

# Tetracarboxylate Ligands as New Chelates Supporting Copper(II) Paddlewheel-Like Structures

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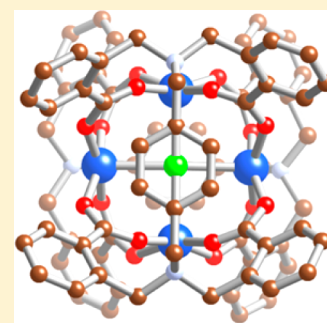
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## Supporting Information

**ABSTRACT:** Two new ligands *N,N,N,N*-tetrakis(2-methylbenzoic acid)-1,4-diaminomethylbenzene, **5H**<sub>4</sub>, and *N,N,N,N*-tetrakis(2-methylbenzoic acid)-4,4'-diaminomethyldiphenyl, **6H**<sub>4</sub>, carrying four carboxylate groups suitable for bridging dinuclear centers have been prepared and their paddlewheel complexes with copper(II) prepared. The phenyl-bridged ligand **5H**<sub>4</sub> gives a cyclic octanuclear species [(Cu<sub>2</sub>)<sub>4</sub>(**5**)<sub>4</sub>], while the diphenyl-bridged ligand **6H**<sub>4</sub> gives a lantern-like tetranuclear species [(Cu<sub>2</sub>)<sub>2</sub>(**6**)<sub>2</sub>]; both were characterized by X-ray crystallography. If the amine functions of **5** are protonated, intramolecular hydrogen bonds position the four carboxylates in such a way as to allow formation of the unusual compound [Cu<sub>4</sub>(SH<sub>2</sub>)<sub>2</sub>Cl]<sup>3+</sup> in which a Cu<sub>4</sub> square centered by a chloro ligand is sandwiched between two (SH<sub>2</sub>)<sup>2-</sup> ligands. The magnetic properties of this compound have been studied and show antiferromagnetic coupling between adjacent coppers (*J* = −33.7 cm<sup>−1</sup>).



## INTRODUCTION

The ability of copper(II) to form paddlewheel-like structures of general formula Cu<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub> with carboxylate ligands has been used in formation of a wide range of molecules such as discrete assemblies,<sup>1–3</sup> polymeric chains,<sup>4–9</sup> and MOFs (metal organic frameworks).<sup>7,10–19</sup> These materials can show useful properties in domains such as catalysis,<sup>20</sup> gas storage,<sup>21–24</sup> and magnetism.<sup>4,25–27</sup> Polycarboxylate ligands such as 1,4-benzene dicarboxylic acid or 1,3,5-benzenetricarboxylic acid<sup>28</sup> are frequently used, and the design of linkers between the carboxylic acids has been discussed.<sup>29</sup> In general, the four carboxylate ligands of a paddlewheel complex belong to different ligands, but one could imagine joining two or more carboxylates to give discrete M<sub>2</sub>(dicarboxylate)<sub>2</sub> or M<sub>2</sub>(tetracarboxylate) species. Dicarboxylate ligands occupying two carboxylate sites of a paddlewheel have indeed been reported previously.<sup>9</sup> A suitably designed tetracarboxylate ligand could, in principle, strongly stabilize the paddlewheel structure, acting as a tetrabridging ligand and allowing synthesis of paddlewheel complexes with metals other than the traditional ions (Mo(II), Rh(II), and Cu(II)).<sup>30,31</sup> This article reports the synthesis of two new tetracarboxylate ligands conceived with this in view and reports their chemistry with copper(II).

## RESULTS

**Ligand Design and Synthesis.** Ligand design requires a certain degree of flexibility to allow the ligand to wrap around the M<sub>2</sub> unit, but it must be sufficiently rigid to prevent formation of simple mononuclear species such as the classic

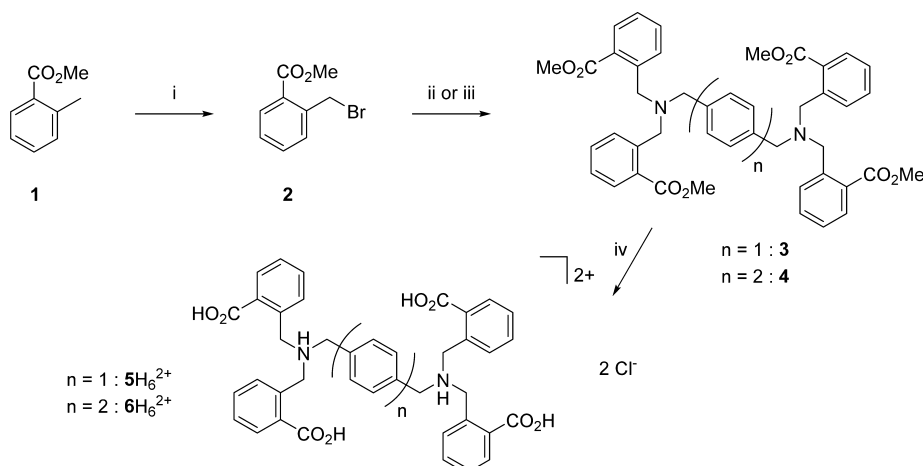
ethylenediaminetetraacetate (EDTA) complexes. Our approach is therefore to use aromatic acids and a partly aromatic linker to give rigidity, with methylene–amino–methylene linkers to allow some flexibility. This led us to *N,N,N,N*-tetrakis(2-methylbenzoic acid)-1,4-diaminomethylbenzene (**5**) as a possible ligand. To study the effect of changing the spacer we also prepared *N,N,N,N*-tetrakis(2-methylbenzoic acid)-4,4'-diaminomethyldiphenyl (**6**).

Both ligands were obtained in three steps following the same route (Scheme 1). The first step involved bromination of methyl-2-methylbenzoic acid **1** to form **2**.<sup>32</sup> Compound **2** undergoes an N-alkylation reaction with 1,4-diaminomethylbenzene or 4,4'-diaminomethyl-biphenyl<sup>33</sup> to form, respectively, the tetraesters **3** or **4**. The yield of the second step is only around 40% due to an intramolecular annelation reaction occurring in parallel with the N-alkylation, decreasing significantly the yield (see Scheme S1, Supporting Information).<sup>34</sup> Hydrolysis of these esters affords the desired tetracarboxylate ligands **5** and **6** in a hexaprotonated form.<sup>35</sup> Ligands **3** and **5** (as a hydrochloride salt) were characterized by X-ray crystallography (see below).

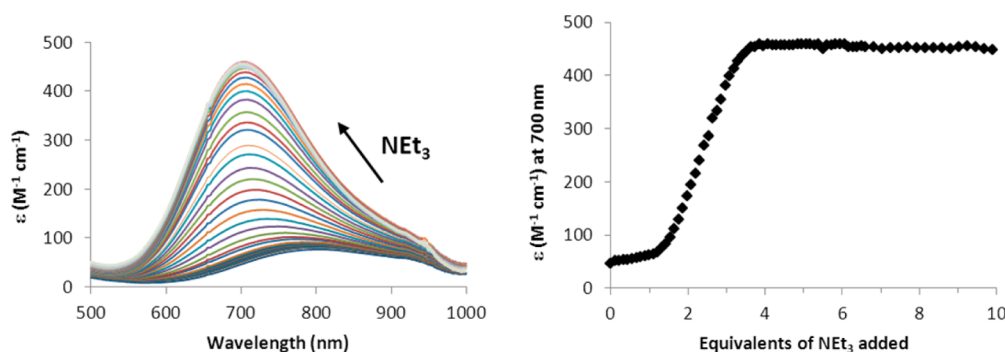
**Copper Complexation Studies.** Complexation of the ligands with copper(II) in solution was followed by observing the d–d transition of the d<sup>9</sup> copper(II) ion. Since it is necessary to deprotonate the carboxylate functions to allow complexation, the reaction was followed by titrating a 2:1 copper/ligand mixture with triethylamine as a base.

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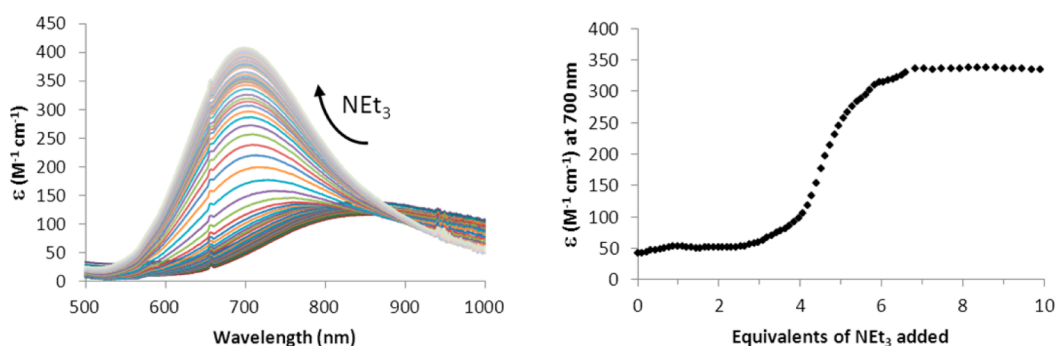
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Scheme 1. Synthetic Pathway for Ligands 5 and 6<sup>a</sup>

<sup>a</sup>(i) NBS (1 equiv), AIBN (0.03 equiv),  $\text{CCl}_4$ , reflux; (ii) 1,4-diaminomethylbenzene (0.2 equiv),  $\text{K}_2\text{CO}_3$  (3 equiv),  $\text{CH}_3\text{CN}$ , reflux; (iii) 4,4'-diaminomethyldiphenyl (0.2 equiv),  $\text{K}_2\text{CO}_3$  (3 equiv),  $\text{CH}_3\text{CN}$ , reflux; (iv) KOH (20 equiv),  $\text{H}_2\text{O}$ , MeOH, reflux, then HCl 6 M.



**Figure 1.** Changes in the visible spectrum upon addition of base (triethylamine) to a mixture of 1 equiv of the salt  $6\text{H}_6\text{Cl}_2$  with 2 equiv of copper(II) perchlorate in DMF. (Left) Change in spectrum; (right) change in extinction at 700 nm.



**Figure 2.** Changes in the visible spectrum upon addition of base (triethylamine) to a mixture of 1 equiv of the salt  $5\text{H}_6\text{Cl}_2$  with 2 equiv of copper(II) perchlorate in DMF. (Left) Change in spectrum; (right) change in extinction at 700 nm.

Ligand 6 showed fairly simple behavior: no change in spectrum was observed for the first equivalent of base, but after 2 equiv per ligand, a strong band ( $\epsilon = 200 \text{ L mol}^{-1} \text{ cm}^{-1}$  per copper), typical of the dicopper–tetracarboxylate chromophore,<sup>36</sup> grew at 700 nm, reaching a plateau after 4 equiv corresponding to deprotonation of the four carboxylate groups (Figure 1). From the DMF solution containing an excess of base, blue crystals of  $[\text{Cu}_4(\text{6})_2(\text{DMF})_4]$ , 9, could be isolated. The infrared spectrum of compound 9 shows several  $\nu_{\text{CO}}$  vibration bands going from 1587 to 1664  $\text{cm}^{-1}$ , establishing the coordination of the carboxylate functions to the copper atoms. The visible spectrum of the solid showed a maximum at

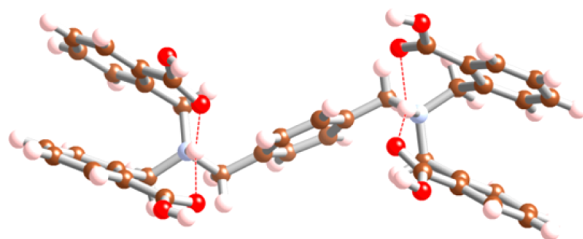
710 nm in agreement with the solution studies and formation of a paddlewheel.

The behavior with ligand 5 was different and showed clear evidence of an intermediate with a maximum around 790 nm, giving a green color to the solution. The dicopper–tetracarboxylate paddlewheel band at 700 nm grows in only after 4 equiv of base per ligand have been added, when deprotonation of the amine functions begins. A maximum is attained when the amines are fully deprotonated after adding 6 equiv of base (Figure 2).

From solutions containing 3 and 10 equiv of base we were able to isolate green crystals of 7,  $[\text{Cu}_4(\mu_4\text{-Cl})(\text{SH}_2)_2(\text{DMF})_4]$ -

(ClO<sub>4</sub>)<sub>3</sub>·DMF, and blue crystals of **8**, [Cu<sub>8</sub>(S)<sub>4</sub>(DMF)<sub>8</sub>·(Et<sub>2</sub>O)<sub>4</sub>], respectively. Use of the stoichiometric quantity of base (4 equiv) to prepare **7** did not give a crystalline product. The infrared spectra of these compounds show several carbonyl stretching bands in the ranges from 1573 to 1669 cm<sup>-1</sup> and 1603 to 1651 cm<sup>-1</sup>, respectively, confirming the coordination of the carboxylate functions to the copper atoms.<sup>37</sup> Compound **7** shows an absorption maximum at 763 nm in the solid state and at 790 nm in solution, while **8** shows an absorption maximum at 710 nm in the solid state and at 715 nm in solution. We conclude that the isolated species are essentially the same as those observed in solution. In high-resolution ESI mass spectrometry compound **7** shows the presence of several polynuclear species with up to three copper atoms, suggesting partial fragmenting of the complex characterized by X-ray crystallography (see below).

**Crystallographic Studies.** The crystal structure of **3** (Figure S1, Supporting Information) shows no particular features of interest. No hydrogen-bonding interactions are seen, but there are stacking interactions between benzoates of different molecules. There appears to be no favored orientation of the ester units. The crystal structure of the tetraacid **5** was obtained in the form of the hydrochloride salt [5H<sub>6</sub>·(Me<sub>2</sub>NH<sub>2</sub>)Cl<sub>3</sub>·2DMF and shows significant differences from that of **3**. All carboxylate and amine functions are protonated, and there is an intramolecular bifurcated hydrogen bond between the N–H<sup>+</sup> group and the carbonyl oxygens of the four acids. This hydrogen bond holds the two toluic acid functions bound to each amine roughly parallel (Figure 3). There are



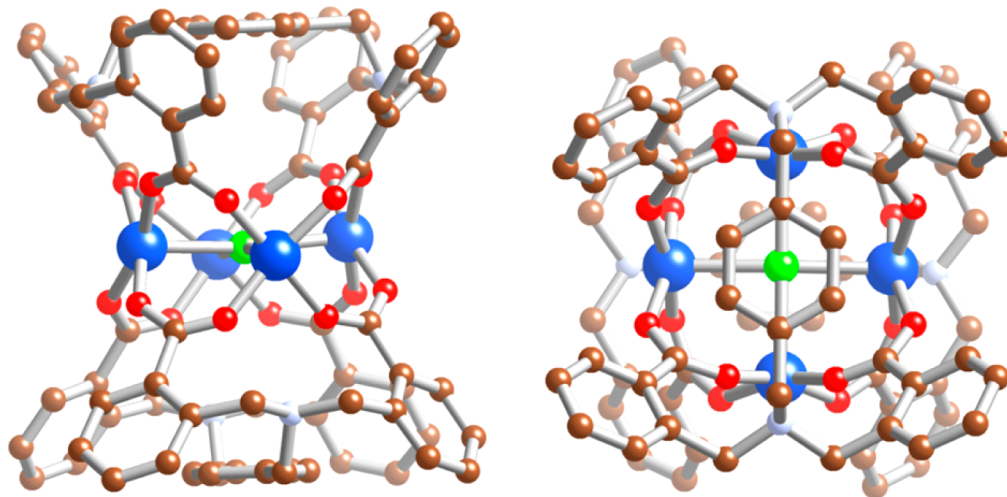
**Figure 3.** Structure of the ligand 5H<sub>6</sub><sup>2+</sup>. Bifurcated hydrogen bonds between the protonated amine function and the carbonyl oxygens are shown as red dashed lines.

stacking interactions between toluic acid functions of neighboring molecules. The three chloride ions are hydrogen bonded to protons of the carboxylic acid functions, the fourth carboxylic acid being hydrogen bonded to a disordered DMF molecule. Two of the chlorides are further hydrogen bonded to the same Me<sub>2</sub>NH<sub>2</sub><sup>+</sup> cation (Figure S2, Supporting Information), which we presume to have been generated by decomposition of DMF during crystallization. Details of hydrogen bonding are given in Table S1, Supporting Information.

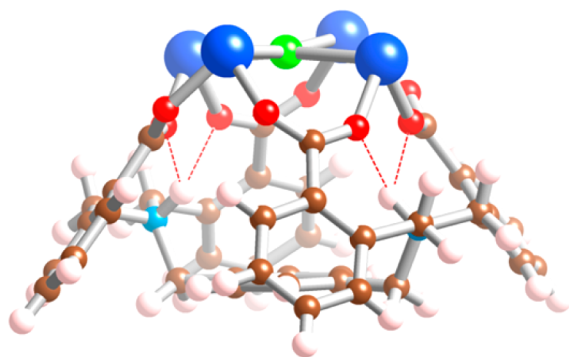
The structure of [Cu<sub>4</sub>(μ<sub>4</sub>-Cl)(5H<sub>2</sub>)<sub>2</sub>(DMF)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>·DMF, **7**, was rather unexpected (Figure 4). It may be regarded as a sandwich containing a Cu<sub>4</sub> square with a chloride ion in the center as a filling. This essentially planar unit lies in between two 5H<sub>2</sub><sup>2-</sup> units where the four deprotonated carboxylate units each bridge one side of the Cu<sub>4</sub> square. The four copper sites are virtually identical. The copper is bound to four oxygen atoms, each belonging to a different carboxylate group with a mean Cu–O distance of 1.957 Å. The four oxygens are essentially planar (maximum deviation 0.02 Å), but the copper is displaced by an average distance of 0.27 Å from the O<sub>4</sub> plane toward the central chloride ion, with a mean Cu–Cl distance of 2.57 Å. Each pair of copper ions is bridged by two carboxylates. Four DMF molecules are weakly coordinated by oxygen (Cu–O > 2.5 Å). The fifth DMF and the three perchlorate anions lie around the complex. The DMF molecules are disordered. Copper–copper distances lie between 3.596 and 3.652 Å.

The amine functions are still protonated, and the bifurcated N–H···O=C hydrogen bonds seen in [5H<sub>6</sub>·(Me<sub>2</sub>NH<sub>2</sub>)Cl<sub>3</sub>·2DMF are still present, although the conformation of the ligand has changed to allow metal binding (Figure 5). The complex as a whole has approximate D<sub>2d</sub> symmetry. Details of hydrogen bonds and selected bond distances and angles are given in the Supporting Information.

Square Cu<sub>4</sub>O systems have been reported in the literature on a number of occasions,<sup>38–43</sup> but the closest to the Cu<sub>4</sub>Cl system reported here is the [Cu<sub>4</sub>(μ<sub>4</sub>-OH)(CO<sub>3</sub>)<sub>8</sub>]<sup>9-</sup> ion reported by Abrahams et al.<sup>44</sup> in which the four copper ions are bridged by eight carbonate ions compared with eight carboxylates as seen here and the μ<sub>4</sub>-bridge occupies an axial position in a square pyramidal (SP) geometry with neighboring Cu planes roughly



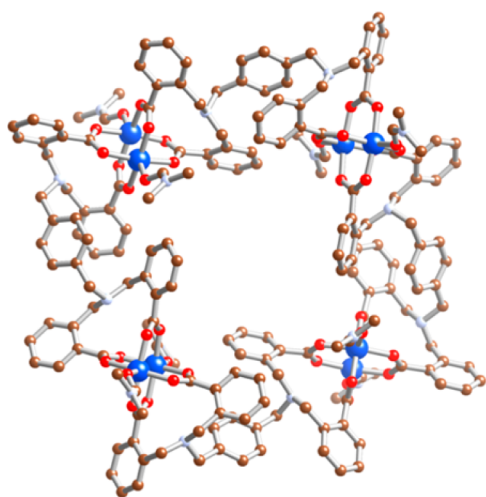
**Figure 4.** Structure of the [Cu<sub>4</sub>(μ<sub>4</sub>-Cl)(5H<sub>2</sub>)<sub>2</sub>(DMF)<sub>4</sub>]<sup>3+</sup> cation in **7**. Hydrogens and the DMF molecules weakly bound on the Cl–Cu axis have been omitted. (Left) View perpendicular to the S<sub>4</sub> axis; (right) view along the S<sub>4</sub> axis.



**Figure 5.** Binding mode of the  $5\text{H}_2^{2-}$  ligand in **7** showing the persistence of the bifurcated hydrogen bonds in the complex.

perpendicular. The copper–copper distances in the carbonate anion are slightly shorter ( $3.155 \text{ \AA}$ ) than those observed here, but this is probably an effect due to the larger central chloride ion in our compound.

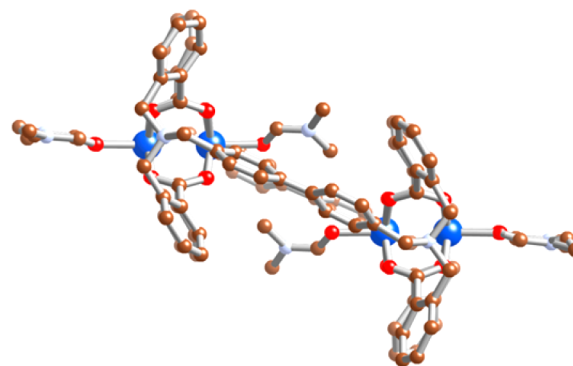
Full deprotonation of the ligand leads to formation of **8**,  $[\text{Cu}_8(\text{S})_4(\text{DMF})_8] \cdot (\text{Et}_2\text{O})_4$ , a tetrameric structure with four  $\text{Cu}_2$  units bridged by four ligands **5** (Figure 6). The amine(bis-



**Figure 6.** Complex  $[\text{Cu}_8(\text{S})_4(\text{DMF})_8]$  in **8** looking along the  $S_4$  axis. Hydrogens and disordered ether molecules in the channels are not shown.

toluic acid) units act as chelates, and the  $\text{Cu}_2(\text{O}_2\text{CR})_4$  unit is thus built up from two coppers and two ligands. The paddlewheel unit shows typical geometry (Cu–Cu distance  $2.6346(7) \text{ \AA}$ , mean Cu–O  $1.966(10) \text{ \AA}$ ), and two DMF molecules are bound in the axial positions. The tetramer has crystallographic  $S_4$  symmetry. Disordered diethyl ether molecules occupy the channels in the center of the tetramer. Selected bond distances and angles are given in the Supporting Information.

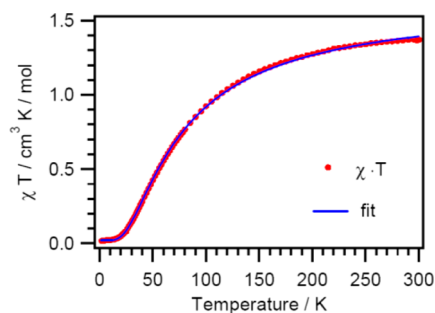
The diphenyl-bridged ligand **6** forms a centrosymmetric double paddlewheel complex  $[\text{Cu}_4(\text{6})_2(\text{DMF})_4]$ , **9** (Figure 7). The two ligands act as bridges between the  $\text{Cu}_2$  units, each ligand providing two carboxylates to each dinuclear unit. The paddlewheel unit shows typical geometry (Cu–Cu distance  $2.6152(4) \text{ \AA}$ , mean Cu–O  $1.970(7) \text{ \AA}$ ). The axial sites are occupied by DMF molecules; those on the outside of the cage are disordered. The two  $\text{Cu}_2$  units are aligned in the same direction as a result of the center of inversion but are not



**Figure 7.** Structural representation of compound  $[\text{Cu}_4(\text{6})_2(\text{DMF})_4]$ , **9**. Only one of the orientations of the disordered external DMF molecules is shown, and hydrogens are omitted.

collinear. Selected bond distances and angles are given in the Supporting Information.

**Magnetic Properties of the Sandwich Complex  $[\text{Cu}_4(\mu_4\text{-Cl})(5\text{H}_2)_2(\text{DMF})_4](\text{ClO}_4)_3 \cdot \text{DMF}$ , **7**.** There have been some magnetic studies on the  $\text{Cu}_4\text{O}$  systems mentioned above<sup>39–41</sup> which concluded that antiferromagnetic coupling was present. We felt it would be of interest to study the  $\text{Cu}_4\text{Cl}$  system prepared here. The  $\chi_m T(T)$  plot (Figure 8) of a



**Figure 8.** Thermal variation of  $\chi_m T$  for **7** (solid line is a fit according to eq 2).

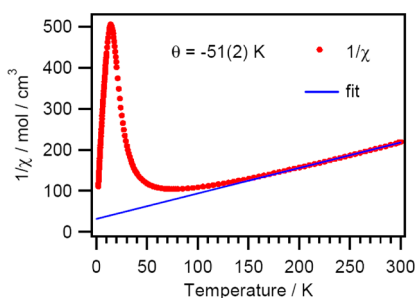
polycrystalline sample of **7** exhibits decreasing  $\chi_m T$  values on cooling, starting from  $1.37 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K and essentially leveling off at a low value of  $0.01 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.9 K; the still slightly positive values at low temperatures are due to a paramagnetic single ion contribution. The high-temperature  $\chi_m T$  value is lower than expected for four noninteracting Cu(II) ions ( $\sim 1.5 \text{ cm}^3 \text{ K mol}^{-1}$  with  $g = 2$ ), which is due to antiferromagnetic exchange interactions; the latter is indicated also by the decreasing  $\chi_m T$  values with lowering temperature. The low-temperature  $\chi_m T$  values correspond to a diamagnetic ground state ( $S = 0$ ).

The inverse magnetic susceptibility curve, given in Figure 9, shows a linear behavior in the temperature range 200–300 K, which results in a Weiss constant  $\Theta = -51(2) \text{ K}$ , in good agreement with the negative slope of the  $\chi_m T$  vs  $T$  curve.

For the tetranuclear entity we can use the following isotropic Hamiltonian to describe the intracluster magnetic exchange interactions (eq 1)

$$H = -2J(S_1 \cdot S_2 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_3 \cdot S_4) \quad (1)$$

This model does not consider “diagonal” coupling constants, which avoids an overparameterization; the quality of the fitting does not depend on it, so that  $J$  can be obtained with



**Figure 9.** Inverse magnetic susceptibility vs temperature for **7** (solid line represents a Curie–Weiss fit in the temperature range 200–300 K).

reasonable accuracy from the susceptibility data. Consequently, the Hamiltonian gives rise to six spin states comprising the total spin values ( $S_T$ ) of 2, 1, 0 with the corresponding energy levels in terms of the magnetic coupling constant  $J$  as given below

$$E_1(S_T = 2) = -2J$$

$$E_2(S_T = 1) = +2J$$

$$E_3(S_T = 1) = 0$$

$$E_4(S_T = 1) = 0$$

$$E_5(S_T = 0) = +4J$$

$$E_6(S_T = 0) = 0$$

In the case of antiferromagnetic coupling ( $J = \text{negative}$ ), the singlet  $E_5$  is the ground state. Applying these energy values to the van Vleck equation gives the following analytical expression (eq 2)

$$\chi_m = [2N\beta^2 g^2 / kT \cdot (A/B)](1 - \rho) + (N\beta^2 g^2 / kT) \cdot \rho \quad (2)$$

$$A = 5\exp(-E_1/kT) + \exp(-E_2/kT) + \exp(-E_3/kT) + \exp(-E_4/kT)$$

and

$$B = 5\exp(-E_1/kT) + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT)$$

where  $\rho$  is the portion of paramagnetic impurity that follows the Curie law. In a straightforward manner it can be deduced that the experimental magnetic susceptibility data can be well represented in the whole temperature range with the parameters  $g = 2.10$ ,  $J = -33.7 \text{ cm}^{-1}$ , and  $\rho = 0.01$  (see Figure 8). The value of the coupling constant  $J$  corresponds to a moderate antiferromagnetic intracenter coupling. There is no indication for magnetic intercluster interactions. In summary, the isotropic HDVV model is a reliable basis for describing this tetranuclear Cu(II) cluster and provides a good overall picture of the spin states.

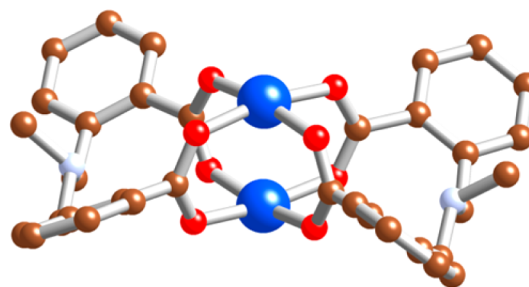
We now turn to the magnetostructural discussion. The four magnetic orbitals of the Cu(II) ions are the  $d_{x^2-y^2}$  orbitals directed roughly along the Cu–O bonds and are perpendicular to the Cu–Cl bond. Magnetic exchange could be mediated either by the bridging chloride ion or by the carboxylate bridges. The Cu–Cl bonds are quite long, and the  $d_{x^2-y^2}$  orbitals have  $\delta$  symmetry with respect to these bonds. There is

consequently no overlap between the magnetic orbitals and the chloro bridge, and we therefore assumed this interaction to be negligible. This is supported by the fact that the data is well fitted by the model neglecting diagonal coupling as mentioned above. Coupling through the carboxylate bridges is well known, most famously in the parent compound dicopper tetracetate dihydrate where the  $J$  value is  $-286 \text{ cm}^{-1}$ .<sup>45</sup> An example of a dicarboxylate bridged system, tricopper hexa(2,4,6-triisopropylbenzoate), has been reported by Clérac, Cotton et al.<sup>46</sup> In this triangular system a  $J$  value of  $-127 \text{ cm}^{-1}$  was reported. This substantial decrease compared to the tetracarboxylate bridge may be attributed to (1) the presence of only two carboxylate bridges, (2) the longer Cu–Cu distances (3.131 Å compared with 2.64 Å), and (3) the fact that the magnetic orbitals are no longer parallel but inclined at  $60^\circ$ . If we move from this system to the one studied here, the number of carboxylate bridges is identical but the Cu–Cu distance increases to around 3.6 Å and the magnetic orbitals are now mutually perpendicular. The still further reduced  $J$  value of  $-33.7 \text{ cm}^{-1}$  is thus physically reasonable. It is close to the values obtained by Alzuet et al.<sup>47</sup> of  $-22.5$  and  $-29 \text{ cm}^{-1}$  for a system with four coppers bridged by either two sulfathiazolato or two hydroxo bridges.

Magnetic studies have been made on two  $\text{Cu}_4-\mu_4$ -hydroxo complexes.<sup>42,43</sup> Both show overall antiferromagnetism, but the two systems are significantly different from each other in their  $\chi T$  against  $T$  curves. They are not directly comparable to our complex since the magnetic orbitals ( $d_{x^2-y^2}$ ) lie in the  $\text{Cu}_4(\text{OH})$  plane and overlap at the OH bridge.

## DISCUSSION

While the two ligands prepared here do form paddlewheel complexes, they do not act as tetradentate ligands to one dinuclear unit as was hoped. If we examine the structures of the two paddlewheel complexes **8** and **9**, the two  $\text{Cu}_2(\text{dicarboxylate})_2$  units are virtually identical (Figure 10),



**Figure 10.** *syn*- $\text{Cu}_2(\text{dicarboxylate})_2$  unit in complex **9**.

the only difference being that one dicarboxylate unit in **8** is rotated about a  $C_2$  axis perpendicular to the dicopper axis to give an *anti* conformation, while in **9** both units are *syn*.

This suggests that the aminebis(toluic acid) units is a good choice for the dicarboxylate unit but that the linker between the two units needs to be improved. The four single bonds between the aryl bridge and the arylcarboxylates offer considerable conformational flexibility as shown by the structures presented here. Rather than a monoligand–dimetal unit, we observe a bis-ligand bis-dimetal unit in **9** and a tetrakis-ligand tetrakis-dimetal compound in **8**. Clearly, since the ligand cannot wrap around the dimetal unit, formation of bis or tetrakis compounds is preferred. The bis–bis compound **9** is a simple solution, but examination of Figure 7 shows no obvious reason why ligand **5**

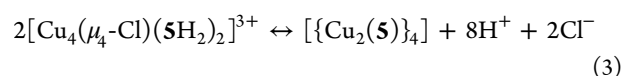
Table 1. Crystallographic Details

	ligand 3	ligand 5	complex 7	complex 8	complex 9
formula	C <sub>44</sub> H <sub>44</sub> N <sub>2</sub> O <sub>8</sub>	C <sub>48</sub> H <sub>60</sub> Cl <sub>3</sub> N <sub>5</sub> O <sub>10</sub>	C <sub>95</sub> H <sub>103</sub> Cl <sub>4</sub> Cu <sub>4</sub> N <sub>9</sub> O <sub>33</sub>	C <sub>203.4</sub> H <sub>231.4</sub> Cu <sub>8</sub> N <sub>18.2</sub> O <sub>45.4</sub>	C <sub>116</sub> H <sub>128</sub> Cu <sub>4</sub> N <sub>12</sub> O <sub>24</sub>
fw	728.81	973.36	2294.82	4165.79	2328.46
temp./K	220	192	180	190	180
cryst syst	triclinic	monoclinic	triclinic	tetragonal	monoclinic
space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub>	<i>P</i> -1	$\bar{I}4$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	11.6522(5)	10.9478(3)	14.2102(6)	31.4137(6)	12.86902(13)
<i>b</i> /Å	12.1177(7)	15.3695(3)	17.3347(9)	31.4137(6)	18.90939(14)
<i>c</i> /Å	13.7807(8)	15.1896(4)	21.6372(9)	10.8904(3)	23.3517(2)
$\alpha$ /deg	104.260(5)	90	95.097(4)	90.00	90.00
$\beta$ /deg	94.848(4)	94.351(2)	102.273(4)	90.00	97.2196(8)
$\gamma$ /deg	91.927(4)	90	106.039(4)	90.00	90.00
vol./Å <sup>3</sup>	1876.11(18)	2548.47(11)	4943.1(4)	10746.9(4)	5637.47(9)
<i>Z</i>	2	2	2	2	2
$\rho_{\text{calcd}}$ (mg/mm <sup>3</sup> )	1.290	1.268	1.542	1.287	1.372
<i>m</i> /mm <sup>-1</sup>	0.721	2.117	2.712	1.473	1.482
<i>F</i> (000)	772.0	1028.0	2368.0	4349.0	2432.0
2 $\theta$ range for data collection	6.648–147.184°	5.836–146.634°	5.372–133.194°	5.62–148.1°	6.04–146.66°
no. of reflns collected	11 918	10 029	30 386	11 334	20 713
no. of independent reflns	7299 [ <i>R</i> <sub>int</sub> = 0.0262]	7204 [ <i>R</i> <sub>int</sub> = 0.0383]	30 386 [twinned]	7956 [ <i>R</i> <sub>int</sub> = 0.0270]	10 996 [ <i>R</i> <sub>int</sub> = 0.0213]
data/restraints/params	7299/350/630	7204/141/601	30 386/400/1486	7956/150/699	10 996/34/759
goodness-of-fit on <i>F</i> <sup>2</sup>	1.038	1.055	1.037	1.040	1.031
final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ]	<i>R</i> <sub>1</sub> = 0.0524, <i>wR</i> <sub>2</sub> = 0.1321	<i>R</i> <sub>1</sub> = 0.0512, <i>wR</i> <sub>2</sub> = 0.1434	<i>R</i> <sub>1</sub> = 0.0981, <i>wR</i> <sub>2</sub> = 0.2609	<i>R</i> <sub>1</sub> = 0.0433, <i>wR</i> <sub>2</sub> = 0.1139	<i>R</i> <sub>1</sub> = 0.0383, <i>wR</i> <sub>2</sub> = 0.0989
final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0782, <i>wR</i> <sub>2</sub> = 0.1522	<i>R</i> <sub>1</sub> = 0.0553, <i>wR</i> <sub>2</sub> = 0.1486	<i>R</i> <sub>1</sub> = 0.1505, <i>wR</i> <sub>2</sub> = 0.3101	<i>R</i> <sub>1</sub> = 0.0483, <i>wR</i> <sub>2</sub> = 0.1199	<i>R</i> <sub>1</sub> = 0.0486, <i>wR</i> <sub>2</sub> = 0.1074
largest diff. peak/hole/e Å <sup>-3</sup>	0.28/−0.22	0.54/−0.24	1.29/−0.96	0.49/−0.27	0.88/−0.29

should not form a similar structure unless it is to avoid repulsion between DMF molecules coordinated axially to the dicopper. This repulsion between axial ligands may explain why **5** forms a tetrameric structure in which the dicopper axes are perpendicular to the main axis of the ligands.

Formation of the sandwich compound **7** was unexpected, but the spectroscopic titrations clearly show that the compound is formed in solution and that **7** is not just an artifact of crystallization. We presume that the partial deprotonation of the ligand gives fully deprotonated carboxylates and protonated amine functions allowing formation of the bifurcated N–H⋯(OC)<sub>2</sub> hydrogen bond. A search of the Cambridge Structural Database (version February 2013) showed that this motif is quite common, 41 examples with H⋯O distances between 1.9 and 2.2 Å. The effect of this hydrogen bond is to pull together two carboxylate groups. With a suitable conformational change, this can bring all four carboxylate groups of ligand **5** to one side of the phenyl spacer with the four O–O vectors of the carboxylates forming a square. It is thus ideally arranged to bind four copper atoms. This is not a possibility for ligand **6** since the diphenyl spacer results in the two pairs of carboxylates being too far apart to form a square.

The competition between metal and proton for a metal binding site is a trivial example of pH-modifying complexation, but in the present case, the protonation/deprotonation equilibrium serves to modify the conformation of the ligand, which binds in both cases using four carboxylates. We confirmed that the changes are reversible. Adding 4 equiv of base (NEt<sub>3</sub>) to a solution of **7** gives the spectrum of the tetrapaddlewheel complex **8**. Similarly, 8 equiv of paratoluene-sulfonic acid added to a solution of **8** give the spectrum of **7**:



## CONCLUSIONS

Both ligands presented here act as dibridging but not as tetrabridging. With ligand **6** a lantern-type complex<sup>48</sup> is found as might be expected. The behavior of ligand **5** is less predictable. When **5** is fully deprotonated, a cyclic tetramer is formed rather than a lantern-type tetranuclear species, possibly to allow the coordination of the axial DMF ligands. The partially deprotonated ligand is surprising, since the intramolecular hydrogen bonding holds the ligand in a conformation suitable to template a Cu<sub>4</sub>(μ<sub>4</sub>-Cl) species, with a structure quite different from previously reported Cu<sub>4</sub>(μ<sub>4</sub>-OH) complexes. The magnetic properties of the compound are significantly different from the previously reported compounds, but this is explicable on careful examination of the structure. The ability of these ligands to act as doubly bridging species is currently under investigation in our laboratory.

## EXPERIMENTAL SECTION

**General.** All chemicals were obtained from Aldrich or Strem and used without further purification. Silica gel (70–230 mesh) for flash-column chromatography was purchased from Aldrich.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Advance 400 spectrometer (400 MHz) at room temperature. Chemical shifts are given with respect to tetramethylsilane. High-resolution mass spectra were obtained on a QSTAR XL (AB/MSD Sciex) instrument on an ESI positive mode by the Mass Spectrometry Laboratory, University of Geneva. Microanalyses were performed using a Varian MICRO Cube instrument at the Microchemical Laboratory of the University of Geneva. IR spectra were recorded on a Perkin-Elmer Spectrum-One spectrometer equipped with a Specac Golden Gate ATR instrument.

UV–vis spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer with an integrating sphere attachment for solid samples. Vis–NIR spectrophotometric titrations were recorded in solution with a Perkin-Lambda 5 spectrophotometer interfaced to a PC and using a probe of 1.0 cm path length. Automated titrations were carried out at 25 °C using a Metrohm buret with a 5 mL syringe and performed by addition of 0.1 and then 0.2 mL aliquots of triethylamine solution (13.0 or 26.0 mM in DMF, respectively, for ligand **5** or **6**) to a mixture of ligands  $5\text{H}_6\text{Cl}_2$  or  $6\text{H}_6\text{Cl}_2$  ( $1.2 \times 10^{-5}$  or  $2.4 \times 10^{-5}$  mol, respectively) and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $2.6 \times 10^{-5}$  or  $5.2 \times 10^{-5}$  mol, respectively, for ligand **5** or **6**). X-ray crystallography: Intensity measurements were made using an Agilent Supernova diffractometer equipped with a CCD bidimensional detector using monochromatic Cu  $K\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Crystal data and structure refinement details are given in Table 1.

**Warning:** Organic salts of perchlorate ion are potentially explosive and care should be taken.

Magnetic susceptibility measurements were made on a Quantum Design MPMS SQUID-XL magnetometer under an applied magnetic field of 2000 Oe between 300 and 1.9 K. The sample was prepared in a gelatin capsule. Diamagnetic corrections were made for the sample using the approximation  $-0.45 \times \text{molecular weight (1997 g/mol)} \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ , and the sample holder was corrected for by measuring directly the susceptibility of the empty capsule.

**Syntheses.** The synthetic procedure for the ligands was shown in Scheme 1.

**Methyl-2-bromomethylbenzoate,  $\text{C}_8\text{H}_9\text{O}_2\text{Br}$ ,<sup>32</sup> **2**.** Methyl-2-methylbenzoic acid, **1** (3.5 g, 23.3 mmol), NBS (4.2 g, 23.5 mmol), and AIBN (0.1 g, 0.6 mmol) were heated together at reflux in 30 mL of  $\text{CCl}_4$  for 24 h under an  $\text{N}_2$  atmosphere. The mixture was cooled to 0 °C and filtered. The organic solution was washed twice with 50 mL of  $\text{Na}_2\text{SO}_3$ , 0.1 M, and the solvent was evaporated under reduced pressure. The solid was taken up in 20 mL of diethyl ether, and the solution was dried over  $\text{Na}_2\text{SO}_4$  and filtered on 5 cm of silica gel. The resulting solution is a mixture of the desired bromide compound, and the starting material in an 80%/20% ratio (ca. from  $^1\text{H NMR}$  signal intensity compared with the published spectrum<sup>32</sup>). The crude product was used without purification for the second step.

$^1\text{H NMR}$  (400 MHz/ $\text{CDCl}_3$ , ppm): 7.97 (d, 1H,  $\text{H}_{\text{ar}}$ ), 7.49 (t, H,  $\text{H}_{\text{ar}}$ ), 7.47 (d, 1H,  $\text{H}_{\text{ar}}$ ), 7.37 (t, 1H,  $\text{H}_{\text{ar}}$ ), 4.97 (s, 2H,  $-\text{CH}_2-$ ), 3.97 (s, 3H,  $-\text{CH}_3$ ).

***N,N,N',N'*-Tetrakis(methyl-2-methylbenzoate)-1,4-diaminomethylbenzene,  $\text{C}_{44}\text{H}_{48}\text{N}_2\text{O}_8$ , **3**.**  $\text{K}_2\text{CO}_3$  (6 g, 43.5 mmol) was added to 1,4-bis(aminomethyl)benzene (0.373 g, 2.74 mmol) under nitrogen atmosphere in 60 mL of freshly distilled  $\text{CH}_3\text{CN}$ . The mixture is refluxed for 30 min, and the crude methyl-2-bromomethylbenzoate, **2** (3.73 g, 14.0 mmol), was added in 30 mL of distilled  $\text{CH}_3\text{CN}$ . The solution was refluxed for 3–4 days, and the solution was filtered while hot. Solvents were evaporated under reduced pressure to give an orange-brown oil. The oil was dissolved in 20 mL of  $\text{CH}_2\text{Cl}_2$ , washed twice with brine, and dried over  $\text{Na}_2\text{SO}_4$ . Solvent was evaporated, and the mixture was purified on silica gel, first by hexane/ $\text{AcOEt}$  2:1 and then the second time by methanol gradient chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$  1–5%) to afford the tetraester pure. Yield: 0.79 g (40%). This product was dissolved in 5 mL of MeOH, and slow evaporation of this solution yielded white crystals suitable for X-ray crystallography.

$^1\text{H NMR}$  (400 MHz/ $\text{CDCl}_3$ , ppm): 7.88 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.81 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.49 (t, 4H,  $\text{H}_{\text{ar}}$ ), 7.30 (s, 4H,  $\text{H}_{\text{ar}}$ ), 7.26 (t, 4H,  $\text{H}_{\text{ar}}$ ), 4.02 (s, 8H,  $-\text{CH}_2-$ ), 3.87 (s, 12H,  $-\text{CH}_3$ ), 3.61 (s, 4H,  $-\text{CH}_2-$ ). MS (ESI-POS-HR):  $m/z$  [ $\text{C}_{44}\text{H}_{44}\text{O}_8\text{N}_2 + \text{H}^+$ ] = 729.3157 (calcd for  $\text{C}_{44}\text{H}_{45}\text{O}_8\text{N}_2^+$  at 729.3170). IR (solid,  $\nu$ ,  $\text{cm}^{-1}$ ): 2950 w br, 1715 s, 1601 w, 1576 w, 1484 w, 1433 m, 1364 w, 1255 s, 1191 w, 1129 m, 1074 s, 966 m, 799 w, 739 s, 672 w.

***N,N,N',N'*-Tetrakis(2-methylbenzoic acid)-1,4-diaminomethylbenzene Dihydrochloride  $\text{C}_{40}\text{H}_{38}\text{N}_2\text{O}_8\text{Cl}_2$ ,  $5\text{H}_6\text{Cl}_2$ , **3**** (0.6 g, 0.82 mmol) was dissolved in 60 mL of MeOH, and 18 mL of KOH 1 M was added to the solution. The mixture was refluxed for 24 h, after which the solvent was evaporated. The solid was then dissolved in 20 mL of water, and the pH was adjusted to 2 with HCl 6 M, resulting in precipitation of a white solid. The solution was left at 0 °C

for 1 h, and the solid was filtered and dried under vacuum for one night at 50 °C. Yield: 0.51 g (92%). This product (10 mg) was dissolved in 2 mL of DMF, and diethyl ether was allowed to diffuse into the solution to give white crystals suitable for X-ray crystallography.  $^1\text{H NMR}$  (400 MHz/ $\text{DMSO}-d_6$ , ppm): 7.76 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.58 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.54 (t, 4H,  $\text{H}_{\text{ar}}$ ), 7.38 (t, 4H,  $\text{H}_{\text{ar}}$ ), 7.29 (s, 4H,  $\text{H}_{\text{ar}}$ ), 4.39 (s, 8H,  $-\text{CH}_2-$ ), 4.29 (sh, 4H,  $-\text{CH}_2-$ ).  $^{13}\text{C NMR}$  (100 MHz/ $\text{DMSO}-d_6$ , ppm): 168.86, 132.77, 131.06, 130.40, 130.04, 129.53, 58.52, 57.76. IR (solid,  $\nu$ ,  $\text{cm}^{-1}$ ): 3371 w br, 1683 s, 1600 w, 1578 w, 1495 w, 1454 m, 1268 s, 1084 m, 1020 w, 912 w, 843 w, 743 s, 699 m, 651 m, 514 m. MS (ESI-POS-HR):  $m/z$  [ $\text{C}_{40}\text{H}_{36}\text{O}_8\text{N}_2 + \text{H}^+$ ] = 673.2545 (calculated for  $\text{C}_{40}\text{H}_{37}\text{O}_8\text{N}_2^+$  673.2544). Anal. Calcd for [ $\text{C}_{40}\text{H}_{38}\text{O}_8\text{N}_2$ ] $\text{Cl}_2 \cdot 9\text{H}_2\text{O}$  found (calcd): C, 53.37 (52.92); N, 2.96 (3.09); H, 5.64 (6.22). The water content found from elemental analysis is consistent with a broad water peak in the  $^1\text{H NMR}$  (3.43 ppm) and a band in the infrared spectrum.

**4,4'-diaminomethyldiphenyl,  $\text{C}_{14}\text{H}_{16}\text{N}_2$ ,<sup>33</sup> 4,4'-Dibromo-1,1'-biphenyl** (1 g, 2.94 mmol) was dissolved in a THF/EtOH/ $\text{H}_2\text{O}$  (16:12:4 32 mL) mixture.  $\text{NaN}_3$  (10.4 g, 160 mmol) in 140 mL of water was added to the solution. The mixture was heated for 1 h. After cooling to room temperature,  $\text{PPh}_3$  (1.54 g, 5.88 mmol) was slowly added. The solution was refluxed 30 min and cooled to room temperature, and then concentrated HCl was added until pH = 1, and the solution was heated a further 2 h.  $\text{Ph}_3\text{PO}$  was eliminated by filtration, and the mixture was washed with  $\text{CHCl}_3$ . The aqueous phase was basified with NaOH 5 M and extracted with  $\text{CHCl}_3$ . The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to afford a white solid ( $m = 0.38$  g, yield = 61%).  $^1\text{H NMR}$  (400 MHz/ $\text{CDCl}_3$ , ppm): 7.56 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.38 (d, 4H,  $\text{H}_{\text{ar}}$ ), 3.92 (s, 4H,  $-\text{CH}_2-$ ).

***N,N,N',N'*-Tetrakis(methyl-2-methylbenzoate)-4,4'-diaminomethyldiphenyl,  $\text{C}_{50}\text{H}_{48}\text{N}_2\text{O}_8$ , **4**.**  $\text{K}_2\text{CO}_3$  (1.72 g, 12.4 mmol) was added to 4,4'-bis(aminomethyl)diphenyl (0.18 g, 0.83 mmol) under nitrogen atmosphere in 30 mL of freshly distilled  $\text{CH}_3\text{CN}$ . Crude methyl-2-bromomethylbenzoate, **2** (1.14 g, 4.28 mmol) was dissolved in 60 mL of distilled  $\text{CH}_3\text{CN}$  and added to the first solution. The mixture was refluxed for 2 days, and the solution was filtered while hot. The solvent was evaporated under reduced pressure to give an orange-brown oil. The oil was dissolved in 20 mL of  $\text{CH}_2\text{Cl}_2$ , washed twice with  $\text{Na}_2\text{S}_2\text{O}_3$ , and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated, and the mixture was purified by silica gel chromatography ( $\text{AcOEt}$ /hexane 1:2) to afford the pure product.  $m = 0.28$  g (yield = 42%).  $^1\text{H NMR}$  (400 MHz/ $\text{CDCl}_3$ , ppm): 7.86 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.79 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.47 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.46 (t, 4H,  $\text{H}_{\text{ar}}$ ), 7.39 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.26 (t, 4H,  $\text{H}_{\text{ar}}$ ), 4.00 (s, 8H,  $-\text{CH}_2-$ ), 3.85 (s, 12H,  $-\text{CH}_3$ ), 3.65 (s, 4H,  $-\text{CH}_2-$ ). MS (ESI-POS-HR):  $m/z$  [ $\text{C}_{50}\text{H}_{48}\text{O}_8\text{N}_2 + \text{H}^+$ ] = 805.3479 (calcd for  $\text{C}_{50}\text{H}_{49}\text{O}_8\text{N}_2^+$  at 805.3483).

***N,N,N',N'*-Tetrakis(methyl-2-methylbenzoic acid)-4,4'-diaminomethyldiphenyl Dihydrochloride  $\text{C}_{46}\text{H}_{40}\text{N}_2\text{O}_8$ ,  $6\text{H}_6\text{Cl}_2$ , **4**** (0.28 g, 0.35 mmol) was dissolved in 30 mL of MeOH, and 18 mL of KOH 1 M was added to the solution. The mixture was refluxed for 24 h. The reaction was stopped, and the solvent was evaporated. The solid was then dissolved in 20 mL of water, and the pH was adjusted to 2 using HCl 6M, resulting in precipitation of a white solid. The solution was left for precipitation at 0 °C for 1 h, and the solid was filtered and dried under vacuum for a night at 50 °C. Yield: 0.26 g (90%).  $^{13}\text{C NMR}$  (100 MHz/ $\text{DMSO}-d_6$ , ppm): 168.92, 134.61, 132.99, 132.04, 131.36, 130.81, 130.60, 130.24, 130.00, 126.64, 57.92, 56.55. IR (solid,  $\nu$ ,  $\text{cm}^{-1}$ ): 1695 m, 1610 w, 1586 w, 1452 w, 1398 w, 1264 m, 1084 w, 921 w, 812 w, 750 s, 727 w, 655 m, 515 m.  $^1\text{H NMR}$  (400 MHz/ $\text{DMSO}-d_6$ , ppm): 7.78 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.68 (broad, 4H,  $\text{H}_{\text{ar}}$ ), 7.57 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.55 (t, 4H,  $\text{H}_{\text{ar}}$ ), 7.43 (d, 4H,  $\text{H}_{\text{ar}}$ ), 7.39 (t, 4H,  $\text{H}_{\text{ar}}$ ), 4.18 (very broad, 8H,  $-\text{CH}_2-$ ), 3.37 (very broad, 4H,  $-\text{CH}_2-$ ). MS (ESI-POS-HR):  $m/z$  [ $\text{C}_{46}\text{H}_{41}\text{O}_8\text{N}_2 + \text{H}^+$ ] = 749.2870 (calcd for  $\text{C}_{40}\text{H}_{37}\text{O}_8\text{N}_2^+$  749.2857). Anal. Calcd for [ $\text{C}_{46}\text{H}_{42}\text{O}_8\text{N}_2$ ] $\text{Cl}_2$ : found (calcd): C, 69.17 (67.24); N, 3.27 (3.41); H, 5.41 (5.15).

**[ $\text{Cu}_4\text{-}\mu_4\text{-Cl}(\text{SH}_2)_2(\text{DMF})_4(\text{ClO}_4)_3 \cdot \text{DMF} \cdot 4\text{H}_2\text{O}$ , **7**.** Suitable crystals for X-ray diffraction were obtained by dissolving the acid  $5\text{H}_6\text{Cl}_2$  (10 mg, 0.015 mmol) and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (11 mg, 0.030 mmol) in 2 mL of DMF. Triethylamine (6.2  $\mu\text{L}$ , 0.045 mmol) was added to the solution that turned from colorless to blue. Finally, diethyl ether was left to

diffuse into the mixture to afford greenish-blue crystals (yield 5 mg, yield = 32%). IR (solid,  $\nu$ ,  $\text{cm}^{-1}$ ): 1669 w, 1624 m, 1595 m, 1573 m, 1451 m, 1382 s, 1302 m, 1080 s, 867 m, 793 m, 762 s, 711 m, 672 m, 619 m, 493 m. Anal. Calcd for  $\text{Cu}_4\text{Cl}(\text{C}_{40}\text{H}_{34}\text{O}_8\text{N}_2)_2(\text{H}_2\text{O})_4(\text{ClO}_4)_3\text{DMF}$ : found (calcd): C, 48.05 (48.04); N, 3.12 (3.38); H, 3.92 (4.00).

$[\text{Cu}_8(\text{DMF})_8]\cdot\text{Et}_2\text{O}$ , **8**. Ligand  $5\text{H}_6\text{Cl}_2$  (10 mg, 0.015 mmol) and  $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$  (11 mg, 0.030 mmol) were dissolved in 5 mL of DMF with addition of  $\text{NEt}_3$  (21  $\mu\text{L}$ , 0.15 mmol). Blue crystals suitable for X-ray analysis appear after diffusing in diethyl ether (10.6 mg, 74%). IR (solid,  $\nu$ ,  $\text{cm}^{-1}$ ): 3400 br, 3043 w, 1610 m, 1590 s, 1561 s, 1451 m, 1370 s, 1289 w, 1151 m, 1089 m, 806 w, 749 s, 707 m, 670 m. Anal. Calcd for  $[\text{Cu}_8(\text{C}_{40}\text{H}_{32}\text{O}_8\text{N}_2)_4(\text{DMF})_8]\cdot 12\text{H}_2\text{O}$ : found (calcd): C, 55.43 (55.47); N, 5.53 (5.63); H, 5.03 (5.26). The water content found from elemental analysis is supported by the IR spectrum where a large band due to water is observed and by the presence of channels in the crystal structure.

$[\text{Cu}_2(\text{DMF})_2]_9$ , **9**. The ligand  $6\text{H}_6\text{Cl}_2$  (15 mg, 0.021 mmol) and  $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$  (15.4 mg, 0.042 mmol) were dissolved in 2 mL of DMF with  $\text{NEt}_3$  (29  $\mu\text{L}$ , 0.21 mmol). Slow diffusion of diethyl ether into the solution affords blue crystals suitable for X-ray analysis. (14.5 mg, 52%). IR (solid,  $\nu$ ,  $\text{cm}^{-1}$ ): 2812 w br, 1668 m, 1613 s, 1494 w, 1453 w, 1412 s, 1384 w, 1255 w, 1155 w, 1093 m, 813 w, 796 w, 745 m, 672 m. Anal. Calcd for  $[\text{Cu}_4(\text{C}_{46}\text{H}_{40}\text{O}_8\text{N}_2)_2(\text{DMF})_4]\cdot 2\text{DMF}$  found (calcd): C, 59.41 (60.32); N, 6.22 (6.39); H, 5.25 (5.61).

## ■ ASSOCIATED CONTENT

### Supporting Information

Scheme S1 and Figures S1 and S2; details of X-ray crystal structures, hydrogen-bond data, and selected bond distances and angles for compounds **7**, **8**, and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 973946–973950 contain the supplementary crystallographic material 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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### Notes

The authors declare no competing financial interest.

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