

# Framework Solids Based on Copper(II) Halides (Cl/Br) and Methylene-Bridged Bis(1-hydroxybenzotriazole): Synthesis, Crystal Structures, Magneto-Structural Correlation, and Density Functional Theory (DFT) Studies

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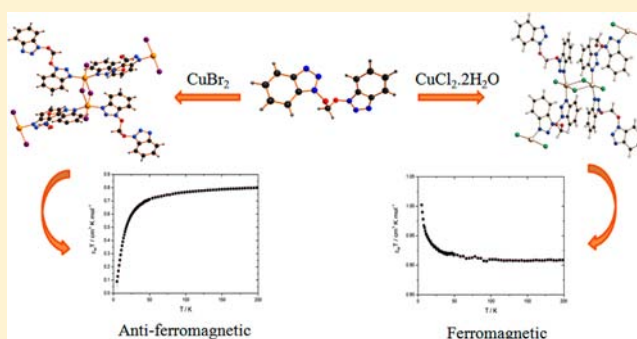
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## S Supporting Information

**ABSTRACT:** A methylene-bridged 1-hydroxybenzotriazole derived ligand **L** [**L** = 1, 3-bis(benzotriazol-1-yl)-1,3-dioxapropane] has been synthesized and characterized by spectroscopic and structural methods. Reaction of **L** with two different copper(II) halides [ $\text{CuX}_2$ ; X = Br, Cl] in an identical condition yields two different compounds of similar compositions,  $\{[\text{Cu}(\mu\text{-Br})(\text{Br})(\mu\text{-L})_2]_n \cdot 2n\text{H}_2\text{O}$  (**1**) and  $\{[\text{Cu}(\mu\text{-Cl})(\text{Cl})(\mu\text{-L})_2]_n \cdot 2n\text{H}_2\text{O}$  (**2**), both being characterized by various physicochemical techniques. Single crystal X-ray studies reveal that they appear as 2D coordination polymers with similar bridging fashion of **L**. Low temperature magnetic susceptibility measurements reveal antiferromagnetic and ferromagnetic behaviors for **1** and **2** with magnetic coupling constants  $J = -15.2$  and  $+1.7 \text{ cm}^{-1}$ , which are in a reasonable agreement with their calculated values ( $J = -9.79$  and  $+0.68 \text{ cm}^{-1}$  respectively, for **1** and **2**). The role of bridging halides in the structure and magnetic properties of the complexes are investigated, and a possible magneto-structural correlation has been established. Influence of spin density of bridging halides on the magnitude of coupling constants has been discussed with the help of density functional theory (DFT) calculations.



## INTRODUCTION

From the past few decades, lots of research has been devoted to inorganic–organic hybrid frameworks due to potential applications in gas absorption,<sup>1</sup> catalysis,<sup>2</sup> magnetic materials,<sup>3</sup> photoluminescence,<sup>4</sup> ion exchange,<sup>5</sup> and nonlinear optical activities.<sup>6</sup> These hybrid frameworks provide a rich structural chemistry and offer novel physical properties as they combine the unique features of inorganic and organic components constructing the frameworks.<sup>7</sup> Due to the diversities in molecular properties, e.g., size, shape, charge, acidity, and abilities to function as proton and electron reservoirs, inorganic components impart novel properties to the hybrid frameworks while the organic components owing to their structural richness and polarizabilities offer diverse structural chemistry and properties. Depending upon the nature of solvent systems and reaction conditions<sup>8</sup> such inorganic and organic components give rise to frameworks of novel architectures within the vast domain of multifunctional materials.<sup>9</sup>

Among the various inorganic components, the family of metal halides or pseudohalides is very important due to their intriguing structures and properties.<sup>10</sup> Moreover, the inorganic counterion X [X = Cl, Br, I, CN, SCN, NNN] may sometimes be incorporated as an essential component to the metal–organic framework leading to high structural complexities and interesting properties.<sup>11</sup> A wide range of organic-connecting components has been used depending upon its coordination properties. The role of a large number of organic molecules with rigid, linear, and bridging ligands such as 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, pyrazine, and 4,4'-bipyridine with few or no conformational modes has been well studied.<sup>12</sup> More recently, flexible ligands able to prolong their arms and weaken steric hindrance effects have been employed to gain access to novel supramolecular structures.

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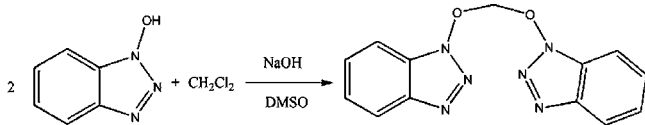
Sometimes incorporation of such flexible components may provide the molecular architectures with potential advantages, for example, a “breathing” ability in the solid state and adaptive recognition properties.<sup>15</sup> However, the inherent conformational properties of these ligands may result in a difficult control of the final supramolecular product.

The easiest technique that has been used to introduce flexibilities into the ligands is the incorporation of alkyl chain spacer groups between 4-pyridyl,<sup>14</sup> 8-quinolyloxy,<sup>15</sup> 1-pyrazolyl,<sup>16</sup> 1-triazolyl,<sup>17</sup> and 2-benzimidazolyl<sup>18</sup> donor groups, and this technique has been reported and used for the construction of many interesting new supramolecular architectures. More recently, focus has been on the ligands containing less commonly studied heterocyclic ring systems,<sup>19</sup> such as benzotriazole. Being a nitrogen containing heterocyclic benzazole derivative with the electron withdrawing imine ( $\text{C}=\text{N}$ ) on its backbone bearing high electron transporting ability,<sup>20</sup> benzotriazole is mostly used in medicinal and organic reactions. However, the presence of three nitrogens in its backbone makes it rich in its coordination properties<sup>21</sup> and has been explored in material science in copper complexes and alloys for its potential corrosion inhibitor properties.<sup>22–24</sup>

A number of organic ligands have been reported incorporating benzotriazole moieties bearing rich topological features<sup>25,26</sup> and few have been explored in their metal complexes.<sup>27</sup> Some substituted benzotriazoles with rigid moieties have also been investigated in supramolecular coordination chemistry because more intermolecular interactions such as hydrogen bonds and  $\pi\cdots\pi$  stacking interactions are often observed in solid structures.<sup>28</sup> Flexible benzotriazole ligands with different spacers so far reported are mainly of the bis(benzotriazole)-alkane<sup>29</sup> and bis(benzotriazole)oxoalkane<sup>30</sup> types. In the metal complexes of these ligands the coordination architectures and topological features have been widely studied while the role of the coordinating counterion of the inorganic components in the overall magnetic properties of the frameworks has not been explored yet. Moreover, the potential of benzotriazole derivatives in designing flexible spacer ligands, and their ability in designing metal–organic frameworks, has yet to be investigated.

In the present work, we have reported the synthesis, spectroscopic, and structural characterizations of a new methylene-bridged ligand **L** [**L** = 1, 3-bis(benzotriazol-1-yl)-1, 3-dioxapropane] (Scheme 1) derived from a benzotriazole

Scheme 1. Synthetic Scheme of the Ligand **L**



derivative, 1-hydroxybenzotriazole, and its ability to form inorganic–organic framework solids with  $\text{CuX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) has been explored. Reaction of **L** with  $\text{CuBr}_2$  and  $\text{CuCl}_2$  in an identical condition yields 2D polymeric compounds  $\{[\text{Cu}(\mu\text{-Br})(\text{Br})(\mu\text{-L})_2]_n \cdot 2n\text{H}_2\text{O}$  (**1**) and  $\{[\text{Cu}(\mu\text{-Cl})(\text{Cl})(\mu\text{-L})_2]_n \cdot 2n\text{H}_2\text{O}$  (**2**), which have been characterized by elemental analyses, FT-IR, UV–vis spectroscopic methods, and single crystal X-ray diffraction technique. Cryomagnetic susceptibility measurements reveal antiferromagnetic ( $J = -15.2 \text{ cm}^{-1}$  for **1**) and ferromagnetic ( $J = +1.7 \text{ cm}^{-1}$  for **2**) behavior of the complexes. The role of the bridging halogens and coordinating

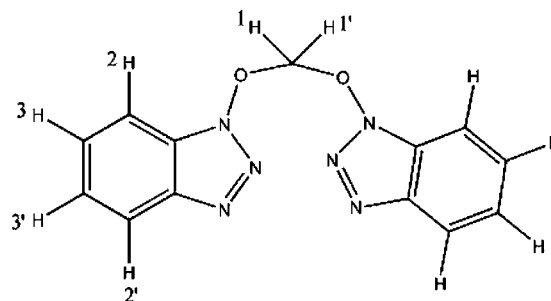
behaviors of the new ligand has been explored to explain their different structures and magnetic properties, and a possible magneto-structural correlation has been established. Density functional theory (DFT) calculations have estimated the  $J$  values of  $-9.79$  and  $+0.68 \text{ cm}^{-1}$  for **1** and **2**, respectively. Thermogravimetric analyses of **1** and **2** are also reported.

## EXPERIMENTAL SECTION

**Materials.** Copper(II) chloride dihydrate, copper(II) bromide, dichloromethane, and sodium hydroxide (NaOH) were purchased from E. Merck, India. 1-Hydroxybenzotriazole (HOBT) was purchased from Spectrochem, India. All solvents and reagents were of reagent grade and used as received without further purification.

**Synthesis of Ligand: [1,3-Bis(benzotriazol-1-yl)-1, 3-dioxapropane] (**L**).** HOBT (1.35 g, 10 mmol) and NaOH (0.40 g, 10 mmol) were taken in 25 mL of dimethylsulfoxide (DMSO). The reaction mixture was heated at  $60^\circ\text{C}$  for 30 min and then cooled to room temperature. Dichloromethane (0.42 g, 5 mmol) was added to the reaction mixture very slowly with constant stirring. The mixture was heated and stirred for 1 h at  $60^\circ\text{C}$  followed by cooling to room temperature. Ice-cooled water was added into it. The resulting white solid was separated, washed with water, and dried in air. Diffraction quality single crystals were obtained by recrystallization from acetonitrile. Yield: 0.84 g (60%). Anal. Calcd (%) for  $\text{C}_{13}\text{H}_{10}\text{N}_6\text{O}_2$  ( $M = 282.26 \text{ g mol}^{-1}$ ): C, 55.32; H, 3.57; N, 29.77%. Found: C, 55.28; H, 3.50; N, 29.70%. FT-IR bands (KBr,  $\text{cm}^{-1}$ ): 3448(s), 3093(s), 3070(m), 1610(w), 1447(m), 1438(s), 1362(s), 1279(s), 1264(m), 1240(s), 1150(w), 1080(s), 984(s), 956(s), 780(w), 773(m), 751(s), 646(w), 601(w), 568(w), 498(w), 463(w), 429(w) (Supporting Information, details labeled S1 and Table S1). UV–vis bands ( $\text{CH}_3\text{CN}$ , nm): 204, 255, 283.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta_{\text{H}}$ : 4.98 ( $^1\text{H}$ s, 2H), 7.43 ( $^2\text{H}$  t,  $J = 7.7 \text{ Hz}$ , 1H), 7.58 ( $^2\text{H}$  t,  $J = 7.68$ , 1H), 7.74 ( $^3\text{H}$  d,  $J = 8.30$ , 1H), 8.05 ( $^3\text{H}$  d,  $J = 4.21$ , 1H) ppm (Scheme 2). ESI-MS,  $m/z$ :  $[\text{M} + \text{H}^+] = 283$ ,  $[\text{M} + \text{Na}^+] = 305$ .

Scheme 2. Proton Numbering of **L**



**Synthesis of  $\{[\text{Cu}(\mu\text{-Br})(\text{Br})(\mu\text{-L})_2]_n \cdot 2n\text{H}_2\text{O}$  (**1**).**  $\text{CuBr}_2$  (0.223 g, 1 mmol) was taken in 20 mL of methanol. Then, 20 mL of an acetonitrile solution of **L** (0.282 g, 1 mmol) was added dropwise for 1 h with constant stirring. The reaction mixture was filtered and filtrate left for slow evaporation. Rhombohedral shaped reddish brown single crystals suitable for X-ray diffraction analysis were obtained after one week. Yield: 0.367 g (70%). Anal. Calcd (%) for  $\text{C}_{13}\text{H}_{12}\text{Br}_2\text{CuN}_6\text{O}_3$  ( $M = 523.65 \text{ g mol}^{-1}$ ): C, 29.82; H, 2.31; N, 16.05%. Found: C, 29.4; H, 2.2; N, 16.0%. FT-IR bands (KBr,  $\text{cm}^{-1}$ ): 3087(m), 3031(m), 2996(s), 2938(s), 1608(w), 1593(m), 1491(m), 1455(s), 1437(w), 1393(m), 1378(m), 1361(w), 1336(w), 1292(s), 1263(m), 1204(s), 1166(s), 1111(w), 1004(m), 981(m), 951(w), 859(w), 750(s), 660(w), 633(w), 601(w), 531(w), 491(w), 432(w) (details labeled S1 and Table S1, Supporting Information). UV–vis bands ( $\text{CH}_3\text{CN}$ , nm): 223, 300, 304, 338, 374, 379, 428.

**Synthesis of  $\{[\text{Cu}(\mu\text{-Cl})(\text{Cl})(\mu\text{-L})_2]_n \cdot 2n\text{H}_2\text{O}$  (**2**).** Complex **2** was synthesized according to the same procedure as adopted for **1** except  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was used instead of  $\text{CuBr}_2$ .  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.170 g, 1 mmol) was taken in 20 mL of methanol. Then 20 mL of an

Table 1. Crystal Structure Parameters for L, 1, and 2

|  | L   | 1   | 2   |
|--|---|---|---|
| empirical formula                        | C <sub>13</sub> H <sub>10</sub> N <sub>6</sub> O <sub>2</sub> | C <sub>13</sub> H <sub>12</sub> Br <sub>2</sub> CuN <sub>6</sub> O <sub>3</sub> | C <sub>13</sub> H <sub>12</sub> Cl <sub>2</sub> CuN <sub>6</sub> O <sub>3</sub> |
| fw (g mol <sup>-1</sup> )                | 282.27  | 523.65  | 434.73  |
| T  | 273(2)  | 294 K   | 293K  |
| cryst syst                               | monoclinic  | monoclinic  | monoclinic  |
| space group                              | P2 <sub>1</sub> /c  | P2 <sub>1</sub> /n  | P2 <sub>1</sub> /n  |
| a (Å)                                    | 7.9486(3)   | 7.9000(7)   | 10.9315(7)  |
| b (Å)                                    | 23.3687(8)  | 13.2679(12)   | 13.7732(8)  |
| c (Å)                                    | 7.9814(3)   | 16.3931(14)   | 11.0552(6)  |
| β (deg)                                  | 119.37(1)   | 98.90(2)  | 95.75(1)  |
| V (Å <sup>3</sup> )                      | 1291.98(8)  | 1697.6(3)   | 1656.12(17)   |
| Z  | 4   | 4   | 4   |
| d <sub>calcd</sub> (g cm <sup>-3</sup> ) | 1.451   | 2.049   | 1.744   |
| μ (mm <sup>-1</sup> )                    | 0.105   | 6.021   | 1.669   |
| F(000)                                   | 584   | 1020  | 876   |
| cryst size (mm <sup>3</sup> )            | 0.22 × 0.18 × 0.16  | 0.14 × 0.18 × 0.22  | 0.23 × 0.22 × 0.21  |
| θ range (deg)                            | 1.7–27.5  | 2.0–26.0  | 2.4–25.5  |
| measured reflns                          | 20 608  | 17 680  | 22 110  |
| independent reflections                  | 2925  | 3344  | 3070  |
| R(int)                                   | 0.031   | 0.030   | 0.032   |
| GOF on F <sup>2</sup>                    | 0.94  | 0.812   | 1.13  |
| final R indices [I > 2σ(I)]              | R1 = 0.0399<br>wR2 = 0.0981                                   | R1 = 0.0187<br>wR2 = 0.0438   | R1 = 0.0346<br>wR2 = 0.1128   |
| R indices (all data)                     | R1 = 0.0657<br>wR2 = 0.0895                                   | R1 = 0.0358<br>wR2 = 0.0464   | R1 = 0.0416<br>wR2 = 0.1172   |
| Δρ <sub>min</sub> and Δρ <sub>max</sub>  | −0.19 and 0.11 (e Å <sup>-3</sup> )                           | −0.38 and 0.41 (e Å <sup>-3</sup> )   | −0.77 and 0.46 (e Å <sup>-3</sup> )   |

acetonitrile solution of L (0.282 g, 1 mmol) was added dropwise for 1 h with constant stirring. The reaction mixture was filtered and filtrate left for slow evaporation. Rhombohedral green single crystals suitable for X-ray diffraction were obtained after one week. Yield: 0.261 g (60%). Anal. Calcd (%) for C<sub>13</sub>H<sub>12</sub>Cl<sub>2</sub>CuN<sub>6</sub>O<sub>3</sub> (*M* = 434.73 g mol<sup>-1</sup>): C, 31.34; H, 2.43; N, 16.87%. Found: C, 30.5; H, 2.21; N, 16.35%. FT-IR bands (KBr, cm<sup>-1</sup>): 3607(s), 3498(s), 3093(s), 1591(s), 1496(s), 1448(s), 1391(w), 1355(s), 1294(w), 1283(m), 1245(s), 1194(m), 1161(m), 1131(m), 1098(s), 999(w), 989(w), 968(s), 936(s), 847(w), 779(m), 764(s), 752(m), 655(w), 644(w), 587(m), 555(w), 518(w), 445(w), 430(w) (details labeled S1 and Table S1, Supporting Information). UV-vis bands (CH<sub>3</sub>CN, nm): 229, 252, 256, 334.

**Physical Measurements.** FT-IR spectra (4000–400 cm<sup>-1</sup>) of the ligand and its complexes were recorded on a Perkin-Elmer RX-I FT-IR spectrophotometer in solid KBr matrix. The electronic spectra of the ligand and complexes in the solid state were recorded at room temperature on a Perkin-Elmer λ 40 UV-Vis spectrometer using Nujol. Elemental analyses (C, H, and N) were carried out with a Perkin-Elmer 2400 II elemental analyzer. <sup>1</sup>H NMR spectrum of the ligand was recorded on a Bruker 300 MHz FT-NMR spectrometer using trimethylsilane as internal standard in CDCl<sub>3</sub>. The positive ion ESI-MS for ligand was performed in a QTOF micromass spectrometer. Variable-temperature magnetic susceptibility measurements were carried out with a Quantum Design MPMS-5S SQUID magnetometer under an applied magnetic field of 5000 Oe. Diamagnetic corrections were estimated from Pascal's tables, and magnetic data were corrected for diamagnetic contributions of the sample holder. The temperature dependence of the molar magnetic susceptibility, χ<sub>M</sub>, was measured on a polycrystalline sample in the temperature range 5–300 K. Thermogravimetric analyses were carried out with a heating rate of 5 °C min<sup>-1</sup> with a Mettler-Toledo Star TGA/SDTA-851 thermal analyzer system in a dynamic atmosphere of N<sub>2</sub> (flow rate 80 mL min<sup>-1</sup>), using aluminum crucible in a temperature range 25–600 °C (details labeled S2 and Figure S1 Supporting Information).

**X-ray Crystallography.** A good quality single crystal of 1 was mounted on a Bruker SMART 1000 CCD diffractometer while 2 and L were mounted on a Bruker APEX II CCD diffractometer, equipped

with graphite monochromatized Mo Kα radiation (λ = 0.710 73 Å) and a fine-focus sealed tube. For 1, intensity data were collected at 294(2) K using ω scan, while for 2 and L, φ and ω scans at 296(2) K were used. Data refinement and reduction were performed using the Bruker SAINT<sup>31a</sup> software. Multiscan absorption corrections were applied empirically to the intensity values (*T*<sub>min</sub> = 0.291 and *T*<sub>max</sub> = 0.425 for 1, *T*<sub>min</sub> = 0.688 and *T*<sub>max</sub> = 0.704 for 2, and *T*<sub>min</sub> = 0.976 and *T*<sub>max</sub> = 0.978 for L) using SADABS.<sup>31a</sup> The structures were solved by direct methods using the program SIR97<sup>31b</sup> and SHELXS-97,<sup>31c</sup> and refined with full-matrix least-squares based on *F*<sup>2</sup> using program SHELXL-97.<sup>31c</sup> All non-hydrogen atoms were refined anisotropically. C-bound hydrogen atoms were placed geometrically and refined using a riding model approximation. Water hydrogen atoms were located in difference Fourier maps and refined with the O–H and H···H distances constrained to 0.86(1) and 1.36(2) Å, respectively. The molecular graphics and crystallographic illustrations for L, 1, and 2 were prepared using Bruker SHELXTL<sup>31d</sup> and ORTEP<sup>31e</sup> programs. Crystallographic data and structure refinement parameters for L, 1, and 2 are summarized in Table 1.

## RESULTS AND DISCUSSION

**Description of Ligand Structure.** A perspective view of the ligand L is shown in Figure 1. In the solid state it adopts an

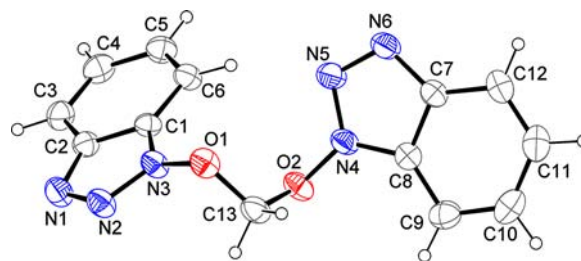
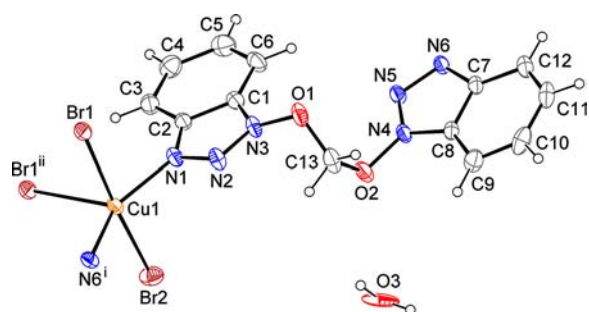


Figure 1. ORTEP view of the molecular structure of L. Displacement ellipsoids are drawn at the 50% probability level.

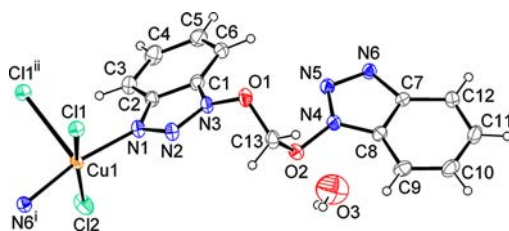


approximately symmetrical conformation about the central methylene spacer group. Specifically, one of the benzotriazole rings exists in a *gauche* conformation [the N3–O1–C13–O2 and N2–N3–O1–C13 torsion angles are 77.7(2)° and 93.4(2)°, respectively], while the other ring has expected *anti* conformation [the N4–O2–C13–O1 and N5–N4–O2–C13 torsion angles are 79.8(2)° and –91.4(2)°, respectively]. The dihedral angle between the mean planes through the benzotriazole ring systems is 53.84(3)°. The molecular conformation is enforced by an intramolecular hydrogen bond involving hydrogen atom attached to the aromatic C6 atom as donor and N5 nitrogen atom as acceptor [C6–H6, 0.96(1) Å; H6···N5, 2.532(14) Å; C6···N6, 3.4240(18) Å; C6–H6···N5, 155(1)°]. This unusual shape results from a complex system of intermolecular forces, comprising face-to-face and edge-to-face aromatic interactions, as well as C–H···N interactions<sup>9</sup> all of which are now well-known to contribute significantly to the solid-state structures of heteroaromatic compounds.

**Description of Crystal Structures of  $\{[\text{Cu}(\mu\text{-Br})(\text{Br}(\mu\text{-L})_2)_n \cdot 2n\text{H}_2\text{O} (1)$  and  $\{[\text{Cu}(\mu\text{-Cl})(\text{Cl}(\mu\text{-L})_2)_n \cdot 2n\text{H}_2\text{O} (2)$ .** ORTEP views of the asymmetric unit of **1** and **2** with atom labels are shown in Figures 2 and 3, respectively. Selected



**Figure 2.** ORTEP view of the asymmetric unit of **1** with displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i)  $-1/2 + x, 1/2 - y, 1/2 + z$ ; (ii)  $-x, 1 - y, 1 - z$ .



**Figure 3.** ORTEP view of the asymmetric unit of **2** with displacement ellipsoids drawn at the 40% probability level. Symmetry code: (i)  $-1/2 + x, 1/2 - y, 1/2 + z$ ; (ii)  $-x, -y, 1 - z$ .

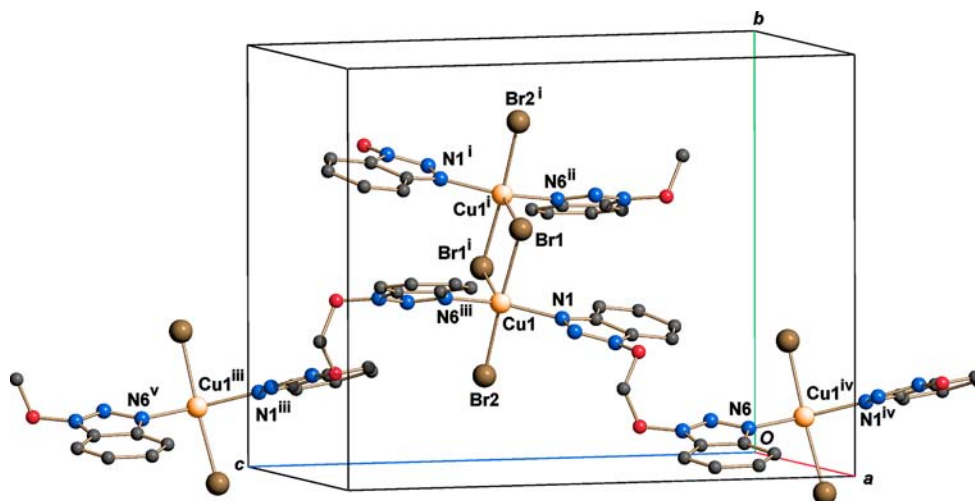
bonding parameters for both complexes are listed and compared (Table 2). The asymmetric units contain one neutral ligand **L**, two halide ions, one copper(II) atom, and one water molecule. Partial packing diagrams (Figures 4 and 5) show that two neighboring asymmetric units connect each other through double  $\mu$ -halide bridges, leading to centrosymmetric  $\text{Cu}(\mu\text{-X})_2\text{Cu}$  building blocks ( $X = \text{Br}$  and  $\text{Cl}$  in **1** and **2**, respectively). The ligand **L** bridges adjacent  $\text{Cu}(\mu\text{-X})_2\text{Cu}$  units by coordinating the metal centers through N1 and N6 nitrogen atoms of the benzotriazole units. In particular, the two benzotriazole moieties of **L** fold over the oxo–methylene bridge into a *gauche*–*gauche* conformation [the N3–O1–C13–

**Table 2.** Selected Bond Lengths [Å] and Angles [deg] for **1** and **2**<sup>a</sup>

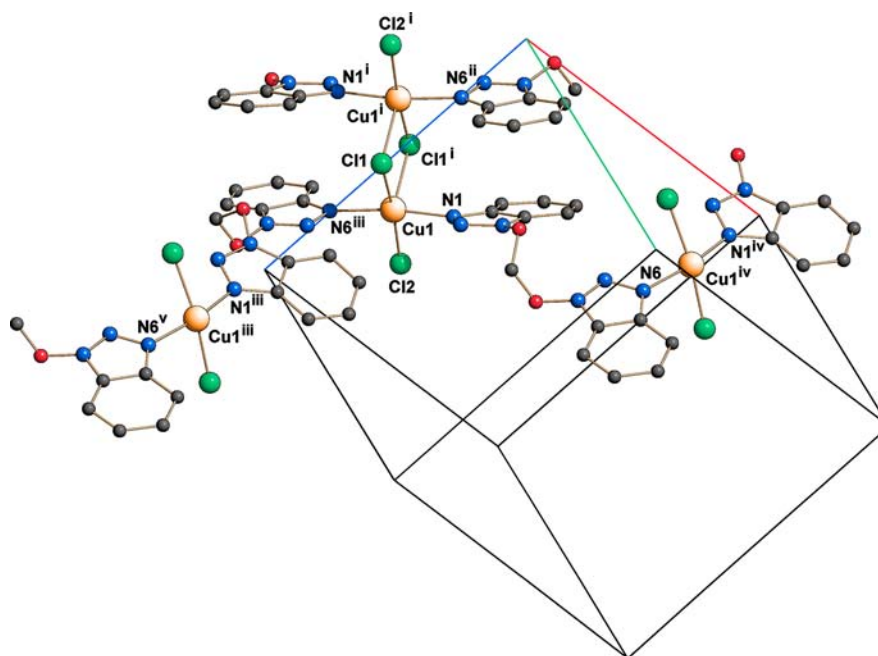
|  | 1           |  | 2          |
|--|-------------|--|------------|
| Cu1–Br1                                | 2.4984(4)   | Cu1–Cl1                                  | 2.3053(8)  |
| Cu1–Br1 <sup>i</sup>                   | 2.6572(4)   | Cu1–Cl1 <sup>iii</sup>                   | 2.6479(8)  |
| Cu1–Br2                                | 2.4439(4)   | Cu1–Cl2                                  | 2.2624(10) |
| Cu1–N1                                 | 2.0014(17)  | Cu1–N1                                   | 2.019(2)   |
| Cu1–N6 <sup>ii</sup>                   | 2.0036(18)  | Cu1–N6 <sup>ii</sup>                     | 2.016(2)   |
| Cu1–Br1–Cu1 <sup>i</sup>               | 92.60(1)    | Cu1–Cl1–Cu1 <sup>iii</sup>               | 89.35(3)   |
| Br1–Cu1–Br2                            | 176.733(14) | Cl1–Cu1–Cl2                              | 169.87(4)  |
| Br1–Cu1–N1                             | 87.88(5)    | Cl1–Cu1–N1                               | 88.76(8)   |
| Br1–Cu1–N6 <sup>ii</sup>               | 89.73(5)    | Cl1–Cu1–N6 <sup>ii</sup>                 | 88.24(7)   |
| Br1–Cu1–Br1 <sup>i</sup>               | 87.401(12)  | Cl1–Cu1–Cl1 <sup>iii</sup>               | 90.65(3)   |
| Br2–Cu1–N1                             | 89.01(5)    | Cl2–Cu1–N1                               | 91.35(8)   |
| Br2–Cu1–N6 <sup>ii</sup>               | 92.30(5)    | Cl2–Cu1–N6 <sup>ii</sup>                 | 89.43(8)   |
| Br1 <sup>i</sup> –Cu1–Br2              | 94.65(1)    | Cl1 <sup>iii</sup> –Cu1–Cl2              | 99.42(4)   |
| N1–Cu1–N6 <sup>ii</sup>                | 146.20(8)   | N1–Cu1–N6 <sup>ii</sup>                  | 167.22(10) |
| Br1 <sup>i</sup> –Cu1–N1               | 110.83(6)   | Cl1 <sup>iii</sup> –Cu1–N1               | 95.58(7)   |
| Br1 <sup>i</sup> –Cu1–N6 <sup>ii</sup> | 102.73(5)   | Cl1 <sup>iii</sup> –Cu1–N6 <sup>ii</sup> | 96.87(7)   |

<sup>a</sup>Symmetry codes: (i)  $-x, 1 - y, 1 - z$ ; (ii)  $-1/2 + x, 1/2 - y, 1/2 + z$ ; (iii)  $-x, -y, 1 - z$ .

O2, N2–N3–O1–C13, N4–O2–C13–O1, and N5–N4–O2–C13 torsion angles are 81.3(2)°, 66.5(2)°, 70.5(2)°, and –101.8(2)°, respectively, in **1**, and 69.8(3)°, 69.4(3)°, 74.0(3)°, and –96.2(3)°, respectively, for **2**]. Thus, two well separated  $\text{Cu}(\mu\text{-X})_2\text{Cu}$  dimeric units are connected by four long spacer organic ligands which extend in a cross-linked fashion resulting in a three-dimensional honeycomb-like metal–organic hybrid architecture (Figure S2, Supporting Information). The Cu···Cu separation in the  $\text{Cu}(\mu\text{-X})_2\text{Cu}$  units in **1** and **2** are 3.7289(4) and 3.4911(5) Å, respectively, while the separation between copper(II) metals bridged by the organic spacer ligand **L** are 10.2294(8) and 9.7649(6) Å, respectively. In both complexes the metal atoms in the dimeric  $\text{Cu}(\mu\text{-X})_2\text{Cu}$  units are coplanar by symmetry requirement. In **1**, copper atoms are five coordinated by two bridging bromides, one terminal bromide, and two terminal nitrogen atoms of benzotriazole moieties of two different **L**. The coordination polyhedron around the copper(II) center could be described as intermediate between distorted square pyramidal and distorted trigonal bipyramidal, with atoms Br1, N1, Br2, and N6<sup>ii</sup> [symmetry code: (ii)  $-1/2 + x, 1/2 - y, 1/2 + z$ ] forming a remarkably tetrahedrally distorted basal plane (maximum displacement 0.5448(16) Å for atom N1) and atom Br1<sup>i</sup> [symmetry code: (i)  $-x, 1 - y, 1 - z$ ] at the apex, with the metal displaced by 0.0571(3) Å toward Br1<sup>i</sup> from the mean basal plane. The relative deviations of bond angles and lengths from the ideal values (Table 2) also support the distorted geometry of the copper(II) center. The distortions of the coordination polyhedron from square pyramidal to trigonal bipyramidal are expressed as  $\tau$ , an index of the degree of trigonality;  $\tau$  is defined as  $(\beta - \alpha)/60$  where  $\beta$  and  $\alpha$  are the two trans-basal angles. For a perfectly square pyramidal geometry the value is equal to 0, while it becomes 1 for perfect trigonal bipyramidal geometry.<sup>32</sup> The  $\tau$  value calculated for **1** is 0.501, and it differs from most previously reported coordination distortions. In **2** the coordination geometry could be described as distorted square pyramidal, with the metal displaced from the Cl1/N1/Cl2/N6<sup>ii</sup> [symmetry code: (ii)  $-1/2 + x, 1/2 - y, 1/2 + z$ ] basal plane (maximum displacement 0.019(2) Å for atom N6) by 0.2032(3) Å toward the apical Cl1<sup>i</sup>



**Figure 4.** Partial crystal packing of **1** showing the formation of the dimeric unit and the bridging role of the ligand. Hydrogen atoms and water molecules are omitted for clarity. Symmetry codes: (i)  $-x, 1 - y, 1 - z$ ; (ii)  $1/2 - x, 1/2 + y, 1/2 + z$ ; (iii)  $-1/2 + x, 1/2 - y, 1/2 + z$ ; (iv)  $1/2 + x, 1/2 - y, -1/2 + z$ .



**Figure 5.** View of the polymer formation in **2**. Hydrogen atoms and water molecules are omitted for clarity. Symmetry codes: (i)  $-x, -y, 1 - z$ ; (ii)  $1/2 - x, -1/2 + y, 1/2 - z$ ; (iii)  $-1/2 + x, 1/2 - y, 1/2 + z$ ; (iv)  $1/2 + x, 1/2 - y, -1/2 + z$ ; (v)  $-1 + x, y, 1 + z$ .

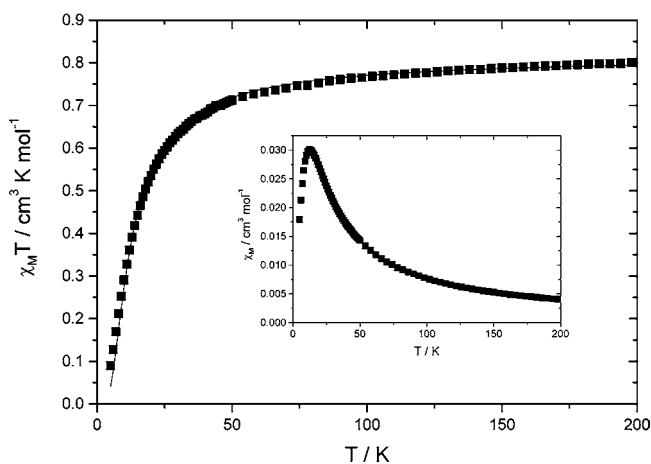
chlorine atom [symmetry code: (i)  $-x, -y, 1 - z$ ]. The index of the degree of trigonality,  $\tau$ , has a value 0.044, indicating a much less distorted structure compared to **1**. The longer Cu–X apical bond lengths (2.6572(4) Å in **1**; 2.6479(8) Å in **2**) as compared to the basal Cu–X distances (weighted mean value 2.47(3) Å in **1**; 2.29(2) Å in **2**) are associated to the pseudo-Jahn–Teller effect on the copper(II) ion. All Cu–X bond distances are in good agreement with those found in the literature for related bis( $\mu$ -bromo)-bis( $\mu$ -chloro)copper(II) complexes.<sup>33–36</sup> The Cu–Cl–Cu bridging angle of 89.35(3)° in **2** is slightly narrower than the corresponding Cu–Br–Cu angle [92.60(1)°] found in **1**, while the Cl1–Cu1–Cl1 angle of 90.65(3)° is slightly larger than the Br1–Cu1–Br1<sup>ii</sup> angle in **1** [87.401(12)°]. It is noteworthy to mention that, in spite of the similar formula units, **1** and **2** are not isostructural. Besides the effect in the coordination geometry of the metal induced by

exchanging Br with Cl as reported above, the lack of isostructurality might be attributed to the different conformations assumed by the L ligand, which results in the formation of different weak interactions. In **1**, the N1–N3/C1–C6 and N4–N6/C7–C12 benzotriazole ring systems form a dihedral angle of 12.33(5)° and are tilted with respect to the basal planes of the coordination polyhedra to which the N1 and N6 nitrogen atoms belong [Br1/N1/Br2/N6<sup>ii</sup> and Br1<sup>iv</sup>/N6/Br2<sup>iv</sup>/N4<sup>iv</sup>; symmetry codes: (ii)  $-1/2 + x, 1/2 - y, 1/2 + z$ ; (iv)  $1/2 + x, 1/2 - y, -1/2 + z$ ] by 91.06(4)° and 62.89(3)°, respectively. In this conformation, no intramolecular hydrogen bond is possible, whereas  $\pi \cdots \pi$  stacking interactions occur involving the aromatic rings of adjacent benzotriazole units [Cg1 $\cdots$ Cg2<sup>v</sup> = 3.6017(14) Å, perpendicular interplanar distance = 3.5529(9) Å, offset = 0.623(8) Å; Cg1 and Cg2 are the centroids of the C1–C6 and C7–C12 rings, respectively; symmetry code: (v)  $1 + x, y, z$ ]. In

**2**, **L** displays a conformation similar to that observed in the free ligand, with the N1–N3/C1–C6 and N4–N6/C7–C12 benzotriazole ring systems forming a dihedral angle of 31.97(6)° and tilted with respect to the basal planes of the coordination polyhedra to which the N1 and N6 nitrogen atoms belong [Cl1<sup>I</sup>/N1/Cl2/N6<sup>II</sup> and Cl1<sup>IV</sup>/N6/Cl2<sup>IV</sup>/N4<sup>IV</sup>; symmetry codes as given for **1**] by 54.91(6)° and 63.62(5)°, respectively. As a consequence, in **2** the intramolecular hydrogen bond reported for **L** is still effective in stabilizing the molecular conformation [C6–H6, 0.93 Å; H6⋯N5, 2.61 Å; C6⋯N6, 3.259(4) Å; C6–H6⋯N5, 127°] and in addition, a further hydrogen interaction is possible involving as donor the H atoms attached to the aromatic C12 carbon atom and as acceptor the bridging Cl1<sup>IV</sup> chlorine atom [C12–H12, 0.93 Å; H12⋯Cl1<sup>IV</sup>, 2.82 Å; C6⋯Cl1<sup>IV</sup>, 3.505(3) Å; C6–H6⋯Cl1<sup>IV</sup>, 131°].

In the crystal packing of **1**, the water molecules are connected to a coordinated bromine atom through O3–H31⋯Br2 hydrogen interactions. In **2**, the lattice water molecule interacts with the polymeric network through bifurcated O3–H31⋯O2 and O3–H31⋯N2 hydrogen bonds. Adjacent layers are linked via O3–H32⋯Cl2 hydrogen interactions involving the lattice water and the nonbridging chloride atom of the asymmetric unit (for details on hydrogen bonding see Table S2 and Figures S3 and S4 of the Supporting Information).

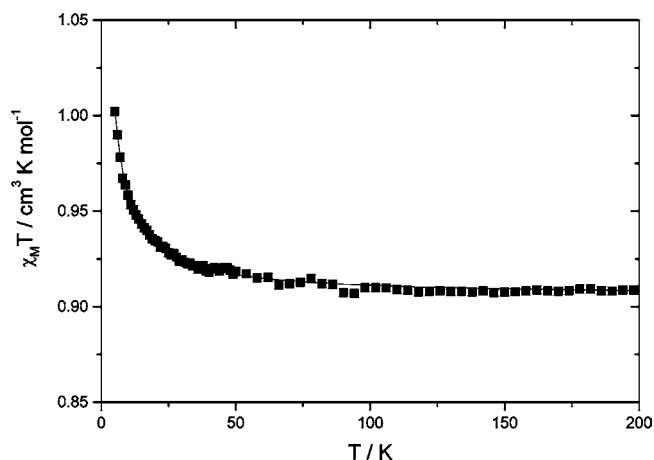
**Magnetic Measurements.** The plots of  $\chi_M T$  versus temperature for both **1** and **2** are shown in Figures 6 and 7,



**Figure 6.**  $\chi_M T$  vs  $T$  for **1**. Solid line shows the best fit of the data set.

respectively. For **1**, the value of  $\chi_M T$  is 0.79 cm<sup>3</sup> K mol<sup>-1</sup> at 200 K which agreed with the value expected for two uncoupled  $S = 1/2$  spins with  $g = 2.05$ .  $\chi_M T$  decreases slowly down to 60 K, then decreases more rapidly to reach the value of 0.09 cm<sup>3</sup> K mol<sup>-1</sup> at 5 K, indicating the presence of an antiferromagnetic interaction between the two copper atoms (Figure 6). This antiferromagnetic interaction can also be evidenced by the  $\chi_M$  versus temperature plot (inset to Figure 6). Starting from 300 K, a decrease in temperature leads to increase of  $\chi_M$ . At 12 K, the curve presents a rounded maximum, a further decrease of the temperature leading to a decrease of  $\chi_M$ . This maximum is clear evidence for antiferromagnetic interaction.

For **2**,  $\chi_M T$  attains the value of 0.91 cm<sup>3</sup> K mol<sup>-1</sup> at 200 K which is in agreement with the value expected for two uncoupled  $S = 1/2$  spins with  $g = 2.20$ .  $\chi_M T$  remains constant upon lowering the temperature to 50 K and then increases very



**Figure 7.**  $\chi_M T$  vs  $T$  for **2**. Solid line shows the best fit of the data set.

slightly to reach the value of 1.00 cm<sup>3</sup> K mol<sup>-1</sup> at 5 K, indicating the presence of weak ferromagnetic coupling between copper atoms (Figure 7).

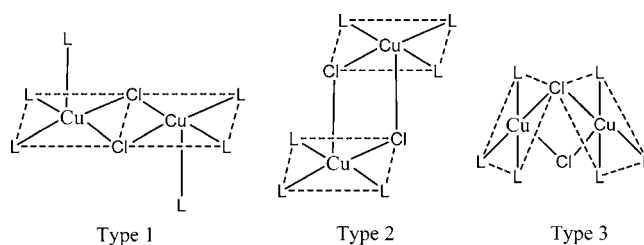
As already previously described, the copper atoms form a chain, two copper atoms being alternatively bridged by two organic ligands and two halogen (Br for **1**, Cl for **2**) atoms. Due to the large size of the ligand **L**, it can be safely assumed that no magnetic interaction can take place through the organic bridge. From a magnetic point of view, the compounds can be considered as copper(II) dimers linked by two halo bridges.

In line with the dimeric nature of the compounds, the magnetism has been fitted using a classical Bleaney and Bowers law:

$$\chi_M T = \frac{N\beta^2}{3k_B} \frac{2g^2}{1 + \exp(-J/k_B T)/3}$$

The best fit of data gives  $J = -15.2$  cm<sup>-1</sup> and  $g = 2.09$  for **1** and  $J = +1.7$  cm<sup>-1</sup> and  $g = 2.20$  for **2**, respectively.

**Magneto-Structural Correlation.** Three different types of square pyramidal geometries (Figure 8) have been exper-



**Figure 8.** Different square pyramidal geometries for dichloro bridged copper(II) dimers.

imentally established: (a) square pyramids sharing a basal edge with coplanar basal planes (type 1); (b) square pyramids sharing a base-to-apex edge with parallel basal planes (type 2); (c) square pyramids that also share a base-to-apex edge but with perpendicular basal planes (type 3). The nature of exchange interaction and magnitude of the coupling constant  $2J$  for Cu( $\mu$ -X)<sub>2</sub>Cu dimers depend mainly on the Cu–X–Cu angle  $\varphi$ , the Cu–X distances, the nature of terminal ligands, and the distortion of the coordination geometry. For an ideal square pyramidal geometry ( $\tau = 0$ ), the unpaired electron spin density lies predominantly in the  $d_{x^2-y^2}$  magnetic orbital on the metal centers. The overlap between copper(II) ions would be

Table 3. Structural and Magnetic Parameters for the Cu( $\mu$ -Br)<sub>2</sub>Cu Dimers<sup>a</sup>

| compd  | Cu–Br <sub>axial</sub> /Å | Cu–Cu/Å | $\Phi$ (Cu–Br–Cu)/deg | $\varphi/R$ (deg/Å) | geometry | type   | $J/\text{cm}^{-1}$ | ref       |
|--|---------------------------|---------|-----------------------|---------------------|----------|--------|--------------------|-----------|
| [Cu(L) <sub>2</sub> Br <sub>2</sub> ] <sub>2</sub>                                     | 2.73                      | 3.61    | 86.31, 87.59          | 31.27               | SP       | type 2 | –11.76             | 34a       |
| [Cu(meox) <sub>2</sub> Br <sub>2</sub> ] <sub>2</sub>                                  | 2.71                      | 3.63    | 86.98                 | 32.09               | SP       | type 2 | –7.6               | 34b       |
| [Cu <sub>2</sub> (dien) <sub>2</sub> Br <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> | 2.89                      | 3.79    | 90.64                 | 31.36               | SP       | type 2 | 1.4                | 34c       |
| [Cu(tmso) <sub>2</sub> Br <sub>2</sub> ] <sub>2</sub>                                  | 3.01                      | 3.75    | 85.97                 | 28.56               | SP       | type 2 | –16.0              | 34d       |
| [Cu <sub>2</sub> (terpy) <sub>2</sub> Br <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub> | 2.82                      | 3.36    | 88.58                 | 31.41               | SP       | type 2 | –3.7               | 34e       |
| (3ap) <sub>2</sub> [Cu <sub>2</sub> Br <sub>6</sub> ] <sub>2</sub> ·H <sub>2</sub> O   | 2.79                      | 3.82    | 93.37                 | 33.46               | SP       | type 2 | –26.9              | 34f       |
| [Cu(tz) <sub>2</sub> Br <sub>2</sub> ] <sub>2</sub>                                    | 3.12                      | 3.99    | 90.20                 | 28.91               |          | type 2 | –10.4              | 34g       |
| [Cu(bp3ca)Br <sub>2</sub> ] <sub>2</sub> ·H <sub>2</sub> O                             | 3.05                      | 3.79    | 87.28                 | 28.61               | SP       | type 2 | 91.52              | 34h       |
| [Cu( $\alpha$ -pic) <sub>2</sub> Br <sub>2</sub> ] <sub>2</sub>                        | 3.87                      | 4.93    | 100.4                 | 25.94               |          | type 2 | –2.5               | 34i       |
| {[Cu( $\mu$ -Br)(Br)( $\mu$ -L)] <sub>2</sub> } <sub>n</sub> ·2nH <sub>2</sub> O       | 2.65                      | 3.72    | 92.60                 | 34.94               | SP       | type 2 | –15.2              | this work |

<sup>a</sup>Abbreviations: meox = 4-methyloxazole; dien = diethylenetriamine; tmso = tetramethylene sulfoxide; terpy = 2,2',6,2'-terpyridyl; 3ap = 3-aminopyridinium cation; tz = thiazole; bp3ca = 2,2'-bipyridine-3,3'-dicarboxylic acid;  $\alpha$ -pic = 2-methylpyridine. Type 2 indicates square pyramids sharing a base-to-apex edge with parallel basal planes.

Table 4. Structural and Magnetic Properties in a Few Cu( $\mu$ -Cl)<sub>2</sub>Cu Dimers<sup>a</sup>

| compd  | Cu–Cl <sub>axial</sub> /Å | Cu–Cu/Å | $\Phi$ (Cu–Cl–Cu)/deg | $\varphi/R$ (deg/Å) | geom | $2J \text{ cm}^{-1}$ | type   | ref       |
|--|---------------------------|---------|-----------------------|---------------------|------|----------------------|--------|-----------|
| [Cu(dmgh)Cl <sub>2</sub> ] <sub>2</sub>  | 3.445                     | 2.698   | 88.0                  | 32.62               | SP   | +0.62                | type 2 | 36a       |
| [Cu(pfsa)Cl] <sub>2</sub>  | 3.825                     | 2.846   | 95.27                 | 33.6                | SP   | +0.30                | type 2 | 36b       |
| [Cu(pmda)Cl] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>                       | 3.396                     | 2.581   | 88.2                  | 34.17               | SP   | +2.24                | type 2 | 36c       |
| [Cu(iyda)Cl] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>                       | 3.494                     | 2.657   | 88.81                 | 33.42               | SP   | +1.16                | type 2 | 36d       |
| [Cu(bpdio)Cl] <sub>2</sub>   | 3.842                     | 2.844   | 96.68                 | 33.99               | SP   | +4.87                | type 2 | 36e       |
| [Cu <sub>2</sub> (baamo) <sub>2</sub> Cl <sub>2</sub> ]                          | 3.418                     | 2.808   | 82.9                  | 29.52               | SP   | +12.0                | type 2 | 36f       |
| {[Cu(MeL)Cl] <sub>2</sub> }[ClO <sub>4</sub> ] <sub>2</sub>                      | 3.821                     | 2.891   | 94.8                  | 32.79               | SP   | –7.78                | type 2 | 36g       |
| [Cu(dmen)Cl] <sub>2</sub>  | 3.458                     | 2.73    | 86.1                  | 31.50               | SP   | –4.2                 | type 2 | 36h       |
| {[Cu(terpy)] <sub>2</sub> (Cl) <sub>2</sub> }(PF <sub>6</sub> ) <sub>2</sub>     | 3.510                     | 2.72    | 89.9                  | 33.1                | SP   | –11.8                | type 2 | 36i       |
| [Cu(2-pic) <sub>2</sub> Cl] <sub>2</sub>   | 4.404                     | 3.36    | 100.6                 | 29.91               | SP   | –14.8                | type 2 | 36j       |
| [Cu <sub>2</sub> Cl <sub>4</sub> (Mebta) <sub>4</sub> ]                          | 3.437                     | 2.64    | 88.1                  | 33.5                | SP   | +13.4                | type 2 | 36k       |
| [Cu(HL1)Cl] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>                        | 3.86                      | 2.92    | 94.7                  | 32.43               | SP   | +21.4                | type 2 | 36l       |
| {[Cu( $\mu$ -Cl)(Cl)( $\mu$ -L)] <sub>2</sub> } <sub>n</sub> ·2nH <sub>2</sub> O | 2.64                      | 3.49    | 89.35                 | 33.84               | SP   | +3.4                 | type 2 | this work |

<sup>a</sup>Abbreviations: dmgh = dimethylglyoxime; pfsa = 3-[N-(2-(pyridylethyl)formimidoyl)salicylic acid; pmda = 1-(2-pyridylmethyl)-1,5-diazacyclooctane; iyda = 1-(imidazol-4-ylmethyl)-1,5-diazacyclooctane; bpdio = 2,2-bis(2-pyridyl)-1,3-dioxolane; baamo = 8-amino-5-aza-4-methyl-3-octene-2-onate; dmen = N,N-dimethylethylenediamine; MeL = methyl [2-(2-pyridyl)ethyl]-(2-pyridylmethyl)amine; HL<sup>1</sup> = 1,5-bis-(pyridin-4-ylmethyl)-1,5-diazacyclooctane; Mebta = 1-methylbenzotriazole. Type 2 indicates square pyramids sharing a base-to-apex edge with parallel basal planes.

zero, and the exchange interaction will be zero. Deviation from the ideal geometries facilitates the overlap of magnetic orbitals antiferromagnetically. Theoretical calculations have been done on suitable model systems of dihalo-bridged copper(II) complexes providing an insight on the nature of magnetic orbital interactions.

Hatfield and co-workers<sup>33</sup> have proposed magneto-structural correlations between  $2J$  and  $\varphi/R$  ratio in Cu( $\mu$ -X)<sub>2</sub>Cu complexes where  $R$  is the longer axial Cu–X distance in a square pyramid. They observed that, for a value of  $\varphi/R$  outside the range 32.6–34.8 (deg/Å), the exchange interaction is antiferromagnetic while for values lying within this range it is ferromagnetic.

In this respect both **1** and **2** belong to type 2 geometries (Figure 8). The  $\varphi/R$  ratios for **1** and **2** are 34.95 and 33.84 (deg/Å), thereby indicating antiferro- and ferromagnetic interactions for **1** and **2**, respectively. These results match well with the observed magnetic properties, and also correlate well with similar dihalo-bridged Cu<sub>2</sub>X<sub>2</sub> systems reported in the literature (Tables 3 and 4). However, in some complexes antiferromagnetic behavior was also observed with  $\varphi/R$  ratios lying in the range 32.6–34.8 (deg/Å). The overall antiferromagnetic behavior of such complexes is due to the fact that antiferromagnetic interaction predominates over ferromagnetic interaction. Thus, it would be difficult to explain satisfactorily

the sign and magnitude of  $J$  values which depend on both  $\varphi$  and  $R$  and not just on their ratio.

The magnetic interaction in halo-bridged dinuclear compounds has been extensively studied, experimentally and theoretically. A complete DFT study has been undertaken by Ruiz et al.<sup>35</sup> In this article, the authors emphasize that when the bridging atom is chlorine, the coupling constant is small in all cases ( $-10 < J < +10 \text{ cm}^{-1}$ ). Indeed, **2** presents a very small and positive  $J$  coupling ( $+1.7 \text{ cm}^{-1}$ ). As far as the bridging atom is bromine, it has been shown that, for type 2 geometry, almost all complexes are antiferromagnetically coupled, with  $J$  varying from  $-27$  to  $-2.5 \text{ cm}^{-1}$ .<sup>36a</sup>

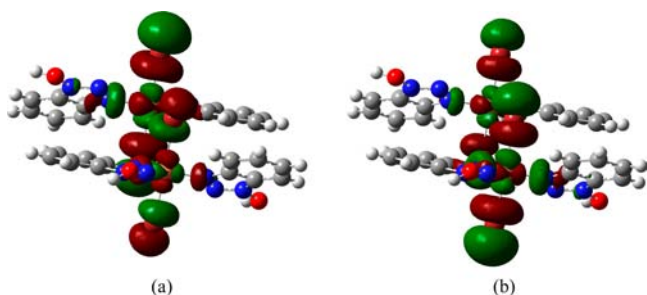
**DFT Methodology.** The calculated coupling constant  $J$  was deduced from two separate DFT computations carried out for the highest spin state and for the broken symmetry state. The hybrid B3LYP<sup>37</sup> functional has been used as implemented in Gaussian98.<sup>38</sup> The basis set used in all calculations was the triple- $\xi$  basis-set proposed by Ahlrichs et al.<sup>39</sup> for transition metals and the double- $\xi$  basis set proposed by the same authors for the other atoms.<sup>40</sup> The obtained  $J$  values were deduced from the energy difference  $E_{\text{HS}} - E_{\text{BS}} = -(2S_1S_2 + S_2)J$  where  $E_{\text{HS}}$  and  $E_{\text{BS}}$  are the energies of high spin and broken symmetry states, respectively,  $S_1$  and  $S_2$  being the spin of the two metal involved ( $S_1 = S_2 = 1/2$  here). We assume that the energy of the broken symmetry state is a good approximation of low spin



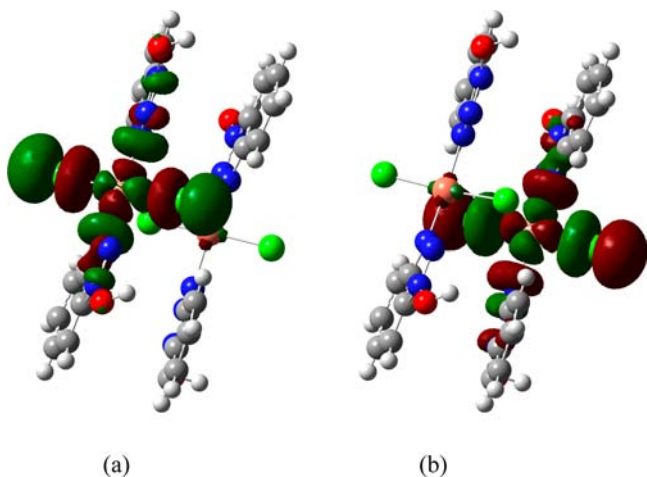
state energy, following Ruiz et al.<sup>41</sup> The spin density reported has been calculated using the Mulliken procedure. The orbitals drawn in this article under the name of magnetic orbitals are the so-called unoccupied magnetic spin orbitals (UMSOs).<sup>42</sup>

In order to get a deeper understanding of the two magnetic coupling constant  $J$ , some DFT calculations have been undertaken. The calculated  $J$  values are of  $-9.79$  and  $+0.68$   $\text{cm}^{-1}$ , respectively, for **1** and **2**, in reasonable agreement with the experimental values ( $-15.2$  and  $+1.7$   $\text{cm}^{-1}$ , respectively). In the case of compound **2**, DFT basically confirms that the interaction is ferromagnetic and very small. In the case of compound **1**, DFT calculations basically give a coupling constant on the same order of magnitude as the one obtained by magnetic measurements, although with a relative error of about 55%. However, if the relative error is large, as an absolute value the error is only  $5.4$   $\text{cm}^{-1}$ . Ruiz et al.<sup>35</sup> have shown on a series of DFT calculations on dichloro- and dibromo-bridged dinuclear copper complexes that the average error between experimental and calculated coupling constant was  $16$   $\text{cm}^{-1}$ . Having an error of  $5.4$   $\text{cm}^{-1}$  is thus in line with previously reported results.

The magnetic orbitals for **1** and **2** are represented in Figures 9 and 10, respectively. The two magnetic orbitals have a



**Figure 9.** (a and b) Different views of unoccupied magnetic spin orbitals (UMSOs) for **1**.



**Figure 10.** (a and b) Different views of unoccupied magnetic spin orbitals (UMSOs) for **2**.

contribution on the two metal atoms. More precisely, this contribution is of the  $d_{x^2-y^2}$  type, with the  $x$  and  $y$  axis being directed toward the four short metal–ligand bonds. These orbitals are also delocalized on the surrounding ligands. The interaction between the metal and the ligand is antibonding in nature, as expected from simple molecular orbital theory

arguments. The shape of magnetic orbitals is basically the same for **2** also.

The  $J$  coupling, either calculated or measured, is relatively weak, especially for **2**. Indeed, for geometries of type **1**,  $J$  can be as high as  $-100$   $\text{cm}^{-1}$ . The relatively weak coupling in **2** can be briefly justified as follows. The two orbitals bearing the unpaired electrons are situated into the two equatorial planes of the copper atoms. These two planes are almost parallel and separated by about  $2.6$  Å. The overlap of magnetic orbitals will be small, according to the so-called Kahn's model.<sup>43</sup>

As there are some geometry differences between the two structures, it is difficult to know if the difference between the two  $J$  couplings is mainly related to the fact that the bromine ligand has been exchanged by the chlorine ligand or due to the geometry changes.

However, one parameter of importance is the spin density delocalized on the bridging atoms. The more important the spin delocalization is, the higher the absolute value of  $J$  is expected to be. The calculated spin density of the two considered molecules has thus been checked. For **1**, the mean spin density in the ferromagnetic state is  $0.473$  for the two copper atoms and  $0.166$  for the Br bridging atoms. As far as **2** is concerned, the mean spin densities on Cu and Cl bridging atoms are, respectively,  $0.556$  and  $0.119$ . As a conclusion of this comparison, the spin density is higher on the bridging atom for compound **1** than for compound **2**, justifying that the absolute value of coupling parameter  $|J|$  is higher for compound **1**.

## CONCLUSION

In this work, we have explored a new methylene bridged 1-hydroxybenzotriazole derived ligand in the formation of metal–organic hybrid framework solids. We observed that the counterions of the salts incorporated in the frameworks play a major role in determining the magnetic properties of the complexes. Flexibilities introduced through the increase of methylene linkages in this class of ligand and its effect on structure and properties of the complexes are also in progress.

## ASSOCIATED CONTENT

### Supporting Information

Additional tables, figures, and details. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 810783, 810784, and 869949 contain the supplementary crystallographic data for **1** and **2**, and **L**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; or e-mail [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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### Notes

The authors declare no competing financial interest.

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