are 8.48 and 8.33 Å and the distance between the two central carbon atoms of bonded PTMMC units are 16.72 Å.



Fig. 3 ORTEP drawing of metal-radical clusters of 2 at the 50% probability level.

Crystal packing of the metal-radical clusters of 2 also leads to micropores stabilized through 16 chlorine-chlorine contacts in the range 3.47-3.33 Å. In this case, four molecules of 2 form repetitive rectangular micropores, where molecules of ethanol are not confronted in comparison with water molecules of 1. Due to the bulky nature of ethanolic and pyrimidine molecules, compared with water molecules, 2 can not adopt the same topology as 1. Indeed, while the PTMMC moieties are confronted in 1, these units undergo a displacement along the [0-11] direction in 2. To illustrate this displacement, the Cu-Cu distance between opposite walls, which forms such micropores, is 15.33 Å. The differences of the self-assembly of 1 and 2 are shown in Fig. 4. This new arrangement creates rectangular micropores with dimensions of 10.7 and 5.9 Å, with an effective size of 7.3×3.0 Å. Furthermore, such micropores are stabilized through additional π - π interactions between the chlorinated

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	1	2	3	4	5
Empirical formula	CuC44Cl28O15H30	CuC ₆₂ Cl ₂₈ O ₁₀ N ₄ H ₄₆	CuC ₇₀ Cl ₂₈ O ₄ N ₃ H ₅₀	Cu ₂ C ₅₂ Cl ₂₈ O ₁₄ H ₃₄	CuC ₇₁ Cl ₂₈ O ₈ N ₃ H ₄₉
Formula weight	1854.82	2063.17	2053.27	2002.47	2128.27
T/K	223(2)	293(2)	223(2)	223(2)	293(2)
λ(Mo-Kα)/Å	0.71069	0.71069	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\overline{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	25.644(4)	16.2920(1)	8.774(1)	26.296(2)	8.8122(3)
b/Å	15.118(3)	16.5722(8)	14.332(1)	16.9040(9)	14.3777(6)
c/Å	18.580(3)	17.9520(1)	17.379(2)	8.5648(6)	17.4037(7)
a/°	90	97.986(4)	84.411(6)	90.00	93.852(2)
β/°	92.18(1)	102.953(4)	79.880(4)	93.760(3)	100.012(2)
γ/°	90	115.831(4)	87.933(6)	90.00	90.004(2)
V/Å ³	7198.(2)	4094.1(4)	2140.8(4)	3798.9(4)	2166.4(2)
Ζ	4	2	1	2	1
$D_{\rm c}/{\rm g~cm^{-3}}$	1.712	1.674	1.593	1.751	1.631
μ/mm^{-1}	1.399	1.236	1.177	1.601	1.169
F(000)	3676	2062	1028	1984	1065
Crystal size/mm	$0.30 \times 0.25 \times 0.03$	$0.31 \times 0.24 \times 0.11$	$0.29 \times 0.16 \times 0.14$	$0.20 \times 0.15 \times 0.02$	$0.30 \times 0.15 \times 0.09$
θ Range/°	1.56-19.00	1.21-22.00	1.20-22.00	1.43-19.75	1.19-22.49
hkl Range	-24/0, -14/13, -16/17	0/17, -17/15, -18/18	0/9, -15/15, -18/19	0/24, -16/16, -8/8	0/9, -15/15, -18/18
Reflections collected	9744	17838	8337	12387	10847
Independent reflections	4617	9965	4972	3413	5663
Parameters	754	894	503	444	506
GOF	1.049	1.049	1.044	1.218	1.104
$R^a \left(I > 2\sigma(I) \right)$	7.07	6.68	4.84	5.95	7.72
$R_{w}^{b}(I \geq 2\sigma(I))$	16.78	18.96	11.54	11.47	21.36
W ()			001 450		515 540

Table 1Crystal data and structure refinement for complexes 1–5.

1		2		3	
 Cu(1)–O(1)	1.967(14)	Cu(1)–O(1)	2.068(8)	Cu(1)–O(1)	1.976(5)
Cu(1) - O(3)	1.99(2)	Cu(1) - O(3)	1.926(6)	Cu(1)-O(2a)	2.147(5)
Cu(1)–O(5)	2.16(12)	Cu(1)-N(1)	2.080(11)	Cu(1)-N(1)	2.184(10)
Cu(1)–O(6)	2.05(7)	Cu(1)-N(3)	1.981(8)	Cu(1)–N(2)	2.334(11)
Cu(1)–O(7)	2.27(9)	Cu(1)–O(5)	2.236(15)	Cu(1)-N(1a)	2.087(9)
O(1)–Cu(1)–O(3)	175.4(9)	O(1)–Cu(1)–O(3)	169.7(3)	O(1)-Cu(1)-O(2a)	158.2(2)
O(1)-Cu(1)-O(5)	92.3(8)	O(1)-Cu(1)-N(1)	88.8(3)	O(1)-Cu(1)-N(1)	89.1(2)
O(3)-Cu(1)-O(5)	92.2(8)	O(3)-Cu(1)-N(1)	86.7(3)	O(2a)-Cu(1)-N(1)	91.1(2)
O(1)-Cu(1)-O(6)	88.9(7)	O(1)-Cu(1)-N(3)	93.4(3)	O(1)-Cu(1)-N(2)	80.0(3)
O(3)-Cu(1)-O(6)	89.8(7)	O(3)-Cu(1)-N(3)	94.3(3)	O(2a)-Cu(1)-N(2)	79.8(3)
O(5)–Cu(1)–O(6)	95.1(12)	N(1)-Cu(1)-N(3)	157.9(5)	N(1)-Cu(1)-N(2)	112.7(5)
O(1)-Cu(1)-O(7)	89.2(6)	O(1)-Cu(1)-O(5)	87.8(5)	O(1)-Cu(1)-N(1a)	97.0(2)
O(3)-Cu(1)-O(7)	91.1(7)	O(3)-Cu(1)-O(5)	83.7(5)	O(2a)-Cu(1)-N(1a)	97.0(3)
O(5)-Cu(1)-O(7)	97.7(11)	N(1)-Cu(1)-O(5)	98.3(6)	N(1)-Cu(1)-N(1a)	139.4(2)
O(6)–Cu(1)–O(7)	167.1(11)	N(3)-Cu(1)-O(5)	103.8(6)	N(2)-Cu(1)-N(1a)	107.9(5)
4		5			
 4 Cu(1)–O(1)	1.971(7)	5 Cu(1)–O(1)	2.288(11)		
 4 Cu(1)–O(1) Cu(1)–O(2)	1.971(7) 1.964(7)	5 Cu(1)–O(1) Cu(1)–O(2a)	2.288(11) 1.978(7)		
 4 Cu(1)–O(1) Cu(1)–O(2) Cu(1)–O(3)	1.971(7) 1.964(7) 1.954(7)	5 Cu(1)–O(1) Cu(1)–O(2a) Cu(1)–N(1)	2.288(11) 1.978(7) 2.110(17)		
 4 Cu(1)–O(1) Cu(1)–O(2) Cu(1)–O(3) Cu(1)–O(4)	1.971(7) 1.964(7) 1.954(7) 1.950(7)	5 Cu(1)–O(1) Cu(1)–O(2a) Cu(1)–N(1) Cu(1)–N(2)	2.288(11) 1.978(7) 2.110(17) 2.340(16)		
 4 Cu(1)-O(1) Cu(1)-O(2) Cu(1)-O(3) Cu(1)-O(4) Cu(1)-O(5)	1.971(7) 1.964(7) 1.954(7) 1.950(7) 2.102(8)	5 Cu(1)-O(1) Cu(1)-O(2a) Cu(1)-N(1) Cu(1)-N(2) Cu(1)-N(1a)	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12)		
 4 Cu(1)-O(1) Cu(1)-O(2) Cu(1)-O(3) Cu(1)-O(4) Cu(1)-O(5) O(1)-Cu(1)-O(2)	1.971(7) 1.964(7) 1.954(7) 1.950(7) 2.102(8) 168.1(3)	5 Cu(1)-O(1) Cu(1)-O(2a) Cu(1)-N(1) Cu(1)-N(2) Cu(1)-N(1a) O(1)-Cu(1)-O(2a)	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4)		
 4 Cu(1)-O(1) Cu(1)-O(2) Cu(1)-O(3) Cu(1)-O(4) Cu(1)-O(5) O(1)-Cu(1)-O(2) O(1)-Cu(1)-O(3)	1.971(7) 1.964(7) 1.954(7) 1.950(7) 2.102(8) 168.1(3) 90.1(3)	$\begin{array}{c} 5 \\ \\ Cu(1)-O(1) \\ Cu(1)-O(2a) \\ Cu(1)-N(1) \\ Cu(1)-N(2) \\ Cu(1)-N(1a) \\ \\ O(1)-Cu(1)-O(2a) \\ O(1)-Cu(1)-N(1) \end{array}$	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4) 98.4(4)		
 4 Cu(1)-O(1) Cu(1)-O(2) Cu(1)-O(3) Cu(1)-O(4) Cu(1)-O(5) O(1)-Cu(1)-O(2) O(1)-Cu(1)-O(3) O(1)-Cu(1)-O(4)	1.971(7) 1.964(7) 1.954(7) 1.950(7) 2.102(8) 168.1(3) 90.1(3) 88.2(3)	$\begin{array}{c} 5 \\ \\ Cu(1)-O(1) \\ Cu(1)-O(2a) \\ Cu(1)-N(1) \\ Cu(1)-N(2) \\ Cu(1)-N(1a) \\ \\ O(1)-Cu(1)-O(2a) \\ O(1)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(1) \end{array}$	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4) 98.4(4) 93.9(4)		
 4 Cu(1)-O(1) Cu(1)-O(2) Cu(1)-O(3) Cu(1)-O(4) Cu(1)-O(5) O(1)-Cu(1)-O(2) O(1)-Cu(1)-O(3) O(1)-Cu(1)-O(4) O(1)-Cu(1)-O(5)	1.971(7) 1.964(7) 1.954(7) 1.950(7) 2.102(8) 168.1(3) 90.1(3) 88.2(3) 97.2(4)	$\begin{array}{c} 5 \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2a) \\ Cu(1)-N(1) \\ Cu(1)-N(2) \\ Cu(1)-N(1a) \\ \hline \\ O(1)-Cu(1)-O(2a) \\ O(1)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(1) \\ O(1)-Cu(1)-N(2) \\ \end{array}$	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4) 98.4(4) 93.9(4) 69.7(5)		
 $\begin{array}{c} \textbf{4} \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2) \\ Cu(1)-O(3) \\ Cu(1)-O(4) \\ Cu(1)-O(5) \\ \hline \\ O(1)-Cu(1)-O(2) \\ O(1)-Cu(1)-O(3) \\ O(1)-Cu(1)-O(4) \\ O(1)-Cu(1)-O(5) \\ O(2)-Cu(1)-O(3) \\ \hline \end{array}$	1.971(7) 1.964(7) 1.954(7) 1.950(7) 2.102(8) 168.1(3) 90.1(3) 88.2(3) 97.2(4) 91.5(3)	$\begin{array}{c} 5 \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2a) \\ Cu(1)-N(1) \\ Cu(1)-N(2) \\ Cu(1)-N(2) \\ Cu(1)-N(1a) \\ \hline \\ O(1)-Cu(1)-O(2a) \\ O(1)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(1) \\ O(1)-Cu(1)-N(2) \\ O(2a)-Cu(1)-N(2) \\ \hline \end{array}$	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4) 98.4(4) 93.9(4) 69.7(5) 83.1(5)		
 $\begin{array}{c} \textbf{4} \\ \hline \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2) \\ Cu(1)-O(3) \\ Cu(1)-O(4) \\ Cu(1)-O(5) \\ \hline \\ O(1)-Cu(1)-O(2) \\ O(1)-Cu(1)-O(3) \\ O(1)-Cu(1)-O(4) \\ O(1)-Cu(1)-O(4) \\ O(2)-Cu(1)-O(3) \\ O(2)-Cu(1)-O(4) \\ \hline \end{array}$	1.971(7) 1.964(7) 1.954(7) 1.950(7) 2.102(8) 168.1(3) 90.1(3) 88.2(3) 97.2(4) 91.5(3) 87.7(3)	$\begin{array}{c} 5 \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2a) \\ Cu(1)-N(1) \\ Cu(1)-N(2) \\ Cu(1)-N(2) \\ Cu(1)-N(1a) \\ \hline \\ O(1)-Cu(1)-O(2a) \\ O(1)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(1) \\ O(1)-Cu(1)-N(2) \\ O(2a)-Cu(1)-N(2) \\ N(1)-Cu(1)-N(2) \\ \end{array}$	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4) 98.4(4) 93.9(4) 69.7(5) 83.1(5) 107.7(7)		
$\begin{array}{c} \textbf{4} \\ \hline \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2) \\ Cu(1)-O(3) \\ Cu(1)-O(4) \\ Cu(1)-O(5) \\ \hline \\ O(1)-Cu(1)-O(2) \\ O(1)-Cu(1)-O(3) \\ O(1)-Cu(1)-O(4) \\ O(1)-Cu(1)-O(5) \\ O(2)-Cu(1)-O(3) \\ O(2)-Cu(1)-O(4) \\ O(2)-Cu(1)-O(4) \\ O(2)-Cu(1)-O(5) \\ \hline \end{array}$	1.971(7) 1.964(7) 1.954(7) 1.950(7) 2.102(8) 168.1(3) 90.1(3) 88.2(3) 97.2(4) 91.5(3) 87.7(3) 94.3(4)	$\begin{array}{c} 5 \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2a) \\ Cu(1)-N(1) \\ Cu(1)-N(2) \\ Cu(1)-N(2) \\ Cu(1)-N(1a) \\ \hline \\ O(1)-Cu(1)-O(2a) \\ O(1)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(2) \\ O(2a)-Cu(1)-N(2) \\ N(1)-Cu(1)-N(2) \\ O(1)-Cu(1)-N(1a) \\ \end{array}$	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4) 98.4(4) 93.9(4) 69.7(5) 83.1(5) 107.7(7) 92.1(4)		
$\begin{array}{c} \textbf{4} \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2) \\ Cu(1)-O(3) \\ Cu(1)-O(4) \\ Cu(1)-O(5) \\ \hline \\ O(1)-Cu(1)-O(2) \\ O(1)-Cu(1)-O(3) \\ O(1)-Cu(1)-O(3) \\ O(1)-Cu(1)-O(4) \\ O(2)-Cu(1)-O(3) \\ O(2)-Cu(1)-O(4) \\ O(2)-Cu(1)-O(4) \\ O(3)-Cu(1)-O(4) \\ O(3)-Cu(1)-O(4) \\ O(3)-Cu(1)-O(4) \\ O(3)-Cu(1)-O(4) \\ \hline \end{array}$	$\begin{array}{c} 1.971(7) \\ 1.964(7) \\ 1.954(7) \\ 1.950(7) \\ 2.102(8) \end{array}$ $\begin{array}{c} 168.1(3) \\ 90.1(3) \\ 88.2(3) \\ 97.2(4) \\ 91.5(3) \\ 87.7(3) \\ 94.3(4) \\ 167.6(3) \end{array}$	$\begin{array}{c} 5 \\\\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2a) \\ Cu(1)-N(1) \\ Cu(1)-N(2) \\ Cu(1)-N(2) \\ Cu(1)-N(1a) \\\\ \hline \\ O(1)-Cu(1)-O(2a) \\ O(1)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(2) \\ O(2a)-Cu(1)-N(2) \\ O(1)-Cu(1)-N(2) \\ O(1)-Cu(1)-N(1a) \\ O(2a)-Cu(1)-N(1a) \\ O(2a)-Cu(1)-N(1a) \\ O(2a)-Cu(1)-N(1a) \\ \end{array}$	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4) 98.4(4) 93.9(4) 69.7(5) 83.1(5) 107.7(7) 92.1(4) 90.4(2)		
$\begin{array}{c} \textbf{4} \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2) \\ Cu(1)-O(3) \\ Cu(1)-O(4) \\ Cu(1)-O(5) \\ \hline \\ O(1)-Cu(1)-O(2) \\ O(1)-Cu(1)-O(3) \\ O(1)-Cu(1)-O(3) \\ O(1)-Cu(1)-O(3) \\ O(2)-Cu(1)-O(3) \\ O(2)-Cu(1)-O(4) \\ O(2)-Cu(1)-O(4) \\ O(3)-Cu(1)-O(4) \\ O(3)-Cu(1)-O(5) \\ \hline \end{array}$	$\begin{array}{c} 1.971(7) \\ 1.964(7) \\ 1.954(7) \\ 1.950(7) \\ 2.102(8) \end{array}$ $\begin{array}{c} 168.1(3) \\ 90.1(3) \\ 88.2(3) \\ 97.2(4) \\ 91.5(3) \\ 87.7(3) \\ 94.3(4) \\ 167.6(3) \\ 98.2(3) \end{array}$	$\begin{array}{c} 5 \\ \hline \\ Cu(1)-O(1) \\ Cu(1)-O(2a) \\ Cu(1)-N(1) \\ Cu(1)-N(2) \\ Cu(1)-N(2) \\ Cu(1)-N(1a) \\ \hline \\ O(1)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(1) \\ O(2a)-Cu(1)-N(2) \\ O(2a)-Cu(1)-N(2) \\ N(1)-Cu(1)-N(2) \\ O(1)-Cu(1)-N(1a) \\ O(2a)-Cu(1)-N(1a) \\ O(2a)-Cu(1)-N(1a) \\ N(1)-Cu(1)-N(1a) \\ \end{array}$	2.288(11) 1.978(7) 2.110(17) 2.340(16) 2.070(12) 152.4(4) 98.4(4) 93.9(4) 69.7(5) 83.1(5) 107.7(7) 92.1(4) 90.4(2) 147.9(2)		

 Table 2
 Selected bond lengths (Å) and angles (°) for complexes 1–5.



Fig. 4 Crystal packing of 1 (top) and 2 (bottom). Water and ethanol for 1 and THF and ethanol solvent molecules for 2 have been omitted for clarity.

rings, which form their walls. The cavities are filled with ethanol and THF molecules. The void volume of the cavities is 1142 Å³, which equals 28% of the unit cell volume.¹⁶

(iii) $[Cu(PTMMC)_2(py)_3]$ -2.5hexane, 3 and $[Cu(HPTM-MC)_2(py)_3]$ -4THF, 5. The molecular structures of 3 and 5 are similar to that of 2, but with three pyridine molecules instead of the two pyrimidine molecules and one molecule of ethanol. ORTEP drawings of metal-radical clusters present in both structures are shown in Fig. 5. As for 2, the Cu(II) ion displays a distorted square pyramidal coordination geometry by binding to the two oxygen atoms of two molecules of PTMMC (or HPTMMC) and the three nitrogen atoms of pyridine mole-



Fig. 5 ORTEP drawing of metal–radical clusters of $3\ (top)$ and $5\ (bottom)$ at the 30% probability level.

cules. The carboxylate groups of PTMMC and HPTMMC moieties are twisted by angles of 79° in **3** and 86° in **5** with respect to the phenyl plane to which they are bonded. In complex **3** the distance between the Cu(II) ion and the central carbon atom of the PTMMC moieties are 8.47 and 8.33 Å and the distance between the two units of PTMMC are 16.72 Å, values that are close to those found for complex **2**.

The self-assembly of metal-radical clusters of **3** and **5** is also similar to that of **2**, forming rectangular pores stabilized through 12 and 16 chlorine-chlorine contacts, respectively, with distances in the range 3.46–3.32 Å, occurring along the three directions. Such channels are filled with *n*-hexane in **3** and THF molecules in **5**. The void volume of the cavities is 632 Å³, which equals 30% of the unit cell volume.¹⁶

(iv) $[Cu_2(PTMMC)_2(MeCOO)_2(H_2O)_2]$ ·4EtOH, 4. Complex 4 crystallizes in the $P2_1/c$ monoclinic space group with the cell parameters reported in Table 1. The crystal structure of 4 shows a paddle-wheel Cu(II) dimer structure, where each Cu metal ion has four O atoms of different carboxylate groups in the equatorial positions, with distances in the range of 1.950–1.971 Å, and a water molecule at 2.102 Å at the apex, completing the square pyramidal coordination geometry (Fig. 6). Two of the O atoms situated at the opposite sites in the base of the square pyramid belong to two different PTMMC ligands, while the other two belong to two distinct acetate groups. The end-to-end distance of such metal–radical paddle-wheel supramolecules is 26 Å.

D. Magnetic properties

The molar paramagnetic susceptibility data of crystalline samples of 1–5 were obtained with a SQUID magneto/ susceptometer in the temperature range 2–300 K at a constant field of 0.1 T using Pascal's constants to calculate the diamagnetic contributions. The results are displayed in the form of the product of the molar paramagnetic susceptibility (χ_{mol}) with temperature (T) vs. the temperature. The principal components of the g-tensors of PTM-based complexes 1–5 (g_1, g_2, g_3) were determined by simulation of EPR spectra of powdered, crystalline samples (see Experimental section), and then the averaged g values $[g_{av} = (g_1 + g_2 + g_3)/3]$ were used in the theoretical calculation, as fixed values.

(i) [Cu(PTMMC)₂(H₂O)₃]·6H₂O·2EtOH, 1, [Cu(PTMMC)₂ (pyrimidine)₂(EtOH)]·THF·4EtOH, 2 and [Cu(PTMMC),-(py)₃]·2.5*n*-hexane, 3. Similar magnetic behavior was observed for complexes 1–3 (Fig. 9). A χT value of 1.12 emu K mol⁻¹ was obtained at 300 K, which is close to the theoretical one (χT = $0.12505 \cdot g \cdot 2[3S(S + 1)] = 0.12505 \cdot 2 \cdot 2[3 \cdot \frac{1}{2}(\frac{1}{2} + 1)] = 1.13$ emu K mol⁻¹) expected for three isolated $S = \frac{1}{2}$ spins in terms of the spin-only equation. As the temperature was decreased, the χT value also decreased until a value of 0.32 emu K mol⁻¹, corresponding to a S = 1/2 doublet fundamental state. The resulting χT vs. T curves for 1–3 were analyzed quantitatively on the basis of a linear three-spin model (Scheme 2), using the following effective Hamiltonian, $H = -2J(S_{R1}S_M + S_MS_{R2})$, modified to take into account the presence of intermolecular interactions (θ) in the molecular field approximation.¹⁷ This model is in accordance with the X-ray molecular and crystal structure analysis previously described. Eqn. (1) for a system with $S_{R1} = S_{R2} = S_M = 1/2$ was applied and fitted to the observed χT vs. T plots by means of a least-square method.

$$\chi T = \frac{N\mu_{\rm B}^2 g^2 T}{3k_{\rm B} (T - \Theta)} \frac{60 e^{3J/T} + 6 e^{2J/T} + 6}{4(4 e^{3J/T} + 2 e^{2J/T} + 2)}$$
(1)

Table 3 Details of the hydrogen bonding distances (Å) and angles (°) of complex 4

		D 1	D.U. A
$D-H \cdots A$	$H \cdots A$	$\mathbf{D} \cdots \mathbf{A}$	$D-H \cdots A$
$O(5)-H(5A) \cdots O(7)$	1.94	2.73	154
$O(5)-H(5B) \cdots O(6)$	1.89	2.74	175
$O(6) - H(6) \cdots O(4)$	2.18	2.95	153
$O(7) - H(7) \cdots O(4)$	2.47	3.09	132

(Table 3). Such hydrogen bonds generate a primary hydrogenbonded cyclic motif between two molecules of ethanol and two molecules (Fig. 7). In a parallel way, four of these cyclic motifs are hydrogen-bonded to create a bigger cyclic pattern composed of four ethanol solvent molecules and four molecules of **4**, which are extended along the *ab* plane generating a two-dimensional hydrogen-bonded network (Fig. 7).

C. Electrochemical properties

Cyclic voltammograms of the radical PTMMC and complexes 1–3 were performed in THF at room temperature with nBu_4NPF_6 (0.1 M) as supporting electrolyte (vs. Ag/AgCl) and a Pt wire as a working electrode. While the radical PTMMC showed only one reversible wave at +0.09 V, assigned to the one-electron reduction of the triphenylmethyl unit, all these complexes revealed two one-electron reversible waves. One of such waves corresponds to the reduction of the perchlorotriphenylmethyl radical ligands (~0 V) and the other to the reduction of the Cu(II) ion (~0.1 V) (Fig. 8). The reversible waves were observed at -0.02 and 0.12 V for 1, -0.03 and 0.13 V for 2, and at -0.03 and 0.10 V for 3 (vs. Ag/AgCl).



Fig. 6 ORTEP plot at the 50% probability level of metal-radical supermolecule (top) and a view of the crystal packing of 4 along the c axes (bottom). Ethanol solvent molecules have been omitted for clarity.

The crystal packing is built up by the self-assembly of such supramolecules in such a way as to form microchannels. A view down in the *c* direction revels an arrangement of square microchannels stabilized by 12 chlorine–chlorine contacts (Fig. 6). Thus, two confronted supramolecules along the *c* direction create a rectangular synthon, which is partially divided in two nearly square micropores, which are separated by a wall formed by the water ligands of both molecules. The dimensions of the micropores are 7.5 and 8.0 Å, with an effective size of 4.2×4.5 Å when van der Waals radius are considered. The void volume is 917 Å³, which equals 24% of the unit cell volume.¹⁶ The cavities are filled with ethanol molecules, strongly bonded through hydrogen bonds with the water and acetate ligands of **4**



Fig. 7 Hydrogen-bonded cyclic pattern formed by two molecules of **4** and two ethanol solvent molecules (left). Two-dimensional hydrogen-bonded layer along the *bc* plane (right). Chlorine atoms (left) and chlorine and carbon atoms (right) have been omitted for clarity.



Fig. 8 Cyclic voltammograms of PTMMC radical (top) and 1 (bottom) in THF.



Scheme 2 Magnetic exchange interactions in the linear three-spin model (a) and in the symmetrical four-spin butterfly model (b).

Fixing the evaluated g values, the resulting parameters for the best fits were $J/k_{\rm B} = -24.9 \pm 0.3$ K and $\theta = -0.68 \pm 0.05$ K for 1, $J/k_{\rm B} = -15.0 \pm 0.1$ K and $\theta = -0.45 \pm 0.02$ K for 2, and $J/k_{\rm B} = -20.7 \pm 0.1$ K and $\theta = -1.70 \pm 0.03$ K for 3. Thus, the values of the copper(II)–radical exchange coupling constants for all complexes were very similar ($J/k_{\rm B} \approx -20$ K) reflecting the presence of relatively strong antiferromagnetic interactions between the Cu(II) ion and the two coordinated radical PTMMC molecules.



Fig. 9 Temperature dependence of the product of the magnetic susceptibility and the temperature for complexes 3 (top) and 5 (bottom).

(ii) [Cu(HPTMMC)₂(py)₃]-4THF, 5. Magnetic measurements of a microcrystalline sample of 5 shows a quasi-ideal paramagnetic behavior (Fig. 9). Thus, the χT value in the range of 300 to 10 K is 0.38 emu K mol⁻¹, which is close to the theoretical value expected for one isolated $S = \frac{1}{2}$ spin. Upon further cooling, χT gradually decreased to a value of 0.33 emu K mol⁻¹ at 2 K. The experimental χT vs. T curve for 5 was analyzed quantitatively using the Curie–Weiss equation. From these data, a molar Curie constant of 0.379 cm³ K mol⁻¹ and a Weiss constant of -0.25 ± 0.01 K were obtained. The latter value is associated to the existence of very weak antiferromagnetic interactions between the supramolecules. (iii) [Cu₂(PTMMC)₂(MeCOO)₂(H₂O)₂]·4EtOH, 4. As can be seen in Fig. 10, the χT value at 300 K is 0.9 emu K mol⁻¹, which is still far from that expected for a system with four noninteracting electrons (1.9 emu K mol⁻¹). Such a divergence is consistent with the presence of strong antiferromagnetic interactions among the two Cu(II) ions and between the Cu(II) ions and the PTMMC coordinated radicals. Upon cooling χT gradually decreases down to 70 K, where it reaches a plateau at a value of 0.7 emu K mol⁻¹. Below 30 K, the χT value decreases abruptly to a χT value of 0.4 emu K mol⁻¹ at 2 K, due to the presence of weak intermolecular interactions.



Fig. 10 Temperature dependence of the product of the magnetic susceptibility and the temperature for complex 4.

The data was nicely fitted to a magnetic model based on a symmetrical butterfly arrangement of the two metal ions and two organic radicals (Scheme 2). The spin Hamiltonian, H, for this butterfly system is given by eqn. (2)¹⁸ where J is the wing-tip/body exchange interaction between the Cu(II) ions and the organic radicals and J_{13} is the body/body interaction between the two Cu(II) ions (Scheme 2).

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_4 \cdot \hat{S}_1) - 2J_{13}\hat{S}_1 \cdot \hat{S}_3 \quad (2)$$

The eigenvalues E deduced from eqn. (2), using the Kambe method, ¹⁹ are:

$$E = -J \cdot [S_{\rm T}(S_{\rm T}+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)] - J_{13}[S_{13}(S_{13}+1)]$$
(3)

where $S_{13} = S_1 + S_3$, $S_{24} = S_2 + S_4$ and $S_T = S_{13} + S_{24}$. A theoretical expression for the χT vs. T behavior was derived from the use of eqn. (3) and the van Vleck equation. The resulting expression, modified to take into account intermolecular interactions (θ) in the molecular field approximation, was then used to least-squares fit the experimental data of 4. Fixing the evaluated g = 2.01, the best fit was obtained for J = -21.3 K, $J_{13} = -350.0$ K and $\theta = -1.7$ K. The value of the body/body [copper(II)–copper(II)] interaction, $J_{13} = -350$ K, is within the range of those previously reported for the same kind of interaction in other paddle-wheel Cu(II) dimers,20 whereas the value of the wing-tip/body [copper(II)-radical interaction], $J_{13} =$ -21.3 K, is similar to that previously reported for the Cu(II)-PTMMC radical interaction in complexes 1-3. The fact that both exchange coupling parameters, J and J_{13} , are negative indicates that any two neighboring spins tend to align antiferromagnetically. However, the topological arrangement of metal ions and organic radicals in the butterfly structure results in a spin-frustration due to the presence of competing antiferromagnetic interactions. The ground state of 4 is therefore degenerated, with two different states that, in the format (S_{T}, S_{13}, S_{24}) , are: the triplet state (1,0,1) and the singlet state (0,0,0). This is one of the scarce examples of a spin-frustrated system composed of organic radicals and metal ions.21

Conclusions

In summary, it has been demonstrated that the carboxylic substituted perchlorotriphenylmethyl radical is an excellent coordinating ligand to obtain new metal complexes with different magnetic properties following the metal-radical approach. The reaction of the PTMMC radical with Cu(II) metal ion gave a series of metal-radical complexes, showing a relatively strong antiferromagnetic exchange coupling between the copper(II) ion and the PTMMC radicals of $J/k_{\rm B} \approx -20$ K. Furthermore, the use of different molar ratios yield different structures for the resulting metal-radical clusters. In particular, a metal-radical paddle-wheel dimer exhibiting a spin frustration phenomenon was obtained. Further studies to expand the range of structural motifs, the structural dimensionality and magnetic behaviours of metal-radical complexes based on polychlorinated triphenylmethyl radicals, either mono-, bi- or trifunctionalised with carboxylic groups, are currently underway.

Experimental

Physical measurements

Microanalyses were performed at the Servei d'Analisi of the Universitat Autònoma de Barcelona. The FT-IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer. The UV-visible spectra were obtained on a VARIAN Cary 5 instrument. Electrochemical experiments were performed with potentiostat Galvanostat 263ª de EG i PAR, using a platinum wire as working electrode and a Ag/AgCl electrode as reference electrode. Anhydrous THF was freshly distilled over sodium/benzophenone under nitrogen. Commercial tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) was used as the supporting electrolyte. The magnetic susceptibility were measured on the bulk materials in the 2-300 K temperature range with a Quantum Design MPMS superconducting SQUID magnetometer operating at a field strength of 0.1 T. The data were corrected for diamagnetism of the constituent atoms using Pascal constants. The EPR spectra have been recorded on X-band Bruker spectrometer (ESP-300E).

Materials

Solvents were distilled before use. In particular, THF was dried over sodium/benzophenone, and distilled under argon. All the reagents were used as received and they were purchased from Aldrich and Panreac. Ligands 1 and 5 were synthesized according to the procedure previously described.^{7b} All reactions were carried out in dark.

Preparation of complexes

(i) [Cu(PTMMC)₂(H₂O)₃]·6H₂O·2EtOH, 1. A solution of Cu₂(O₂CMe)₄·2H₂O (0.032 g, 0.080 mmol) in 8 mL of water was added dropwise to a solution of PTMMC (0.250 g, 0.320 mmol) in 14 mL of ethanol and stirred for 15 min at room temperature. A red microcrystalline solid (0.246 g) was isolated through filtering. The remaining solution was allowed to stand in air for slow evaporation. After 5 days, 0.011 g of red plate crystals of 1 were obtained, suitable for X-ray analysis. The total yield of the reaction was 97%. Elemental analysis (%): Calc. for C40H6O7Cl28Cu: C 29.04, H 0.36; Found: C 29. 41, H 0.47. FT-IR (KBr, cm⁻¹): 3393 (m), 1707 (w), 1607 (m), 1407 (m), 1335 (s), 1324 (s), 1260 (m), 1038 (w), 819 (w), 768 (w), 734 (m), 718 (m), 697 (w), 675 (w), 642 (m), 617 (w), 522 (m). UV-Vis (THF, λ/nm , ϵ/M^{-1} cm⁻¹): 223 (153800), 385 (62150), 508 (2412), 564 (2347). EPR (RT, powder crystalline sample): g-factors: $g_1 = 2.040$, $g_2 = 2.060$, $g_3 = 2.090$.

(ii) $[Cu(PTMMC)_2(pyrimidine)_2(EtOH)]$ ·THF·4EtOH, 2. A solution containing 15.7 µL of pyrimidine in 20 mL of ethanol was layered onto a solution of 1 (0.100 g, 0.060 mmol) in 20 mL

of THF. Slow diffusion over 19 days yielded 0.041 g (37%) of red prism crystals of 2. Elemental analysis (%): Calc. for C₅₀H₁₄O₅Cl₂₈N₄Cu: C 33.24, H 0.77, N 3.10; Found: C 32.87, H 0.47, N 2.73. FT-IR (KBr, cm⁻¹): 2970 (w), 1737 (w), 1611 (m), 1594 (m), 1564 (w), 1506 (w), 1470 (w), 1334 (s), 1324 (s), 1259 (m), 1226 (w), 1173 (w), 1038 (w), 819 (w), 770 (w), 734 (w), 715 (m), 674 (w), 642 (m), 616 (w), 577 (w), 540 (w), 522 (m). UV-Vis (THF, λ/nm , ϵ/M^{-1} cm⁻¹): 222 (176200), 385 (67340), 512 (1770), 565 (1802). EPR (RT, powder crystalline sample): g-factors: $g_1 = 2.018$, $g_2 = 2.032$, $g_3 = 2.090$.

(iii) [Cu(PTMMC)₂(py)₃]·2.5hexane, 3. A solution containing 3 mL of pyridine in 15 mL of hexane was layered onto a solution of 1 (0.095 g, 0.057 mmol) in 20 mL of THF. Slow diffusion over 4 days yielded 0.040 g (39%) of red prism crystals of 3. Elemental analysis (%) Calc. for C₅₇H₂₂O₄Cl₂₈N₃Cu: C 37.03, H 1.17, N 2.23; Found: C 36.93, H 1.85, N 1.70. FT-IR (KBr, cm⁻¹): 2951 (w), 2927 (w), 2859 (w), 1617 (m), 1610 (m), 1450 (m), 1397 (m), 1334 (s), 1324 (s), 1258 (m), 1073 (m), 1048 (w), 1037 (w), 917 (w), 876 (w), 820 (w), 812 (w), 769 (m), 733 (w), 718 (w), 694 (m), 674 (w), 645 (w), 617 (w), 579 (w), 537 (w), 522 (m). UV-Vis (THF, λ/nm , ε/M^{-1} cm⁻¹): 222 (163800), 385 (67530), 512 (2615), 565 (2715). EPR (RT, powder crystalline sample): g-factors: $g_1 = 2.019$, $g_2 = 2.028$, $g_3 = 2.088$.

(iv) [Cu₂(PTMMC)₂(MeCOO)₂(H₂O)₂]·4EtOH, 4. A solution of PTMMC (0.075 g, 0.098 mmol) in 40 mL of ethanol was added dropwise to a solution of Cu₂(O₂CMe)₄·2H₂O (0.051 g, 0.127 mmol) in 9 mL of water and 1 mL of ethanol during 2 h and stirred for 5 min at room temperature. The reaction mixture was filtered and the remaining solution was allowed to stand in air for slow evaporation. After 15 days, 0.009 g (14%) of red prism crystals of complex 4 were obtained. Elemental analysis (%): Calc. for C44H10O10Cl28Cu2: C 31.19, H 1.70; Found: C 31.26, H 1.64. FT-IR (KBr): 1624 (m), 1607 (m), 1417 (m), 1335 (s), 1324 (s), 1259 (m), 1039 (w), 819 (w), 767 (w), 734 (m), 717 (W), 675 (w), 642 (m), 616 (w), 522 (m). EPR (110 K, powder crystalline sample): g-factors: $g_1 = 2.008$, $g_2 = 2.009$, $g_3 = 2.018$.

(v) [Cu(HPTMMC)₂(py)₃]·4THF, 5. A solution of Cu₂-(O₂CMe)₄·2H₂O (0.026 g, 0.130 mmol) in 7 mL of water was added dropwise to a solution of 13 mL of ethanol and 0.5 mL of ether of HPTMMC (0.200 g, 0.260 mmol) and stirred for 15 min at room temperature. A green solid was isolated through filtration and 100 g of this was dissolved in 20 mL of THF. A solution of 30 mL of hexane containing 3 mL of pyridine was layered onto a solution of THF. Slow diffusion over 6 days yielded 0.033 g of blue prism crystals of 6. Elemental analysis (%): Calc. for C₅₅H₁₇O₄Cl₂₈N₃Cu: C 35.90, H 0.92, N 2.28; Found: C 36.46, H 1.13, N 1.82. FT-IR (KBr, cm⁻¹): 2950 (w), 2926 (w), 1742 (w), 1628 (m), 1618 (m), 1609 (m), 1556 (w), 1534 (w), 1489 (w), 1469 (w), 1450 (m), 1438 (w), 1405 (m), 1371 (m), 1334 (s), 1314 (s), 1300 (s), 1240 (m), 1218 (w), 1152 (w), 1123 (w), 1048 (w), 912 (w), 872 (w), 804 (mw), 763 (m), 719 (w), 694 (m), 676 (m), 652 (w), 634 (w), 619 (w), 579 (w), 543 (w), 521 (m). UV-Vis (THF, λ/nm , $\varepsilon/\text{M}^{-1}$ cm⁻¹): 223 (264900). EPR (RT, powder crystalline sample): g-factors: $g_1 = 2.052$, $g_2 = 2.070, g_3 = 2.094.$

X-Ray data collection and structure determination

X-Ray single-crystal diffraction data were collected on a Nonius KappaCCD diffractometer with graphite-monochromized Mo-K α radiation ($\lambda = 0.7106$ Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK. Several scans in ϕ and ω directions were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces an empirical absorption correction. The

structures were solved and refined using the SHELXTL software.22

For 4, the refinement was run in a normal way, all nonhydrogen atoms were refined with anisotropic displacement parameters, all hydrogen atoms were calculated or found on their positions and refined isotropically. In the refinement of the other structures the hydrogen atoms of the water, ethanol, hexane and THF molecules were omitted, because of poorer crystal data owing to disorder problems.

Two kinds of disorder were observed around the environment of the well ordered PTMMC radicals, one for 1 and 2, the other for 3 and 5. In 1, there is a 5 : 1 positional disorder of the $Cu(H_2O)_3$ -unit. The Cu(1) atom of the major part coordinates to O1 and O3 (as shown in Fig. 2) and in the minor part the Cu(1a) atom coordinates to O2 and O4 with an apparent Cu(1)–Cu(1a) distance of 2.60 Å. The oxygen atoms of the minor part and the solvent water and ethanol were refined with isotropic displacement parameters, all other non-hydrogen atoms were refined anisotropically. A similar disorder of 3:1 occurs for the Cu(pyrimidine)₂(EtOH)-unit of 2 with an apparent Cu(1)-Cu(1a) distance of 1.34 Å. This short distance between the disordered Cu atoms leads to nearly overlying pyrimidine rings with highly distorted anisotropic displacement parameters and separate ethanol groups in opposite directions. The ethanol molecule of the minor part and the solvent ethanol and THF were refined with isotropic displacement parameters, all other non-hydrogen atoms were refined anisotropically. In 3 and 5 there is only a half molecule in the asymmetric unit and the Cu(py)₃-unit lies nearby a symmetry centre, which produces a second Cu(py)₃-unit in a 1 : 1 disorder with an apparent Cu(1)–Cu(1a) distance of 1.48 Å for 3 and 1.15 Å for 5, respectively. Similarly to 2, there are two nearly overlying pyridine rings with distorted displacement parameters and one separate pyridine ring for each Cu atom. In 3 all non-hydrogen atoms were refined with anisotropic displacement parameters, except the solvent hexane, which was refined isotropically. In 5 there additionally exists a 1:1 positional disorder of the methane group of the HPTMMC molecule. The solvent THF were refined isotropically and also the carbon atoms of the separate pyridine ring, because of a nearly overlying with a THF molecule from the disordered part, all other atoms were refined with anisotropic thermal parameters.

Interestingly, 2, 3 and 5 have nearly the same packing motifs in the crystal lattice, although the cell volume of 2 is twice as large. An examination of the intensities of 2 shows that all reflections with h + k = 2n + 1 are systematically weak suggestive of a C-centred unit cell, which is not defined in the triclinic system. The relationship to 3 and 5 is, that the 1:1 disorder of the Cu-units leads to a complete extinction of these weak reflections and formally to a C-centred unit cell. The transformation matrix from the C-centered to the correct primitive P cell is $0.5\ 0.5\ 0;\ -0.5\ 0.5\ 0;\ 0.5\ 0.5\ 1$ (row by row). If the unit cell of 2 is transformed in this manner, the cell constants are comparable to those of 3 and 5 with cell constants a = 8.729, b = 13.923, c = 17.076 Å, a = 86.52, $\beta = 81.22$ and $\gamma = 88.91^{\circ}$. This shows that a simple 1 : 1 disorder from a small part of the molecule can generate a new unit cell.

CCDC reference numbers 186141 (1), 226899 (2), 226900 (3), 186142 (4) and 226898 (5).

See http://www.rsc.org/suppdata/dt/b3/b316458f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This work was supported by the Dirección General de Investigación (Spain), under project MAT2003-04699 and the 3MD Network of the TMR program of the EU (contract ERBFMRX CT980181).D. R.-M. thanks the Programa Ramón y Cajal for financial support. D. M. is grateful to the Generalitat de Catalunya for a predoctoral grant. D. M. is

enrolled in the PhD program of the Universitat Autònoma de Barcelona. We warmly thank Dr Carlos Gómez-García and J. M. Martínez (Universitat de Valencia) for the magnetic susceptibility measurements.

References

- (a) A. Caneschi, D. Gatteschi and P. Rey, *Prog. Inorg. Chem.*, 1991, 39, 331; (b) H. Iwamura, K. Inoue and T. Hayamizu, *Pure Appl. Chem.*, 1996, 68, 243.
- 2 For a review of nitroxide-based complexes, see: H. Iwamura and K. Inoue, *Magnetism: Molecules to Materials II*, ed. J. S. Miller and M. Drillon, Wiley-VCH, Weinheim, 2001.
- 3 For examples of complexes with nitroxide radicals, see: (a) L. M. Field, P. M. Lahti and F. Palacio, *Chem. Commun.*, 2002, 636; (b) F. Mathevet and D. Luneau, *J. Am. Chem. Soc.*, 2001, **123**, 7465; (c) P. Rabu, M. Drillon, H. Iwamura, G. Görlitz, T. Itoh, K. Matsuda, N. Koga and K. Inoue, *Eur. J. Inorg. Chem.*, 2000, 211; (d) H. Kumada, A. Sakane, N. Koga and H. Iwamura, *J. Chem. Soc., Dalton Trans.*, 2000, 911.
- 4 For examples of complexes with α-nitronyl nitroxide radicals, see: (a) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, Angew. Chem., Int. Ed., 2001, 40, 1760; (b) M. Minguet, D. Luneau, E. Lhotel, Vincent Villar, C. Paulsen, D. B. Amabilino and J. Veciana, Angew. Chem., Int. Ed., 2002, 41, 586; (c) G. Stroh, P. Turek, P. Rabu and R. Ziessel, Inorg. Chem., 2001, 21, 5334; (d) C. Rancurel, J.-P. Sutter, T. Le Hoerff, L. Ouahab and O. Kahn, New. J. Chem., 1999, 1333; (e) M. G. F. Vaz, L. M. M. Pinehiro, H. O. Stumpf, A. F. C. Alcantara, S. Goleen, L. Ouahab, O. Cador, C. Mathonière and O. Kahn, Chem. Eur. J., 1999, 5, 1486; (f) K. Fey, D. Luneau, T. Ohm, C. Paulsen and P. Rey, Angew. Chem., 1998, 37, 1270.
- 5 For examples of complexes with imino nitroxide radicals, see: (a) K. E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey and M. Verdaguer, J. Am. Chem. Soc., 2000, **122**, 718; (b) H. Oshio and T. Ito, Coord. Chem. Rev., 2000, **198**, 329; (c) A. Marvilliers, Y. Pei, J. Cano, K. E. Vostrikova, C. Paulsen, E. Rivière, J.-P. Audière and T. Mallah, Chem. Commun., 1999, 1951; (d) H. Oshio, T. Wanabe, A. Ohto and T. Ito, Inorg. Chem., 1997, **36**, 1608.

- 6 R. G. Hicks, M. T. Lemaire, L. K. Thompson and T. M. Barclay, J. Am. Chem. Soc., 2000, **122**, 8077.
- 7 (a) A. Caneschi, A. Dei, H. Lee, D. A. Shultz and L. Sorace, *Inorg. Chem.*, 2001, 40, 408; (b) D. Ruiz-Molina, J. Veciana, K. Wurst, D. N. Hendrickson and C. Rovira, *Inorg. Chem.*, 2000, 39, 617.
- 8 K. I. Pokhodnya, N. Petersen and J. S. Miller, *Inorg. Chem.*, 2002, **41**, 1996.
- 9 S. Karasawa, H. Kumada, N. Koga and H. Iwamura, J. Am. Chem. Soc., 2001, **123**, 9685.
- 10 (a) D. Maspoch, L. Catala, P. Gerbier, D. Ruiz-Molina, J. Vidal-Ganzedo, K. Wurst, C. Rovira and J. Veciana, *Chem. Eur. J.*, 2002, **8**, 3635; (b) M. Ballester, J. Castañer, J. Riera, A. Ibáñez and J. Pujadas, *J. Org. Chem.*, 1982, **47**, 259.
- 11 A preliminary communication has already been reported; see: D. Maspoch, D. Ruiz-Molina, K. Wurst, C. Rovira and J. Veciana, *Chem. Commun.*, 2002, 2958.
- 12 A similar tendency to form mononuclear complexes have already been shown in transition metal complexes with highly sterically hindered carboxylate ligands encapsulated by arene groups: F. A. Chavez, L. Que and W. B. Tolman, *Chem. Commun.*, 2001, 111.
- 13 M. Ballester, J. Riera, J. Castañer, C. Badia and J. M. Monsó, J. Am. Chem. Soc., 1971, 93, 2215.
- 14 R. C. Mehrotra, *Metal Carboxylates*, Academic Press Inc., New York, 1983.
- 15 M. Ballester, J. Riera, J. Castañer, A. Rodríguez, C. Rovira and J. Veciana, J. Org. Chem., 1982, 47, 4498.
- 16 A. L. Spek, A.M.C.T. PLATON, Utrecht University, Utrecht, The Netherlands, 1998.
- 17 Y. Ishimaru, M. Kitano, H. Kumada, N. Koga and H. Iwamura, Inorg. Chem., 1998, 37, 2273.
- 18 J. B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P. D. Boyd, J. C. Huffman, D. N. Hendrickson and G. Christou, J. Am. Chem. Soc., 1989, 111, 2086.
- 19 K. Kambe, J. Phys. Soc., Jpn., 1950, 5, 48.
- 20 O. W. Steward, B. S. Johnston, S.-C. Chang, A. Harada, S. Ohba, T. Tokii and M. Kato, Bull. Chem. Soc. Jpn., 1996, 69, 3123.
- 21 (a) D. Ruiz-Molina, C. Sporer, K. Wurst, P. Jaitner and J. Veciana, *Angew. Chem., Int. Ed.*, 2000, **39**, 3688; (b) M. Tanaka, K. Matsuda, T. Itoh and H. Iwamura, *Angew. Chem.*, 1998, **110**, 866; M. Tanaka, K. Matsuda, T. Itoh and H. Iwamura, *Angew. Chem., Int. Ed.*, 1998, **37**, 810.
- 22 G. M. Sheldrick: SHELXL-97, Program for Crystal Structure refinement, University of Göttingen, Germany 1997.