

X-ray Crystal Structures, Electron Paramagnetic Resonance, and Magnetic Studies on Strongly Antiferromagnetically Coupled Mixed  $\mu$ -Hydroxide- $\mu$ - $N^1,N^2$ -Triazole-Bridged One Dimensional Linear Chain Copper(II) ComplexesKrzysztof Drabent,<sup>\*,†</sup> Zbigniew Ciunik,<sup>†</sup> and Andrzej Ozarowski<sup>‡</sup>

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Four new metal-organic polymeric complexes,  $\{[\text{Cu}(\mu\text{-OH})(\mu\text{-ClPhtrz})](\text{H}_2\text{O})(\text{BF}_4)]_n$  (**1**),  $\{[\text{Cu}(\mu\text{-OH})(\mu\text{-BrPhtrz})](\text{H}_2\text{O})(\text{BF}_4)]_n$  (**2**),  $\{[\text{Cu}(\mu\text{-OH})(\mu\text{-ClPhtrz})(\text{H}_2\text{O})](\text{NO}_3)]_n$  (**3**), and  $\{[\text{Cu}(\mu\text{-OH})(\mu\text{-BrPhtrz})(\text{H}_2\text{O})](\text{NO}_3)]_n$  (**4**) (ClPhtrz =  $N$ -[(*E*)-(4-chlorophenyl)methylidene]-4*H*-1,2,4-triazol-4-amine; BrPhtrz =  $N$ -[(*E*)-(4-bromophenyl)methylidene]-4*H*-1,2,4-triazol-4-amine), were synthesized in a reaction of substituted 1,2,4-triazole and various copper(II) salts in water/acetonitrile solutions. The structures of **1–4** were characterized by single-crystal X-ray diffraction analysis. The Cu(II) ions are linked both by single  $N^1,N^2$ -1,2,4-triazole and hydroxide bridges yielding one dimensional (1D) linear chain polymers. The tetragonally distorted octahedral geometry of copper atoms is completed alternately by two water and two  $\text{BF}_4^-$  anion molecules in **1** and **2** but solely by two water molecules in **3** and **4**. Magnetic properties of all complexes were studied by variable temperature magnetic susceptibility measurements. The Cu(II) ions are strongly antiferromagnetically coupled with  $J = -419(1) \text{ cm}^{-1}$  (**1**),  $-412(2) \text{ cm}^{-1}$  (**2**),  $-391(3) \text{ cm}^{-1}$  (**3**), and  $-608(2) \text{ cm}^{-1}$  (**4**) (based on the Hamiltonian  $\mathbf{H} = -J[\sum \mathbf{S}_i \cdot \mathbf{S}_{i+1}]$ ). The nature and the magnitude of the antiferromagnetic exchange were discussed on the basis of complementarity/countercomplementarity of the two competing bridges.

## Introduction

Substituted 1,2,4-triazole ligands can bridge transition metal ions through an  $N^1,N^2$ -coordination mode to afford polynuclear compounds with unique magnetic properties.<sup>1</sup> The current interest is focused on the spin-crossover phenomena in iron(II) triazole complexes because of their potential applications as molecular switches and memory devices.<sup>2–4</sup> On the other hand, considerable progress has been achieved in revealing the magneto-structural correlations in copper(II) compounds with substituted 1,2,4-triazoles. De-

pending on the synthesis conditions, triazole substituents, and the kind of anion used, the Cu(II) ions form a variety of polynuclear compounds including triply triazole-bridged linear chains<sup>5–8</sup> and linear trinuclear entities,<sup>9–12</sup> as well as

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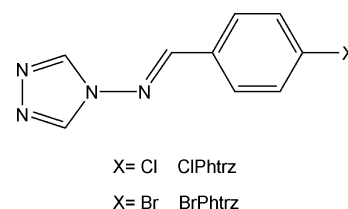
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doubly triazole-bridged chains, trimers, and dimers.<sup>13–21</sup> In addition, triangular trinuclear,<sup>22–26</sup> cyclic hexanuclear complexes,<sup>27</sup> linear chains,<sup>28,29</sup> trimers,<sup>13</sup> and dimers<sup>26,30</sup> with a single 1,2,4-triazole bridge have been reported. In this case, the metal ions are usually bridged additionally by small anions such as Cl<sup>–</sup>,<sup>28</sup> F<sup>–</sup>,<sup>29</sup> N<sub>3</sub><sup>–</sup>,<sup>13</sup> SO<sub>4</sub><sup>2–</sup>,<sup>30</sup> or OH<sup>–</sup>.<sup>22–27</sup> Two different bridges may either enhance or attenuate their effect on Cu–Cu exchange interactions.

The problem of two different bridges in copper(II) dimers and their effect on magnetic interactions between Cu(II) ions was noticed for the first time by Nishida et al.<sup>31–34</sup> and

Chart 1



McKee et al.<sup>35–37</sup> The *J* value calculated for  $\mu$ -alkoxido- $\mu$ -acetato-dicopper(II) complexes appeared to contradict the rules<sup>38–41</sup> relating the *J* value and Cu–O–Cu angle. The discrepancies between observed and theoretical *J* values were explained on the basis of orbital complementarity or countercomplementarity. This model was successfully applied to explain magnetic properties of Cu(II) dimers containing both  $\mu$ -alkoxido/hydroxido and  $\mu$ -pyrazolato bridges.<sup>37,42–46</sup> Linear polynuclear complexes containing  $\mu$ -OH and  $\mu$ -1,2,4-triazole ligands are not known.<sup>1</sup> Only one cyclic hexanuclear copper(II) complex, [Cu<sub>6</sub>(OH)<sub>6</sub>(admtz)<sub>6</sub>(H<sub>2</sub>O)<sub>5</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>6</sub>·4H<sub>2</sub>O<sup>27</sup> (where admtz = 4-amino-3,5-dimethyl-1,2,4-triazole) was characterized by X-ray crystallography and by magnetic methods. Strong antiferromagnetic exchange was reported for that compound.

Because the properties of triazole-containing copper(II) complexes are highly affected by the substituents on triazole ring, we decided to investigate the complexes with Schiff-base containing triazole ligands (Chart 1). In this paper, we report the synthesis, crystal structure, electron paramagnetic resonance (EPR), and magnetic properties of polymeric chains: {[Cu( $\mu$ -OH)( $\mu$ -XPhtrz)](H<sub>2</sub>O)(BF<sub>4</sub>)]<sub>n</sub> (compound 1 XPhtrz = ClPhtrz = N-[(E)-(4-chlorophenyl)methylidene]-4H-1,2,4-triazol-4-amine; compound 2 XPhtrz = BrPhtrz = N-[(E)-(4-bromophenyl)methylidene]-4H-1,2,4-triazol-4-amine) and {[Cu( $\mu$ -OH)( $\mu$ -XPhtrz)(H<sub>2</sub>O)](NO<sub>3</sub>)]<sub>n</sub> (compound 3 XPhtrz = ClPhtrz; compound 4 XPhtrz = BrPhtrz).

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## Experimental Section

**General.**  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ,<sup>47</sup>  $N$ -[(*E*)-(4-chlorophenyl)methylidene]-4*H*-1,2,4-triazol-4-amine (ClPhtrz),<sup>48</sup> and  $N$ -[(*E*)-(4-bromophenyl)methylidene]-4*H*-1,2,4-triazol-4-amine (BrPhtrz)<sup>49</sup> were prepared by the literature methods. All other reagent were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N, Cl, and Br) were carried out at the Microanalytical Laboratory of this university. Infrared spectra of Nujol mulls and KBr pellets were recorded on a Bruker IFS 113V FT-IR spectrometer over the 4000–400  $\text{cm}^{-1}$  range. Magnetic susceptibilities were measured on a Quantum Design MPMS-XL5 SQUID magnetometer over the 300–2 K range. Magnetic data were corrected for diamagnetic contributions, which were estimated from the Pascal's constants and for temperature independent paramagnetism estimated at  $60 \times 10^{-6}$  emu/mol for Cu(II) ion.

High-frequency EPR spectra were recorded on a home-built spectrometer at the EMR facility of NHMFL.<sup>50</sup> The instrument was a transmission-type device in which waves are propagated in cylindrical lightpipes. The microwaves were generated by a Gunn oscillator, operating at  $95 \pm 3$  GHz. Frequencies higher by a factor 2, 3, or 4 were obtained using a Schottky diode-based multiplier and appropriate high-pass filters. A phase-locked oscillator (Virginia Diodes) generating frequency of  $13 \pm 1$  GHz and its 8th, 16th, and 24th harmonics was also used. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.<sup>50</sup>

**Preparation of  $\{[\text{Cu}(\mu\text{-OH})(\mu\text{-ClPhtrz})](\text{H}_2\text{O})(\text{BF}_4)\}_n$  (1).** Aqueous solution (2 mL) of  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.115 g, 0.3 mM) was added dropwise to a hot acetonitrile solution (10 mL) of ClPhtrz (0.208 g, 1 mM). The resulting dark blue solution was stirred at room temperature for 2 h and then filtered and allowed to stand at room temperature overnight. The resulting dark blue crystals were filtered off, washed with water, and dried under vacuum. Dark blue crystals suitable for X-ray analysis were selected from this sample. Yield: 0.028 g, 21.7% (based on  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ). Anal. Calcd for  $\text{C}_9\text{H}_{10}\text{N}_4\text{ClO}_2\text{BF}_4\text{Cu}$  (%): C, 27.58; H, 2.57; N, 14.29; Cl, 9.04. Found: C, 27.71; H, 2.54; N, 14.15; Cl, 8.99. IR (KBr pallet,  $\text{cm}^{-1}$ ): 3586, 3554, 3505, 3452, 3173, 3149, 1613(s), 1595(m), 1567(w), 1540(m), 1494(w), 1412(vw), 1337(w), 1305(vw), 1287(vw), 1228(w), 1177(w), 1124(m), 1084(vs), 1072(vs), 1014(s), 987(m), 970(m), 897(w), 874(w), 834(w), 822(m), 767(w), 630(w), 532(m), 497(w), 466(w), 424(w).

**Preparation of  $\{[\text{Cu}(\mu\text{-OH})(\mu\text{-BrPhtrz})](\text{H}_2\text{O})(\text{BF}_4)\}_n$  (2).** Compound 2 was prepared in a similar manner using BrPhtrz instead of ClPhtrz. Yield: 0.039 g, 26.7% (based on  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ). Anal. Calcd for  $\text{C}_9\text{H}_{10}\text{N}_4\text{BrO}_2\text{BF}_4\text{Cu}$ : C, 24.78; H, 2.31; N, 12.84; Br, 18.32. Found: C, 25.13; H, 2.40; N, 13.04; Br, 18.30. IR (KBr pallet,  $\text{cm}^{-1}$ ): 3589, 3557, 3502, 3457, 3426, 3169, 3146, 1613(s), 1591(s), 1564(m), 1540(s), 1490(w), 1411(w), 1397(vw), 1385(vw), 1336(m), 1303(w), 1286(w), 1227(m), 1204(w), 1179(m), 1140(m), 1124(s), 1084(vs), 1071(vs), 1029(s), 1012(vs), 971(s), 896(w), 873(w), 819(m), 762(m), 708(vw), 679(vw), 631(w), 628(m), 532(m), 522(m), 494(m), 423(w).

**Preparation of  $\{[\text{Cu}(\mu\text{-OH})(\mu\text{-ClPhtrz})(\text{H}_2\text{O})_2](\text{NO}_3)\}_n$  (3).** Aqueous solution (3 mL) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.242 g, 1 mM) was added dropwise with stirring to a hot acetonitrile solution (15 mL) of ClPhtrz (0.208 g, 1 mM). A light-blue amorphous precipitate

formed after addition of first few drops of copper nitrate solution but dissolved upon addition of the full amount of reactants. The resulting dark-blue limpid solution was filtered. Dark blue crystals precipitated after cooling the solution to room temperature. The crystals were filtered off, washed with acetonitrile and dried in vacuo. Yield 0.189 g, 49.2%. Anal. Calcd for  $\text{C}_9\text{H}_{12}\text{N}_5\text{ClO}_6\text{Cu}$ : C, 28.06; H, 3.14; N, 18.18; Cl, 9.20. Found: C, 28.32; H, 3.25; N, 18.24; Cl, 9.11. IR (KBr pallet,  $\text{cm}^{-1}$ ): 3560, 3408, 3252, 3167, 3147, 1620(w), 1596(m), 1566(vw), 1539(m), 1493(w), 1425(m), 1385(vs), 1330(s), 1320(s), 1304(m), 1282(w), 1232(w), 1207(w), 1183(vw), 1085(m), 1074(m), 1042(w), 1019(w), 983(w), 883(vw), 866(w), 831(w), 766(w), 712(vw), 626(m), 540(w), 518(w), 464(w).

**Preparation of  $\{[\text{Cu}(\mu\text{-OH})(\mu\text{-BrPhtrz})(\text{H}_2\text{O})_2](\text{NO}_3)\}_n$  (4).** Aqueous solution (4 mL) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.242 g, 1 mM) was added dropwise with stirring to a solution of BrPhtrz (0.251 g 1 mM) in 20 mL of acetonitrile. Formation of an amorphous, light blue precipitate was observed. The resulting reaction mixture was refluxed until the precipitate dissolved and dark blue solution was obtained. Dark blue crystals deposited after cooling to RT were filtered, washed with acetonitrile and dried in vacuo. Yield 0.156 g, 36.3%. Anal. Calcd for  $\text{C}_9\text{H}_{12}\text{N}_5\text{BrO}_6\text{Cu}$ : C, 25.16; H, 2.81; N, 16.30; Br, 18.60. Found: C, 25.23; H, 2.71; N, 16.17; Br, 18.52. IR (KBr pallet,  $\text{cm}^{-1}$ ): 3554, 3455, 3412, 3244, 3159, 3146, 1620(w), 1590(m), 1563(w), 1539(m), 1493(w), 1431(m), 1385(vs), 1353(w), 1332(m), 1315(s), 1305(m), 1281(w), 1230(w), 1206(vw), 1184(vw), 1069(m), 1039(w), 1013(m), 980(w), 882(vw), 867(w), 826(w), 762(w), 708(vw), 626(m), 534(w), 518(w).

**X-ray Crystallographic Studies.** X-ray data for compounds **1–4** were collected at 100 K using an Oxford Cryosystem device on a Kuma KM4CCD  $\kappa$ -axis diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystals were positioned at 65 mm from the CCD camera. With this setup, 612 frames were measured at  $0.75^\circ$  intervals with a counting time of 30–40 s. Accurate cell parameters were determined and refined by a least-squares fit of 2200–2700 of the strongest reflections. The data were corrected for Lorentz and polarization effects. Analytical absorption corrections were applied. Data reduction and analysis were carried out using the Oxford Diffraction (Poland) Ltd. programs. Structures were solved by direct methods (program SHELXS97<sup>51</sup>) and refined by the full-matrix least-squares method on all  $F^2$  data using the SHELXL97<sup>52</sup> programs. Nonhydrogen atoms were refined with anisotropic displacement parameters. Three fluorine atoms of tetrafluoroborate anion in **2** were found disordered over two sites, and the site occupation factors were refined yielding 0.83 and 0.17, respectively. Hydrogen atoms were included according to the geometry of molecules and  $\Delta\rho$  maps. They were treated as riding groups with fixed isotropic displacement parameters. Final  $\Delta\rho$  maps showed no hydrogen atoms from water molecules in **2** and **4** which suggest some disorder phenomena in crystals. Crystal data for **1–4** are given in Table 1, together with refinement details.

## Results and Discussion

**Syntheses and General Characterization.** Generally, depending upon the experimental conditions, reactions of 4-R-substituted 1,2,4-triazole ligands with Cu(II) salts of potentially noncoordinating anions either yield linear chain<sup>5–8</sup> or linear trinuclear entities,<sup>9–12</sup> where Cu(II) ions are triply bridged by the ligands. The compounds **1–4** described in the present study, obtained in reaction of 4-amino-triazole

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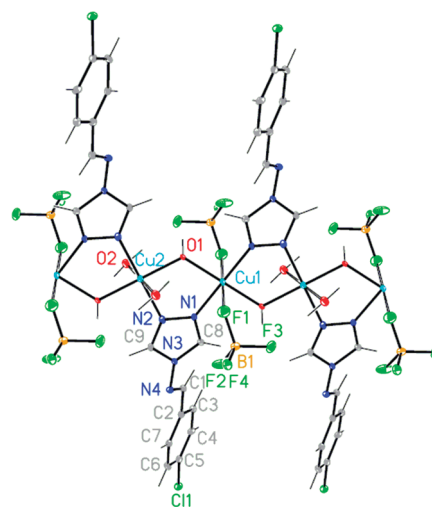
**Table 1.** Summary of Crystallographic Data for the Structures of **1–4**

	1	2	3	4
empirical formula	C <sub>9</sub> H <sub>10</sub> BClCuF <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>9</sub> H <sub>10</sub> BBrCuF <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>9</sub> H <sub>12</sub> ClCuN <sub>5</sub> O <sub>6</sub>	C <sub>9</sub> H <sub>12</sub> BrCuN <sub>5</sub> O <sub>6</sub>
fw	392.02	436.47	385.23	429.69
cryst. syst.	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
<i>a</i> , Å	6.728(1)	6.755(1)	6.788(1)	6.813(2)
<i>b</i> , Å	7.136(1)	7.174(1)	7.062(1)	7.163(2)
<i>c</i> , Å	14.786(3)	14.894(3)	15.772(1)	16.039(3)
$\alpha$ , deg	90.25(3)	90.52(1)	86.65(1)	85.12(3)
$\beta$ , deg	96.24(3)	96.09(1)	86.35(1)	87.33(3)
$\gamma$ , deg	108.62(3)	108.10(1)	67.23(1)	64.32(3)
<i>V</i> , Å <sup>3</sup>	668.2(2)	681.5(2)	695.2(2)	702.8(2)
<i>Z</i>	2	2	2	2
<i>D</i> <sub>calcd</sub> , g cm <sup>−3</sup>	1.948	2.127	1.840	2.030
$\mu$ , mm <sup>−1</sup>	1.893	4.592	1.801	4.435
<i>T</i> , K	100(2)	100(2)	100(2)	100(2)
$\lambda$ , Å	0.71073	0.71073	0.71073	0.71073
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0415	0.0551	0.0432	0.0801
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.0976	0.1308	0.0869	0.1600
<i>R</i> <sub>1</sub> (all data)	0.0644	0.0833	0.0591	0.1197
<i>wR</i> <sub>2</sub> (all data)	0.1066	0.1454	0.0927	0.1732
<i>R</i> <sub>int</sub>	0.0538	0.0779	0.0447	0.0651
GO <sub>F</sub>	0.979	0.951	1.073	1.138
<i>N</i> <sub>total</sub>	3971	4620	9979	4834
<i>N</i> <sub>ind</sub>	2394	2839	3609	2963
<i>N</i> <sub>obs</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	1738	1962	2957	2104
no. params.	202	215	202	202
$\Delta\rho_{\text{min,max}}$ (e Å <sup>−3</sup> )	0.660/−0.564	2.336/−1.023	0.538/−0.635	1.079/−0.930

<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

containing Schiff base (see Chart 1) and appropriate copper(II) salts, have 1:1 ligand/metal composition and are clearly different from those mentioned above. Indeed, the composition of these compounds is unaffected by the ligand/metal molar ratio used in synthesis procedure (1:1, 2:1, or 3:1), but for **1** and **2**, the best crystals for X-ray analysis were obtained when the 3:1 ratio was applied. The compounds are insoluble in commonly used solvents. Crystallographic data clearly indicate the 1D polymeric nature of the compounds where copper(II) ions are asymmetrically bridged by  $N^1,N^2$ -coordinated triazole ligand and  $\mu$ -hydroxide anion. The electroneutrality of the crystals is accomplished by one anion ( $\text{BF}_4^-$  in **1** and **2** or  $\text{NO}_3^-$  in **3** and **4**) molecule per Cu(II) ion.

**Description of the Structures of 1 and 2.** The structures of the isostructural complexes **1** and **2** consist of polymeric cationic  $[\text{Cu}(\mu\text{-OH})(\mu\text{-XPhtrz})]^+$  units. The polymeric structure of **1** is shown in Figure 1, together with the atom numbering scheme. Selected bond distances and angles are given in Table 2. The polymeric structure consists of two symmetry-unrelated copper(II) atoms Cu1 and Cu2. Both Cu atoms lie on inversion centers giving a linear chain of equally spaced copper(II) ions running along the *a* axis. Adjacent, essentially square planar copper(II) centers are bridged equatorially by the XPhtrz ligand and hydroxide. Additionally, each copper(II) forms much longer axial bonds with water molecules (2.539(3) and 2.547(5) Å for **1** and **2**, respectively) and with anions (2.590(3) and 2.620(5) Å for **1** and **2**, respectively). Therefore, the copper environment can be described as an elongated (4 + 2) octahedron. The unique feature of this interaction is its asymmetric character—two  $\text{BF}_4^-$  anions are bound to Cu1 whereas two molecules of water are bound to Cu2. As a result, the differentiation of the copper-oxygen(hydroxide) distances [1.941(3) and



**Figure 1.** View of the polymeric structure of **1** showing the atom-labeling scheme and 30% thermal ellipsoids. In the isomorphous structure of **2**, the chloride atom Cl1 is replaced by bromide atom Br1 (see Figure S1 in the Supporting Information).

1.925(3) Å for **1** and 1.945(4) and 1.924(4) Å for **2**] as well as of the related angles is observed. Similar differentiation is observed in the copper-nitrogen(triazole) distances [1.973(3) and 2.021(4) Å for **1** and 1.980(5) and 2.023(5) Å for **2**]. The most pronounced consequences of these are the values 22.6(4)° and 21.5(6)° for **1** and **2**, respectively, observed for torsion angle defined by Cu1–N1–N2–Cu2 atoms (Table 2). The values of Cu–N–N angles are slightly less than 120° reflecting the differences mentioned above (see Table 2).

The copper atoms in the polymer are separated by 3.364(1) Å for **1** and 3.377(1) Å for **2**, which is significantly longer than the 3.236 Å (average value) found in cyclic  $[\text{Cu}_6(\text{OH})_6(\text{admtz})_6(\text{H}_2\text{O})_5(\text{C}_2\text{H}_5\text{OH})_2](\text{ClO}_4)_6 \cdot 4\text{H}_2\text{O}$ .<sup>27</sup> These separations are close to that of 3.405 Å for Cu(II) ions linked

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **1–4**

	1	2	3	4
Cu1–O <sub>OH</sub>	1.940(3)	1.945(4)	1.923(2)	1.930(6)
Cu2–O <sub>OH</sub>	1.926(3)	1.924(4)	1.929(2)	1.934(6)
Cu1–N1	1.973(3)	1.980(5)	2.021(2)	2.020(8)
Cu2–N2	2.021(4)	2.023(5)	2.024(2)	2.020(7)
N1–N2	1.375(5)	1.379(7)	1.381(3)	1.380(3)
Cu1–Cu2	3.364(1)	3.377(1)	3.394(1)	3.406(2)
Cu1–F1	2.590(3)	2.620(5)		
Cu1–O <sub>w</sub>			2.525(2)	2.509(7)
Cu2–O <sub>w</sub>	2.539(3)	2.547(5)	2.436(2)	2.465(7)
Cu1–O <sub>OH</sub> –Cu2	121.0(1)	121.6(2)	123.6(1)	123.6(3)
Cu1–N1–N2	119.5(2)	119.3(4)	119.8(2)	120.9(6)
Cu2–N2–N1	117.9(2)	118.5(4)	119.5(2)	119.2(6)
N1–Cu1–O <sub>OH</sub>	88.0(1)	87.7(2)	87.9(1)	87.2(3)
N2–Cu2–O <sub>OH</sub>	88.5(1)	88.1(2)	87.5(1)	87.6(3)
O1–Cu1–N1 <sup>i</sup>	92.0(1)	92.3(2)	92.1(1)	92.8(3)
O1–Cu2–N2 <sup>ii</sup>	91.5(1)	91.9(2)	92.5(1)	92.4(3)
C8–N3–N4–C1	–39.0(6)	–41.2(9)	–10.3(4)	–10.0(2)
C9–N3–N4–C1	139.2(4)	139.6(6)	177.6(3)	178.7(9)
N3–N4–C1–C2	–179.6(4)	179.7(5)	178.0(2)	177.4(8)
N4–N3–C8–N1	178.2(4)	179.8(6)	–173.9(3)	–173.7(9)
N4–N3–C9–N2	–178.0(3)	180.0(5)	175.1(2)	174.1(8)
Cu1–N1–N2–Cu2	22.6(4)	21.5(6)	9.4(3)	6.8(9)

<sup>i</sup>  $-x + 1, -y + 1, -z$ . <sup>ii</sup>  $-x, -y + 1, -z$ .

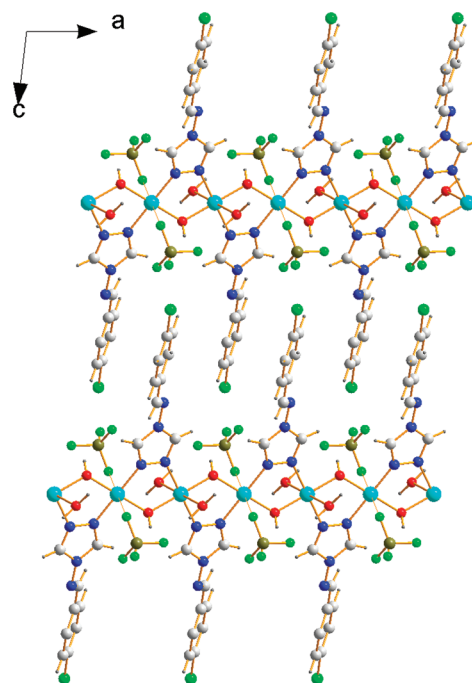
by a single  $\mu$ -N<sup>1</sup>,N<sup>2</sup>-1,2,4-triazole bridge and two  $\mu$ -chloride anions in the linear complex  $[\text{Cu}(\text{trz})\text{Cl}_2]_\infty$ <sup>28a</sup> and are shorter than the 3.521 and 3.490 Å found in the  $[\text{Cu}(\text{atrz})\text{Cl}_2]_\infty$ <sup>28b</sup> (where Htrz = 1,2,4-1H-triazole, atrz = 4-amino-1,2,4-4H-triazole).

The bond angles of Cu–O(H)–Cu of 121.0(1) and 121.6(2)° for **1** and **2**, respectively, are much larger than that found in the cyclic hexanuclear complex<sup>27</sup> (average value 114.9°). On the other hand, they are close to the angles found in dimeric copper(II) complexes with hydroxide and pyrazolato bridges: 123.9° in  $[\{\text{Cu}(\text{mepirazole})\text{Br}\}_2(\mu\text{-OH})(\mu\text{-pz})]$ <sup>44</sup> (mepirazole = 4-methoxy-2-(5-methoxy-3-methyl-1H-pyrazol-1-yl)-6-methylpyrimidine; pz = pyrazolate) and 121.3° in  $[\text{Cu}_2(\text{DBM})_2(\mu\text{-pz})(\mu\text{-OH})]$ <sup>45</sup> (DBM = dibenzoylmethanate).

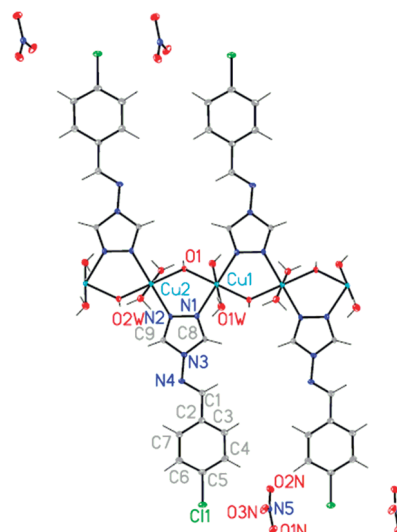
Generally, the distances between the copper(II) ions as well as Cu–O–Cu angles in **1** and **2** lie within the ranges observed in dimeric complexes with  $\mu$ -pyrazolato and  $\mu$ -methoxide bridges (3.359–3.401 Å and 118.9–125.6°, respectively<sup>44</sup>).

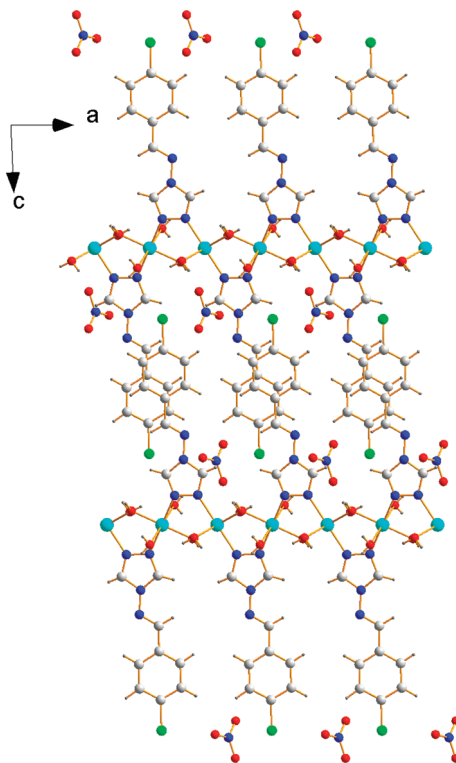
The bond distances of triazole ligands do not show significant deviations from those observed in similar compounds.<sup>53,54</sup> In **1** and **2**, the XPhtrz coordinates as a nonplanar ligand. The angles between planes defined by triazole ring and phenyl carbon atoms are 47.1(2) and 47.6(3)° for **1** and **2**, respectively (Figure 2). Phenyl ring stacking<sup>55</sup> along the *a* direction is observed (sym. *x*, *y*, *z* and 1 – *x*, –*y*, 1 – *z*) with distances 3.34 and 3.37 Å and offsets 1.60 and 1.56 Å, for **1** and **2**, respectively.

**Description of the Structures of 3 and 4.** The structures of the isostructural complexes **3** and **4**, as well as of complexes **1** and **2**, consist of polymeric cationic  $[\text{Cu}(\mu\text{-OH})(\mu\text{-XPhtrz})(\text{H}_2\text{O})_2]^+$  units arranged in polymeric chains



**Figure 2.** Packing diagram of **1** along the *b* axis. The color scheme is as follows: Cu, turquoise; N, blue; C, gray; O, red; B, olive; Cl/F, green.





**Figure 4.** Packing diagram of **3** along the *b* axis. The color scheme is as follows: Cu, turquoise; N, blue; C, gray; O, red; Cl, green.

**Table 3.** Hydrogen Bond Distances (Å) and Angles (deg) for **3**

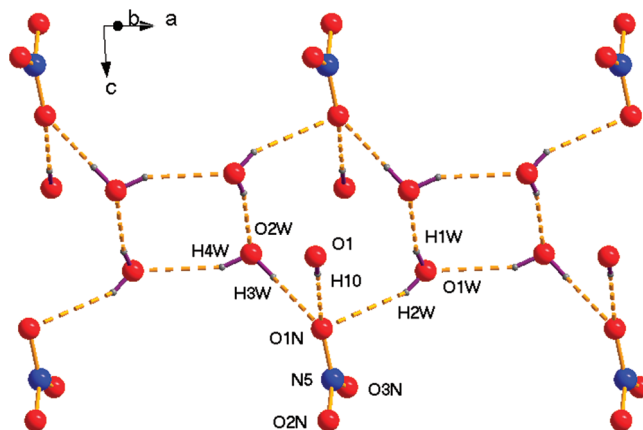
	D—H	H···A	D···A	<(DHA)
O1W—H1W···O2W <sup>i</sup>	0.72	2.04	2.743(3)	167
O1W—H2W···O1N <sup>ii</sup>	0.67	2.52	3.093(4)	145
O2W—H3W···O1N <sup>iii</sup>	0.76	2.03	2.756(3)	159
O2W—H4W···O1W <sup>iii</sup>	0.75	2.06	2.769(3)	158
O1—H10···O1N <sup>iv</sup>	0.82	2.11	2.929(3)	172

<sup>i</sup>  $-x, -y + 2, -z$ . <sup>ii</sup>  $-x + 1, -y + 1, -z + 1$ . <sup>iii</sup>  $x - 1, y, z$ . <sup>iv</sup>  $x - 1, y + 1, z - 1$ .

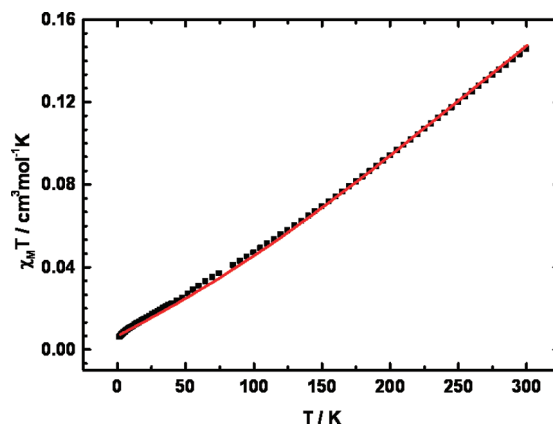
Similar environment of all copper(II) ions results in equal (within the error limit) distances Cu—N(triazole) (avg 2.022(2) Å for **3** and 2.020(7) Å for **4**) and Cu—O(hydroxide) (av. 1.926(2) Å for **3** and 1.932(6) Å for **4**). The Cu—O—Cu angles in both complexes are 123.6(3)°. The repercussions of a more regular geometry around copper(II) are smaller values of Cu—N1—N2—Cu torsion angles (9.4(3) and 6.8(9)° for **3** and **4**, respectively) when compared to those observed for **1** and **2** (see Table 2). On the other hand, the Cu—N—N angles are close to 120° and are similar to those observed for **1** and **2**.

The XPhtrz ligands are coordinated in an almost planar configuration and the angles between planes defined by triazole ring and phenyl carbon atoms are equal to 8.3(1) and 10.8(4)° for **3** and **4**, respectively (Figure 4). As a result, stacking of phenyl rings<sup>55</sup> along *b* direction (sym. *x*, *y*, *z* and  $1 - x, -y, 1 - z$ ) with distances 3.38 and 3.43 Å and offsets 1.36 and 1.31 Å (for **3** and **4**, respectively) is observed.

In crystals of **3**, the water molecules, hydroxide bridges, and nitrate ions are involved in formation of extended systems of hydrogen bonds. The water molecules are arranged in cyclic tetrameric clusters. Within the clusters,



**Figure 5.** Hydrogen bond scheme for **3**.



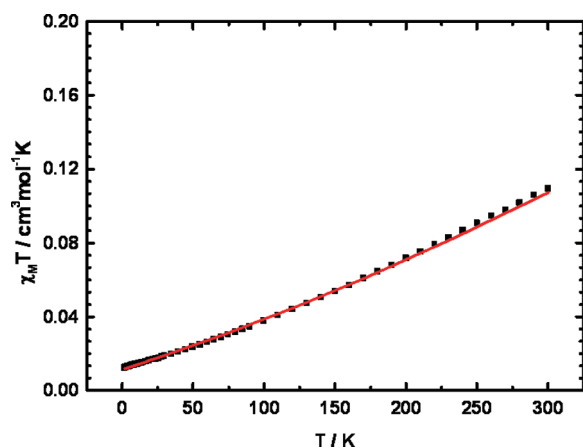
**Figure 6.** Plot of  $\chi_M T$  vs *T* for **1**. The red solid line was calculated using the best-fit parameters.

each water molecule acts both as a single hydrogen-bond donor and as a single hydrogen-bond acceptor and has another hydrogen atom oriented above or below the ring.<sup>56</sup> Four oxygen atoms of the water molecules are coplanar and suitable metric data are presented in Table 3. Some of the water clusters also forms hydrogen bonds with O1N oxygen atoms of nitrate anions. The same O1N atom is involved as an acceptor in hydrogen bond with bridging hydroxide group. The atoms mentioned above form tapes located between the coordination polymer chains (Figure 5).

Crystals of **3** and **4** are isomorphous, and the distances between oxygen atoms are similar suggesting that the hydrogen bond networks are almost identical in both (Figure S7 and Table S1).

**Magnetic Properties.** The magnetic susceptibility studies were carried out over the temperature range 2.0–300 K. The magnetic behavior of **1** and **4** is shown in Figures 6 and 7, respectively, in the form of  $\chi_M T$  vs *T* plots. The room-temperature values of  $\chi_M T$  are 0.141, 0.142, 0.173, and 0.106 cm<sup>3</sup> K/mol (1.06, 1.07, 1.18, and 0.92  $\mu_B$ ) for **1–4**, respectively. They decrease upon temperature lowering to reach values of 0.0062, 0.0064, 0.0246, and 0.012 cm<sup>3</sup> K mol<sup>−1</sup> (0.22, 0.23, 0.24, and 0.31  $\mu_B$ ) at 2.0 K indicating strong

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**Figure 7.** Plot of the  $\chi_M T$  vs  $T$  for **4**. The red solid line was calculated using the best-fit parameters.

antiferromagnetic interactions between the metal centers. Because well-isolated copper(II) chains are the dominant magnetic units in the compounds under investigations, the magnetic susceptibility of **1–4** may be treated in terms of eq 1 derived by Bonner and Fisher for a uniform  $S = 1/2$  infinite chain model:<sup>57</sup>

$$\chi' = \left( \frac{Ng^2\beta^2}{kT} \right) \left( \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \right) \quad (1)$$

in which  $x = |J|/kT$ .  $J$  is the isotropic interaction parameter occurring in the spin Hamiltonian  $\mathbf{H} = -J(\sum \mathbf{S}_i \cdot \mathbf{S}_{i+1})$ .

In eq 1,  $N$ ,  $g$ ,  $\beta$ ,  $k$ , and  $T$  have their usual meanings. However, taking into account the possible chain breaking which may introduce some unlinked copper ions and/or short odd-numbered chains, the experimental  $\chi T$  of **1–4** is actually fitted by eq 2 in which  $p$  is the percentage of paramagnetic ions.

$$\chi = (1 - p)\chi' + \frac{Ng^2\beta^2}{4kT}p \quad (2)$$

The  $g$  values found from EPR were used ( $g_{\text{average}} = 2.15$ ). The best-fit parameters are the following:  $J = -419(1) \text{ cm}^{-1}$ ,  $p = 1.2(2)\%$ ,  $R = 2.19 \times 10^{-4}$  for **1**;  $J = -412(2) \text{ cm}^{-1}$ ,  $p = 1.2(2)\%$ ,  $R = 2.7 \times 10^{-4}$  for **2**;  $J = -391(3) \text{ cm}^{-1}$ ,  $p = 3.9(1)\%$ ,  $R = 1.6 \times 10^{-3}$  for **3**; and  $J = -608(3) \text{ cm}^{-1}$ ,  $p = 2.00(1)\%$ ,  $R = 3.7 \times 10^{-4}$  for **4** (where agreement factor  $R = \Sigma[(\chi T)_{\text{exp}} - (\chi T)_{\text{calc}}]^2 / \Sigma(\chi T)_{\text{exp}}^2$ ).

**EPR Spectra.** “Infinite” chains of strongly antiferromagnetically coupled copper ions chains are not expected to exhibit EPR, and thus, the extremely weak spectra, particularly for compounds **1** and **2**, that could only be observed at low temperatures, are most likely due to short odd-membered chains mentioned above. No zero-field splitting effects were observed and the spectra were characteristic for spin  $1/2$  with no resolved hyperfine structure. If the spectra were due to “monomers” diluted in polynuclear complexes which are essentially diamagnetic at low temperatures then copper hyperfine structure should be observed. The  $g_z$  values were

within a narrow range 2.31–2.32 and the  $g_{x,y}$  values were 2.06–2.07. In **1**, the equatorial planes  $\text{N}_2\text{O}_2$  of Cu1 and Cu2 are tilted versus each other by only  $14.4^\circ$ , and thus, the observed  $g$  values should be close to the monomer  $g$ . The  $g$  magnitudes for Cu1 and Cu2 are expected to be similar because they are typically not strongly affected by axial coordination of copper. The corresponding tilt angles are  $14.3^\circ$ ,  $10.7^\circ$ , and  $11.1^\circ$  in **2**, **3**, and **4**, respectively.

It is well-known that the magnitude and nature of the interaction in bis(hydroxide) dinuclear copper(II) complexes depends on the Cu–O–Cu angle.<sup>38–41,58</sup> Antiferromagnetic interaction was observed for angles above  $97.5^\circ$  with ferromagnetic coupling at smaller angles. Moreover, the antiferromagnetic coupling increases with increasing angle. This correlation is obeyed in the case of the symmetrical, planar copper(II) dimers bridged by two hydroxides. The Cu–O–Cu angles exceeding  $120^\circ$ , as found in complexes **1–4** are observed in systems where one of the two bridging ligands is a hydroxide group and the other a different bridging ligand.<sup>42–46</sup> On the other hand, similar empirical magnetostructural correlation has been found in dicopper complexes doubly bridged by symmetrically substituted 1,2,4-triazole.<sup>17b,59</sup> The Cu–N<sub>trz</sub>–N<sub>trz</sub> angles of ca.  $135^\circ$  in the systems lead to the largest possible coupling with  $J$  about  $-240 \text{ cm}^{-1}$ . The largest  $J$  value ( $-236 \text{ cm}^{-1}$ ) has been observed for  $[\text{Cu}_2(\text{bpt})_2(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_2]^{18}$  (bptH = 3,5-bis(pyridin-2-yl)-1H-1,2,4-triazole), and only slightly lower values have been detected for 4-substituted triazoles in  $[\text{Cu}(\text{aamt})\text{Br}(\text{H}_2\text{O})]_2\text{Br}_2(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})^{19}$  (aamt = 4-amino-3,5-bis(aminomethyl)-4H-1,2,4-triazole) ( $J = -220 \text{ cm}^{-1}$ ) and in  $\text{Cu}_2(\text{ibdpt})_2(\text{ClO}_4)_4(\text{MeCN})^{20}$  (ibdpt = 4-isobutyl-3,5-di(2-pyridyl)-4H-1,2,4-triazole) ( $J = -210 \text{ cm}^{-1}$ ). The asymmetric bridging mode (Cu1–N1–N2  $\approx 125^\circ$ , Cu2–N2–N1  $\approx 140^\circ$ ), observed in  $[\text{Cu}_2(\text{pt})_2(\text{SO}_4)(\text{H}_2\text{O})_3] \cdot (\text{H}_2\text{O})_3^{17b}$  (ptH = 3-pyridin-2-yl-1H-1,2,4-triazole)] reduces the interaction by about one-half ( $J = -98 \text{ cm}^{-1}$ ).

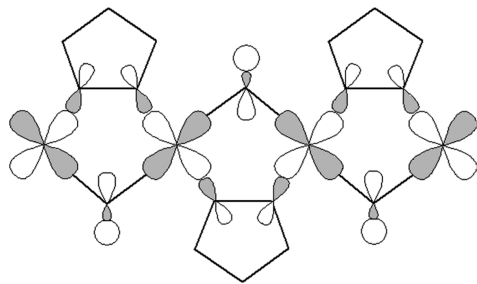
Less ambiguous magnetostructural correlation can be made when two copper(II) ions are bridged by single triazole and a second, different ligand. In the dimeric compound  $[\text{Cu}_2(\mu\text{-abpt})(\mu\text{-SO}_4)(\text{SO}_4)(\text{H}_2\text{O})_4](\text{H}_2\text{O})^{30}$  (abpt = 4-amino-3,5-bis(pyridine-2-yl)-1H-1,2,4-triazole) the copper(II) ions are linked in the equatorial plane by an  $N^1, N^2$ -bridging chelating abpt ligand (with Cu1–N1–N2 and Cu2–N2–N1 angles equal to  $136.6$  and  $138.3^\circ$ , respectively) and a bidentate bridging sulfate anion. The magnetic data for this complex yield  $J = -69 \text{ cm}^{-1}$ . However, for linear, trinuclear compound  $[\text{Cu}_3(\text{atr})_2(\text{N}_3)_6]^{13a}$  where besides the  $N^1, N^2$  bridges from triazole ligands the  $\text{N}_3^-$  bridging anions are present, the copper(II) ions are strongly antiferromagnetically coupled with  $J = -217.6 \text{ cm}^{-1}$ . In the latter complex, the atr ligands bridge copper(II) ions in asymmetrical mode with

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**Figure 8.** Orbital models for the  $\mu$ -OH and  $\mu$ -triazole bridging in 1D polymeric systems.

$\text{Cu}-\text{N}_{\text{trz}}-\text{N}_{\text{trz}}$  angles at central Cu atom equal to  $119.3^\circ$  and at external Cu atoms equal to  $123.4^\circ$ , markedly smaller than optimal value  $135^\circ$ .

The above magnetostructural correlations could be used to rationalize the magnetic properties of **1–4** on the basis of simple orbital symmetry considerations (Figure 8). Additionally, the fact that the magnitude of the antiferromagnetic coupling  $J$  is proportional to the overlap integral between the magnetic orbitals must be taken into account. The unpaired electron of each copper(II) ion is located in the  $d_{x^2-y^2}$  orbital, which is situated in the plane of the equatorially coordinated triazole and  $\text{OH}^-$  bridges (N1 and N1A from triazole molecules, O1 and O1A from hydroxide groups [sym  $A = -x + 1, -y + 1, -z$ ] and Cu1 are located in the plane). Because the  $x$  and  $y$  axes are generally aligned with the copper-ligand bonds and the angles between the planes are equal to  $14.4$  and  $14.3^\circ$  for **1** and **2**, respectively ( $10.7^\circ$  and  $11.1^\circ$  for **3** and **4**, respectively), the magnetic orbitals have strong sigma overlap. Thus, the magnetic interactions transferred by the bridging hydroxide and bridging  $N^1,N^2$ -triazole ligands are indeed expected to be strongly antiferromagnetic.

Escriva et al.<sup>44</sup> have performed theoretical calculations to explain the strong antiferromagnetic interaction ( $J = -770 \text{ cm}^{-1}$ ) observed in dimeric  $[\{\text{Cu}(\text{mepirizole})\text{Br}\}_2(\mu\text{-OH})(\mu\text{-pz})]$ . It is noteworthy that this compound has very similar structural parameters ( $\text{Cu}\cdots\text{Cu}$   $3.378 \text{ \AA}$ ,  $\text{Cu}-\text{O}-\text{Cu}$   $123.9^\circ$ ,  $\text{Cu}-\text{N}-\text{N}$   $120.6^\circ$  and  $120.8^\circ$ ) to those found in polymers investigated by us (see Table 2). They have examined three models: In models 1 and 2 the hydroxide or pyrazolate is the only bridging ligand, respectively. In model 3, the hydroxide and pyrazolate ligand are both present. When only the hydroxide anion bridges two copper(II) ions (model 1), the calculated  $J$  value is  $-215 \text{ cm}^{-1}$ . For the single pyrazolate bridge (model 2), the calculated  $J$  value is equal to  $-71 \text{ cm}^{-1}$ . Because the  $J$  values for models 1 and 2 carry the same sign, the dimer  $[\{\text{Cu}(\text{mepirizole})\text{Br}\}_2(\mu\text{-OH})(\mu\text{-pz})]$  can be treated as an orbital *complementary* case where two antiferromagnetic interactions add constructively to provide a significantly

stronger one. This conclusion arises directly from calculations accomplished for model 3, for which  $J = -440 \text{ cm}^{-1}$ .

The antiferromagnetic exchange integrals observed for coordination polymers **1** and **2** fit in very well with that calculated for model 3 presented above. The discrepancy between  $J$  calculated for a markedly simplified model and the values observed for compounds **3** and **4** ( $J = -391$  and  $-608 \text{ cm}^{-1}$ , respectively) can be explained by the fact that  $J$  depends on the relative position of hydrogen of the hydroxide group.<sup>39,40,60</sup> On the other hand, the presence of the  $\text{NO}_3^-$  ions affects the ligand configuration (torquing and planarity) as well as the OH bridge geometry (hydrogen atom deviation from the  $\text{Cu}\cdots\text{O}\cdots\text{Cu}$  plane). It appears that the main factor deciding about the  $J$  magnitude in nitrate-containing complexes is the C–X bond polarizability ( $X = \text{Cl}, \text{Br}$ ) resulting from the presence of the nitrate anion at a short distance from X. That effect is possible thanks to planar conformation of the triazole ligand. In the case of  $\text{BF}_4^-$ , the ligand is tilted and cannot interact with C–X resulting in much smaller C–X bond polarization.

## Conclusions

The syntheses, structures, and magnetic properties of four polynuclear copper(II) complexes with derivatives of Schiff base containing 1,2,4-triazole ligands have been presented. All complexes exhibit linear chain 1D structures with unique asymmetric  $\mu$ -hydroxide and  $\mu$ - $N^1,N^2$ -triazole bridges whereas the ligand configuration (torqued in **1** and **2** or planar in **3** and **4**) is affected by the anion used ( $\text{BF}_4^-$  or  $\text{NO}_3^-$ , respectively). The magnetic susceptibility data show strong antiferromagnetic exchange in **1–4**, as expected from their structures. The exchange interactions are discussed in terms of *complementarity/countercomplementarity* of the two competing bridges.

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**Supporting Information Available:** Crystallographic files in CIF format for compounds **1–4**, Figures S1–S4 showing the atom labeling scheme and crystal packing for compounds **2** and **4**, Figures S5 and S6 showing magnetic behavior for compounds **2** and **3** (in the form of  $\chi_M T$  vs  $T$  plots), Figure S7 showing the scheme of  $\text{O}\cdots\text{O}$  interactions in **4**, and Table S1 containing  $\text{O}\cdots\text{O}$  distances in **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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