New Mononuclear Cu(II) Complexes and 1D Chains with 4-Amino-4H-1,2,4-triazole

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Abstract: The crystal structures of two mononuclear Cu(II) NH2trz complexes [Cu(NH2trz)4(H2O)](AsF6)2 (I) and [Cu(NH2trz)4(H2O)](PF6)2 (II) as well as two coordination polymers [Cu(μ2-NH2trz)2Cl]Cl·H2O (III) and [Cu(μ2-NH2trz)2Cl](SiF6)0.5·1.5H2O (IV) are presented. Cationic 1D chains with bridging bis-monodentate μ2-coordinated NH2trz and bridging μ2-coordinated chloride ligands are present in III and IV. In these coordination polymers, the Cu(II) ions are strongly antiferromagnetically coupled with $J = -128.4$ cm$^{-1}$ for III and $J = -143$ cm$^{-1}$ for IV ($H = -\sum S_i S_{i+1}$), due to the nature of the bridges between spin centers. Inter-chain interactions present in the crystal structures were taken into consideration, as well as $g$ factors, which were determined experimentally, for the quantitative modeling of their magnetic properties.

Keywords: coordination polymers; copper; 1,2,4-triazole; magnetic properties; crystal engineering
1. Introduction

There is constant interest in 1,2,4-triazoles and their derivatives, which are known as useful drugs thanks to their outstanding biological activities being used as, antifungal agents [1], plant protection fungicides [2], etc. On the other hand, 1,2,4-triazoles are also synthesized for other purposes, for instance in coordination chemistry as metal-azolate frameworks [3], or azole coordination polymers [4,5]. A variety of coordination networks can be designed thanks to the various coordination modes of 1,2,4-triazole-containing building blocks [4]. In particular, numerous oligonuclear and polymeric Cu(II) complexes have been reported with 4-amino-4H-1,2,4-triazole (NH$_2$trz) [6–17], presumably because it contains a primary –NH$_2$ group, which might be further used to functionalize the obtained products. In particular, a few examples of 1D chains were proposed as structural models of the corresponding Fe(II) complexes, which are known to present exceptional spin transition behavior, sometimes occurring around room temperature [18–20]. This includes [Cu(μ$_2$-NH$_2$trz)$_3$](BF$_4$)$_2$H$_2$O [21], [Cu(μ$_2$-NH$_2$trz)$_3$](BF$_4$)(SiF$_6$)$_{0.5}$·2H$_2$O [21], [Cu(μ$_2$-NH$_2$trz)$_3$]SiF$_6$·H$_2$O [21], [Cu(μ$_2$-NH$_2$trz)$_3$](NO$_3$)$_2$·2H$_2$O [18] and [Cu(μ$_2$-NH$_2$trz)$_3$]ZrF$_6$·2H$_2$O [22], which all exhibit a polymeric structure where Cu(II) atoms are linked in a 1D chain by the bridging bis-monodentate nitrogen atoms of the 1,2,4-triazole cycles. Interestingly, only two mononuclear Cu(II) NH$_2$trz complexes [23,24] are known. Following our continuing interest on the magnetic properties of these systems, we report on the synthesis and crystal structures of two new mononuclear Cu(II) complexes [Cu(NH$_2$trz)$_4$(H$_2$O)](AsF$_6$)$_2$ (I) and [Cu(NH$_2$trz)$_4$(H$_2$O)](PF$_6$)$_2$ (II). We also present the crystal structures and magnetic properties of two 1D chains [Cu(μ$_2$-NH$_2$trz)$_2$Cl]Cl·H$_2$O (III) and [Cu(μ$_2$-NH$_2$trz)$_2$Cl](SiF$_6$)$_{0.5}$·1.5H$_2$O (IV) whose magnetic properties were studied quantitatively. We also detail the synthesis of a new bis-triazole molecule: N,N'-bis-(1,2,4-triazole-4-yl)formamidine hydrochloride (L·HCl) and describe its crystal structure.

2. Results and Discussion

2.1. Synthesis

Two synthetic pathways were followed. Path A is classic with the reaction of [Cu(H$_2$O)$_6$](AsF$_6$)$_2$ or a mixture of Cu(CH$_3$COO)$_2$ H$_2$O and (NH$_4$)$_2$CuCl$_4$ 2H$_2$O, with NH$_2$trz in aqueous MeOH, leading to complexes I and III, respectively. Path B is more original. It requires first the synthesis of the formamidine L·HCl which was obtained by reacting NH$_2$trz with NaN$_3$ and HC(OEt)$_3$ in AcOH in an attempt to get the corresponding triazole-tetrazole molecule. The elemental analysis data suggest the resulting product to be a hydrochloride salt of a novel molecule (Scheme 1). Its $^1$H NMR spectrum recorded in DMSO-$d_6$ contains two singlet signals at 8.65 and 8.83 ppm, corresponding to the formamidine and triazole CH protons, respectively.
During our attempts to react Cu(II) salts with L·HCl, not surprisingly we noticed that this molecule was hydrolyzed in aqueous solution, and proves to be effective to slowly release NH₂trz and obtain crystals of Cu(II) complexes II–IV. It should be noted that the formulation of complex IV is rather unusual. In addition to the L·HCl hydrolysis, SiF₆²⁻ anions were identified. These anions are actually generated in situ by the reaction of BF₄⁻ anions (provided by the Cu(II) salt) with the glass of the H-tube used to grow crystals of the complex [21]. Furthermore, since L·HCl was introduced as a hydrochloride salt, complex IV contains Cl⁻ ions, which were provided by the ligand. This might be also true for III although CuCl₂ 2H₂O was used as a source of Cu(II) ions.

2.2. IR and Diffuse Reflectance Spectroscopy

IR spectra of I–IV each contain a band at about 1630 cm⁻¹, corresponding to the amide band of the NH₂ group (Figure S1). The spectra of I and II also exhibit an absorption band for the CuOH fragment at around 1000 cm⁻¹. There are also bands for the CH, NH₂ and H₂O groups in the range from 3000 to 3700 cm⁻¹. Additionally, the IR spectra of I, II and IV contain intense broad bands at about 740–800 cm⁻¹, arising from AsF₆⁻, PF₆⁻ and SiF₆²⁻ anions, respectively (Figure S1). Diffuse reflectance -spectra of I–IV exhibit two broad bands in the range 400–900 nm corresponding to d-d transitions (Figure S2). A band from 200 to 400 nm has been attributed to the intraligand NH₂trz transitions. It should be noted that the IR and diffuse reflectance spectra of I and II are almost identical (Figures S1 and S2), testifying to isomorphous structures of these two complexes, as was also concluded from X-ray diffraction (see next Section).

2.3. Structural Aspects

Recrystallization of L·HCl from an aqueous acetone solution leads to the formation of X-ray suitable crystals of L, which structure was initially solved and refined in the triclinic space group P1, and finally transformed to the monoclinic space group Cc. The molecular structure of L is shown in Figure 1. Table S1 in Supplementary Information contains the bond and angle values for L. The structure of L is stabilized by an intermolecular N–H···N hydrogen bonds between the NH hydrogen atom of the formamidine fragment and the triazole nitrogen atom of a neighboring molecule (Table S2 in Supplementary Information). As a result, the formation of 1D polymeric chains is observed in the structure of L.

Scheme 1. Synthesis of N,N'-bis-(1,2,4-triazole-4-yl)formamidine hydrochloride.
Figure 1. Thermal ellipsoid (50%) plot of L along the $a$-axis. The nitrogen and carbon atoms are depicted in blue and grey, respectively. H-atoms were omitted for clarity.

Complexes I–IV were obtained as X-ray suitable blue crystals by slow evaporation of a solvent from their solutions. It should be noted that several crystals of each complex have been checked by a single crystal X-ray analysis, indicating their full identity. Both complexes I and II crystallize in the tetragonal space group $I4_1/a$ and are isomorphous. Therefore, only the crystal structure of complex II will be described. Complexes III and IV crystallize in the monoclinic space group $P2_1/a$ and triclinic space group $P\overline{1}$, respectively, and each exhibit 1D cationic Cu(II) containing polymeric chains. The molecular structures of II and III are shown in Figure 2.

Figure 2. Thermal ellipsoid (50%) plot of II (left) and III (right). H-atoms and PF$_6^-$ anions in II, and non-coordinated Cl$^-$ anions and water molecules in III were omitted for clarity. The nitrogen atoms are depicted in blue, the carbon atoms in grey, the chloride ions in green and the copper atoms in red.

The discrete mononuclear complex II exhibits a distorted square pyramidal coordination polyhedron (Figure 2). In the basal plane, the Cu(II) atom is coordinated by four nitrogen atoms arising from four different NH$_2$trz ligands, while the apical position is occupied by a water oxygen atom (Figure 2). The Cu(II) atom in II is almost in the basal plane of the square pyramid and only slightly deviated above the plane (0.1890(4) Å). This is a surprising feature as in square pyramidal complexes the metal atom is usually located significantly above the basal plane [25]. This feature can be explained by the Cu⋯F interaction between the metal center and one of the fluorine atoms of the PF$_6^-$ anion noted in II. Indeed, since the fluorine atom is located below the basal plane, it tends to drag the Cu(II) atom towards the bottom of the pyramid. The average Cu–N bond length is about 2.0 Å.
(Table S3 in Supplementary Information). The Cu–O bond length is 2.263(3) Å. The N–Cu–N bond angles formed by the nitrogen atoms, corresponding to the NH$_2$trz ligands coordinated in a cis-arrangement are close to 90°, while the N–Cu–N bond angles formed by the nitrogen atoms in trans-position are about 170° (Table S3 in Supplementary Information). The N–Cu–O bond angles are about 95° (Table S3 in Supplementary Information).

Complexes III and IV each consist of 1D cationic Cu(II)-containing polymeric chains (Figures 2 and 3). The asymmetric unit of IV contains two non-equivalent Cu(II) atoms. Cu···Cu separations (~3.60–3.65 Å) in both complexes exceed the sum of van der Waals radii of Cu(II) which indicates the absence of any distinct intramolecular Cu···Cu interactions. Each metal center in III and IV is coordinated by two chlorine atoms in trans-configuration and by four nitrogen atoms arising from four different NH$_2$trz ligands (Figure 3). As a result, the formation of the distorted coordination octahedron is observed for both polymeric complexes. It should be highlighted that the structures of III and IV are unusual, with only one bridging μ$_2$-coordinated chloride ligand linking two neighboring Cu(II) atoms in a polymeric chain, because incorporation of chlorine into the coordination sphere of a transition metal in the triazole chains is known to result in triple bridges containing two μ$_2$-coordinated chloride ligands [4]. The latter situation is encountered in the crystal structure of [Cu(Htrz)Cl$_2$] (Htrz = 4H-1,2,4-triazole) [26], which was the first one for a triazole complex elucidated by single crystal X-ray analysis, and in the related chain of [Cu(μ$_2$-NH$_2$trz)(μ$_2$-Cl)$_2$] [10]. Thus, depending on the synthesis conditions, it is possible to obtain one or two μ$_2$-coordinated chloride ligands in the triple bridge, giving rise to charged or neutral chains, respectively.

**Figure 3.** Thermal ellipsoid (50%) plot of III along the a (top) and c axes (bottom). The nitrogen atoms are depicted in blue, the carbon atoms in grey, the chloride ions in green and the copper atoms in red. H-atoms were omitted for clarity.
The Cu–N bond lengths in III and IV are similar to those found in the crystal structures of I and II, being about 2.0 Å (Tables S4 and S5 in Supplementary Information). The Cu–Cl bond lengths in III are about 2.69–2.78 Å (Table S4 in Supplementary Information), while the same bond lengths in IV are slightly shortened, about 2.65–2.72 Å (Table S5 in Supplementary Information). Thus, the equatorial positions on the octahedron are occupied by nitrogen atoms, while the chlorine atoms are in apical positions. Each coordinated Cl\(^-\) anion exhibits a bridging μ\(_2\)-coordination mode, while NH\(_2\)trz ligands exhibit a bridging bis-monodentate μ\(_2\)-N\(_1\),N\(_2\)-coordination mode, linking two neighboring Cu(II) atoms (Figure 2). The N–Cu–N bond angles in each coordination octahedron of III and IV, formed by nitrogen atoms of the NH\(_2\)trz ligands coordinated in a cis-arrangement, are similar to those observed for I and II and are about 90°. The N–Cu–N bond angles formed by the nitrogen atoms in trans-position are significantly enlarged, 178–180° (Tables S4 and S5 in Supplementary Information). The N–Cu–Cl bond angles are in the range 85–95° both in III and IV (Tables S4 and S5 in Supplementary Information). The Cl–Cu–Cl bond angles are almost straight, 178–180°. The Cu–N–N bond angles defined by the Cu(II) atoms with NH\(_2\)trz ligands are 122–124°, while the Cu–Cl–Cu bond angles are about 84° in both polymeric complexes (Tables S4 and S5 in Supplementary Information). The Cu(II) atoms are located almost in the same plane with the triazole rings. There are two distinguishable octahedron orientations along the polymeric chains resulting in alternate ababa... order. Depending on the presence of intrachain ligand interactions, both ababa... [18,21,22] and abcbab... [27] order may be found in Cu(II) chains with triple μ\(_2\)-N\(_1\),N\(_2\)-triazole bridges. In complexes, III and IV, the lack of direct intrachain ligand···ligand interactions, leads to the more regular ababa... order. It should be noted, that the angles between the planes formed by the triazole fragments coordinated to two Cu(II) atoms within a chain in III and IV are 74.23(13) and 66.55(12)°, respectively. This is considerably higher compared to Cu(II) μ\(_2\)-N\(_1\),N\(_2\)-1,2,4-triazole chain complexes (e.g., 50.9(2)° for [Cu(μ\(_2\)-NH\(_2\)trz)]ZrF\(_6\) H\(_2\)O [21]). The supramolecular aggregation in the structure of II consists of head-to-tail double sheets of mononuclear building units (Figure 4). Counter anions are located between double sheets, which are linked by a dense hydrogen bonding network involving amino groups of NH\(_2\)trz and the PF\(_6\)^- anions (Table S2 in Supplementary Information). Each amine group is hydrogen bonded to two counter anions and one neighboring amine group. The hydrogen bonding between amine groups links mononuclear complexes of the same sheet (Figure 4). Each counter anion forms N–H···F hydrogen bonds with several mononuclear species, generating links between complexes of the same sheet and complexes corresponding to different double planes. Although the hydrogen atoms of coordinated H\(_2\)O were not located, interatomic distances between oxygen atoms of the water molecules of the sheet and the lone pair of the amine groups, corresponding to a further sheet of the same double plane, indicate the possible existence of hydrogen bonding between these ligands (predicted by the Mercury [28] software). Such hydrogen bonding was proposed by Yi et al. [24] to explain the double sheet structure.
Figure 4. Thermal ellipsoid (50%) plot of II along the b axis. The nitrogen atoms are depicted in blue, the carbon atoms in grey, the fluoride atoms in green, copper atoms in red and the phosphorus atoms in orange. H-atoms were omitted for clarity.

The crystal packing in III and IV is made of parallel Cu(II) chains, between which non-coordinated counter anions and water molecules are located (Figures 3 and 5). The Cu···Cu distances in III are 3.6532(16) Å, while the same separations in IV are insignificantly shortened to 3.5994(16) and 3.6106(16) Å (Table 1), which was expected since no change of the first coordination sphere is noticed between III and IV. These values are about 0.08–0.14 Å longer than those for the similar Cu(II) chains, containing μ2-O or μ2-N bridging atoms, [11–13] but significantly shorter than the Cu···Cu distances in the Cu(II) chains with three μ2-1,2,4-triazole derivatives [27,29]. A shorter Cu···Cu distance of 3.40 Å is found when only one μ2-N₁,N₂-1,2,4-triazole is bridging as observed for [Cu(Htrz)Cl₂] [26]. The dihedral angles, formed by the μ2-NH₂trz ligands linking two neighboring Cu(II) atoms, are about 5° and 12° in III. The former angle in IV is significantly reduced and of 0–2°, while the latter angle is very similar, 12–14°. These values are in a range characteristic for similar Cu(II) chains [12–14]. However, incorporation of the third μ2-1,2,4-triazole derivative into the Cu(II) chain leads to a significant increase of the third dihedral angle, which might be explained by steric demands [27,29].

The presence of the amine groups, chloride ions and water molecules favors hydrogen bonding (Table S2 in Supplementary Information). Each chain is linked to a further two chains by the N–H···Cl(coordinated) and N–H···Cl(non-coordinated) ···H–N hydrogen bonding. Moreover, the N–H···Cl···H–O···Cl···H–N hydrogen bonds create connections to four neighboring chains. Thus, each chain is hydrogen bonded to six others in the structure of III. The crystal packing of IV consists of a dense hydrogen bonding network, which links neighboring chains (Table S2 in Supplementary Information). Parallel chains are linked by the multiples N–H···Cl and N–H···N hydrogen bonds. The N–H···O···F–Si–F···H–N hydrogen bonds connect the NH₂trz ligands throughout the whole network. Finally, rows of the SiF₆²⁻ anions are bound by F···H–O···H···F hydrogen bonding. As a result of dense hydrogen bonding network is observed.

In III, voids between metal-containing chains are occupied by water-chloride {Cl(H₂O)}ₙ supramolecular chains propagated by hydrogen bonds in a meander-like manner (Figure 6, Table S2 in Supplementary Information). These clusters are connected to cationic chains through hydrogen bonds formed between non-coordinated chloride ions and one of the NH₂ hydrogen atoms of the NH₂trz ligands (marked by red dash lines in Figure 6, Table S2 in Supplementary Information). Similar
structural arrangements of the water-chloride clusters, but in a pure zigzag manner, were observed for Co(II) and Pd(II) complexes [30,31].

Table 1. Overview of structural characteristics and magnetic data for 1D Cu(II) chains with 1,2,4-triazole ligands.

| Complex | \(d(\text{Cu}^{2+}-\text{Cu})\) (Å) | \(\angle(\text{Cu–N–N–Cu})\) (°) | \(g\) (cm\(^{-1}\)) | \(P\) (%) | \(\chi_T \times 10^6\) (cm\(^3\) mol\(^{-1}\)) | \(zJ/kB\) (cm\(^{-1}\)) | Ref. |
|---------|---------------------------------|---------------------------------|----------------|----------|---------------------------------|----------------|------|
| [Cu(\(\mu_2\)-Htrz)(\(\mu_2\)-Cl)]\(_2\) | 3.405 | -4.67 | 2.013 | -12.4 | - | - | [26,32] |
| [Cu(\(\mu_2\)-NH\textsubscript{2}trz)](\(\mu_2\)-Cl)]\(_2\) | 3.489(5), 8.7(2) | 2.26 | -20.4 | - | - | - | [10,32] |
| [Cu(\(\mu_2\)-NH\textsubscript{2}trz)\(_2\)Cl] | 3.653(2) | 5.2(3), 11.7(2) | 2.13 | -128.4 | 0.65 | 390 | 11(5) | This work |
| [Cu(\(\mu_2\)-NH\textsubscript{2}trz)\(_2\)Cl] | 3.599(2), 1.5(5), 13.9(4) | 2.13 | -143.0 | 1.02 | 270 | 80(4) | This work |
| (SiF\textsubscript{4})\(_6\)-1.5H\textsubscript{2}O (IV) | 3.611(2) | 0.6(5), 11.5(4) | 2.13 | -139.9 | 0.90 | 350 | 0 | work |
| [Cu(\(\mu_2\)-NH\textsubscript{2}trz)] | 3.503(8) | -7.8(4), -13.0(4) | 2.22(1) | -17.7 | - | - | - | [11] |
| [Cu(\(\mu_2\)-NH\textsubscript{2}trz)\(_2\)] | 3.470(2) | 1.5(6), 2.0(5) | 2.21 | -51 | - | - | - | [12] |
| (\(\mu_2\)-N\(_3\)-N\(_3\))NO\(_3\) | 3.5035(8) | -7.8(4), -13.0(4) | 2.22(1) | -51 | - | - | - | [11] |
| [Cu(\(\mu_2\)-NH\textsubscript{2}trz)\(_2\)] | 3.5301(5) | -11.4(3), -13.8(3) | 2.12 | -75.1 | - | - | -1.1 | [11] |
| (\(\mu_2\)-NO\(_3\))NO\(_3\) | 3.532(2), 8.4(7), 10.7(9), 37.5(7) | 2.03(1) | -1.1(2) | - | - | - | [27] |
| (\(\mu_2\)-hydroxyethytrz)]\(_3\) | 3.829(2), 3.0(7), -11.5(8), -38.0(6) | 2.20(1) | 1.45(3) | - | - | - | [29] |
| (CF\textsubscript{3}SO\textsubscript{3})\(_2\)-H\textsubscript{2}O | 3.8842(4), 33.2(2), -16.3(2), 28.98(19), -11.3(2), -13.8(2), -20.2(2) | 2.20(1) | 1.45(3) | - | - | - | [29] |

\(^a\) Dihedral angles must be compared by their magnitudes; \(^b\) hyetrz = 4-(2'-hydroxyethyl)-1,2,4-triazole.

2.4. Magnetic Properties

Since no cooperative magnetism was expected for the mononuclear complexes I and II, magnetic properties were only investigated for polymeric complexes III and IV. Electron Paramagnetic Resonance (EPR) spectroscopy at X-band was used to determine the Lande g-factors that were thereafter used for a quantitative analysis of the magnetic properties. Room temperature X-band EPR spectra from powdered samples of III and IV are shown in Figure 7. The spectra consist of broad derivative-like signals with widths of \(\Delta H_{pp} = 350\) and 245 G for III and IV, respectively. Both complexes are characterized by a g value of 2.13.
**Figure 5.** Thermal ellipsoid (50%) plot of IV along the $a$ (**top**) and $b$ (**bottom**) axes. The nitrogen atoms are depicted in blue, the carbon atoms in grey, the fluoride atoms in light green, the chloride ions in green, the copper atoms in red, the silicium atoms in yellow and the oxygen atoms are depicted in red. H-atoms were omitted for clarity.

**Figure 6.** Thermal ellipsoid (50%) plot of the 1D polymeric chain formed by the $\{[\text{Cl(H}_2\text{O)}]\}_n$ cluster in the structure of III.

**Figure 7.** Room temperature X-band EPR spectra from powdered samples of III and IV.

Magnetic susceptibility measurements were recorded for powdered samples of III and IV over the 5–300 K temperature range at an applied field of 0.1 T (Figure 8). At room temperature, the $\chi_M T$ values are 0.40 and 0.39 cm$^3$ mol$^{-1}$ K for III and IV, respectively, comparable with that expected for one Cu(II) ion ($S = 1/2$). The temperature profiles of the magnetic susceptibility for both complexes are
very similar. As the temperature decreases, $\chi_M$ increases smoothly reaching a rather broad maximum at ca. 125 K for III and ca. 130 K for IV. Below these temperatures, $\chi_M$ decreases going through a minimum at ca. 25–30 K before increasing again abruptly (Figure 8).

**Figure 8.** Temperature dependence of molar susceptibility $\chi_M$ for powdered samples of III and IV at 0.1 T. Red solid lines are simulations based on the fitting procedure as discussed in the text. For IV the blue line corresponds to the fit obtained assuming $zJ' = 0$.

On the basis of the crystal structures of III and IV, the magnetic behavior of both complexes was approximated assuming a 1D antiferromagnetic (AF) chain governed by the exchange coupling Hamiltonian: $H = -J \sum S_i S_{i+1}$, where $J$ is the isotropic interaction parameter. The temperature dependence of the magnetic susceptibility for such a 1D system is adequately described by the Bonner-Fischer approximation [33]:

$$
\chi_M = \frac{N \beta^2 \gamma^2}{k_B T} \left( \frac{0.25 + 0.074975 x + 0.075235 x^2}{1 + 0.9931 x + 0.172135 x^2 + 0.757825 x^3} \right)
$$

with $x = |J|/k_B T$ and the other terms having their usual meanings.

Since the crystal packing for these 1D chains reveals several inter-chain interactions (Figures 3 and 5), a mean field correction was considered using a corrected susceptibility $\chi_{cor}$, where $zJ'$ corresponds to the interchain interaction parameter [34]:

$$
\chi_{cor} = \frac{\chi_M}{1 - \frac{zJ' \chi_M}{Ng^2 \beta^2}}
$$

The increase of $\chi_M$ below 30 K is attributed to paramagnetic monomeric impurities and/or short chains after chain breaking [35,36] with $S = 1/2$, for which the magnetic susceptibility, $\chi_{IMP}$, follows
the Curie law. Overall, the susceptibility data were best fitted following the equation:

$$\chi_M = (1 - \rho)\chi_{\text{cor}} + \rho\chi_{\text{IMP}} + \chi_{\text{TIP}},$$

where $\rho$ is the fraction of paramagnetic impurities and $\chi_{\text{TIP}}$ is the temperature independent paramagnetism (TIP). The parameters obtained from these simulations are listed in Table 1, considering two situations for IV, with or without intermolecular interactions, the second situation being the less favorable according to fitting results (Figure 8).

Despite the similar nature of the $[\text{Cu}(\mu_2-\text{NH}_2\text{trz})_2\text{Cl}]$ polymeric unit in III and IV, the latter exhibits stronger inter-chain magnetic interactions $zJ$ (Table 1). The strong AF intra-dimer coupling $J$ determined in III and IV is much higher than those of previously reported 1D Cu(II) complexes made of two $\mu_2-N_1,N_2-\text{NH}_2\text{trz}$ and another bridging atom, i.e., N in $[\text{Cu}(\mu_2-\text{NH}_2\text{trz})_2(\mu_2-\text{N}_1,N_1,N_2)]\text{NO}_3$ [11], or $[\text{Cu}(\mu_2-\text{NH}_2\text{trz})_2(\mu_2-\text{NCS-N})]\text{ClO}_4\cdot 0.5\text{H}_2\text{O}$ [12], and O in $[\text{Cu}(\mu_2-\text{NH}_2\text{trz})_2(\mu_2-\text{NO}_3)]\text{NO}_3$ (Table 1) [13]. These results allow us to evidence an intermediate case between two structural situations by disclosing the crystal structures of the chain compounds III and IV which show a new bridge type of formula $[\text{Cu}(\text{NH}_2\text{trz})_2\text{Cl}]^+$. Interestingly, this configuration reveals higher intra-dimer coupling constants compared to the initial case where Cu(II) chains, of formula $[\text{Cu(Rtrz)}]^2+$, made of three Rtrz bridges show very weak $|J|$ values [27,29], and the third case where neutral Cu(II) chains $[\text{Cu(NH}_2\text{trz})\text{Cl}]_2$, show weak $J$ values [10,32]. Despite the high $J$ values of III and IV, the record ones reported so far for this sub-class are hold by Drabent et al. for $[\text{Cu}(\mu_2-\text{OH})(\mu_2-\text{Xphtrz})]\text{BF}_4\cdot \text{H}_2\text{O}$ and $[\text{Cu}(\mu_2-\text{OH})(\mu_2-\text{Xphtrz})(\text{H}_2\text{O})]\text{NO}_3$ (X = Cl, Br; Xphtrz = N-[(E)-(4-3-methylidene]-4H-1,2,4-triazol-4-amine) which range from $-391(3)$ to $-608(2)$ cm$^{-1}$ [35]. Ab initio calculations would be useful to appreciate the origin of the magnitude of the coupling constants in these model Cu(II) chain compounds.

3. Experimental Section

3.1. General Procedures

Infrared spectra (KBr) were recorded with a FTIR-8400S SHIMADZU spectrophotometer (Shimadzu, Kyoto, Japan) in the range 400–3600 cm$^{-1}$. $^1$H NMR spectra in DMSO-$d_6$ were obtained on a Bruker Avance 300 MHz spectrometer (Billerica, MA, USA) at 25 °C. Chemical shifts are reported with reference to SiMe$_4$. Diffuse reflectance spectra were obtained with a Varian Cary 5E spectrometer (Palo Alto, CA, USA) using polytetrafluoroethylene (PTFE) as a reference. Elemental analyses were performed at University College London, UK. Magnetic susceptibility measurements were performed on a MPMS-5500 Quantum Design instrument (San Diego, CA, USA) in the temperature range 5–300 K. Experimental data were corrected for the sample holder and for the diamagnetic contribution of the sample using Pascal’s constants. X-band EPR spectra at room temperature were recorded on a Bruker ER 200D-SRC X-band spectrometer (Billerica, MA, USA) equipped with an NMR Gaussmeter, and an Anritsu microwave frequency counter. The following conditions were applied: microwave power 59 mW, modulation amplitude 25 Gpp, microwave frequency 9.42 GHz.

3.2. Syntheses

$N,N'$-bis(1,2,4-triazole-4-yl)formamidine hydrochloride (L$\cdot$HCl): A solution of NH$_2$trz (4.9 g, 58.3 mmol), HC(OEt)$_3$ (9.8 g, 66.1 mmol) and NaN$_3$ (3.9 g, 60 mmol) in AcOH (25 mL) was heated at
105 °C for 3 h. The reaction mixture was then cooled and 37% aqueous HCl (5.8 g, 58.3 mmol) was added. The resulting solution was filtered and concentrated under reduced pressure to give a yellowish solid, which was washed by hot EtOH (80 mL) to afford a white solid. Yield: 1.5 g (12%).

mp > 200 °C. IR: ν = 3105 (m), 3095 (m), 3068 (m), 3025 (w), 2971 (vw), 1657 (s), 1491 (m), 1447 (w), 1447 (m), 1393 (m), 1362 (w), 1318 (m), 1285 (m), 1264 (m), 1173 (m), 1055 (s), 990 (m), 959 (m), 947 (m), 899 (w), 872 (m), 833 (m), 764 (m), 614 (s), 532 (w) cm⁻¹. 1H NMR: δ = 8.65 (s, 1H, CH), 8.83 (s, 4H, CH, 1,2,4-triazole) ppm. Anal. Calc. for C₅H₇ClN₈ (214.62): C 27.98, H 3.29, N 52.21. Found: С 27.63, Н 2.99, N 51.11. Crystals of L suitable for a single crystal X-ray analysis were obtained by dissolving 0.2 g of L·HCl in H₂O–acetone (5 mL; 50:50, v/v) solution, which was slowly evaporated at room temperature affording single crystal on standing (4 days).

[Cu(NH₂trz)₄(H₂O)](AsF₆)₂ (I): A solution of NH₂trz (0.252 g, 3 mmol) in MeOH (10 mL) was added drop wise to a solution of [Cu(H₂O)₆](AsF₆)₂ (0.550 g, 1 mmol) in MeOH (5 mL). The resulting blue precipitate was filtered off, washed with MeOH and dried in a desiccator. A small amount of a solid material (0.050 g) was dissolved in water (100 mL). Crystals suitable for a single crystal X-ray analysis were obtained on standing (12 months) with slow evaporation of the solvent. Yield: 0.376 g (63%). Anal. Calc. for C₈H₁₈As₂CuF₁₂N₁₆O (795.71): C 12.08, H 2.28, N 28.16. Found: С 12.17, Н 2.23, N 28.24.

[Cu(NH₂trz)₄(H₂O)](PF₆)₂ (II): L·HCl (0.300 g, 1.39 mmol) was dissolved in water (10 mL). Then a solution of KPF₆ (0.208 g, 1.13 mmol) and CuCl₂·2H₂O (0.097 g, 0.57 mmol) in water (10 mL) was added dropwise leading to the formation of a precipitate. To the resulting mixture, additional water (500 mL) was added and the solution was heated until the precipitate completely dissolved. Crystals suitable for a single crystal X-ray analysis were obtained on standing (8 months) with slow evaporation of the solvent and slow delivery of NH₂trz by hydrolysis of L. Yield: 0.285 g (74%). Anal. Calc. for C₈H₁₈CuF₁₂N₁₆OP₂ (707.8): C 13.57, H 2.56, N 31.64. Found: C 14.37, H 2.52, N 33.30.

[Cu(μ₂-NH₂trz)₂Cl]Cl·H₂O (III): Path A: A solution of Cu(CH₃COO)₂·H₂O (0.106 g, 0.053 mmol) in water (5 mL) was added to a solution of (NH₄)₂CuCl₄·2H₂O (0.147 g, 0.053 mmol) in the same solvent (5 mL). The resulting blue solution was added to a solution of NH₂trz (0.134 g, 0.159 mmol) in MeOH (5 mL). Then the mixture was cooled in ice till the blue solid was precipitated. The obtained solid material was filtered off and dissolved in water (50 mL) upon heating. Crystals suitable for a single crystal X-ray analysis were obtained on standing (several weeks) after slow evaporation of the solvent. Yield: 0.114 g. Path B: L·HCl (0.300 g, 1.39 mmol) was dissolved in water (10 mL). Then a solution of CuCl₂·2H₂O (0.097 g, 0.57 mmol) in water (10 mL) was added dropwise leading to the formation of a precipitate. To the resulting mixture, additional water (450 mL) was added and the solution was heated until the precipitate completely dissolved. Crystals suitable for a single crystal X-ray analysis were obtained on standing (6 months) after slow evaporation of the solvent and slow delivery of NH₂trz by hydrolysis of L. Yield: 0.128 g (75%). Anal. Calc. for C₆H₁₄Cl₂CuN₈O (320.63): C 14.98, H 3.14, N 34.95. Found: C 15.11, H 3.19, N 34.82.

[Cu(μ₂-NH₂trz)₂Cl](SiF₆)₀.₅·1.₅H₂O (IV): L·HCl (0.300 g, 1.39 mmol) was dissolved in water (6 mL) and inserted in the left arm of a H-tube. A 50% wt. aqueous solution of Cu(BF₄)₂ (260 μL, 0.55 mmol) was placed in the right arm of a H-tube. Then the tube was carefully filled with water and...
sealed to prevent evaporation of the solvent. Crystals suitable for a single crystal X-ray analysis were obtained on standing (5 months) after slow delivery of NH$_2$trz by hydrolysis of L and formation of SiF$_6^{2−}$ by the reaction of BF$_4^{−}$ with the glass tube. Yield: 0.137 g (34%). Anal. Calc. for C$_8$H$_{32}$Cl$_2$Cu$_2$F$_6$N$_{16}$O$_3$Si (730.44): C 13.15, H 3.04, N 30.68. Found: C 13.28, H 2.97, N 30.53.

### 3.3. X-ray Crystallography

The X-ray intensity data were collected with a MAR345 image plate (Norderstedt, Germany) using Mo-K$_\alpha$ ($\lambda = 0.71069$ Å) radiation. The crystal was chosen, mounted in inert oil and transferred quickly to the cold gas stream for flash cooling. Crystal data and data collection parameters are summarized hereafter. The unit cell parameters were refined using all the collected spots after the integration process. The data were not corrected for absorption (for L, III, IV), but the data collection mode partially takes the absorption phenomena into account. All non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were placed on calculated positions with temperature factors 1.2 times higher than their parent atoms (1.5 for methyl and OH hydrogens). The Fourier density map for II reveals a high residual peak next to the copper coordinated oxygen atom. Inspection of the native Patterson map reveals a large off origin peak (peak height > 50% origin peak) positioned at 0.5 0 0.25, which is believed to indicate translational disorder. Applying the translation to the Cu atom situated on the 2-fold axis this gives a peak at 0.0000 0.7500 0.0901 or 0.5000 0.2500 0.5901 (+1/2 +1/2 +1/2) (given the I centering), which is also the position of the high residual peak in the Fourier map. The crystals (in total three full datasets were measured all giving the same outcome) have all some degree of non-crystallographic translational symmetry and thus consists of two domains which are translated by 1/2 in the z-direction. Figures were generated using the Mercury software [14].

**Crystal data for L:** C$_5$H$_6$N$_8$, $M_t = 178.18$ g mol$^{-1}$, Monoclinic, space group Cc, $a = 3.7400(7)$, $b = 21.081(4)$, $c = 9.2000(18)$ Å, $\beta = 100.00(3)^\circ$, $V = 714.3(2)$ Å$^3$, $Z = 4$, $\rho = 1.657$ g cm$^{-3}$, $T = 293(2)$ K, $\mu$(Mo-K$\alpha$) = 0.122 mm$^{-1}$, reflections: 3630 collected, 1345 unique, $R_{int} = 0.0466$, $R_1$(all) = 0.0399, $wR_2$(all) = 0.0958.

**Crystal data for II:** C$_8$H$_{16}$CuF$_{12}$N$_{16}$OP$_2$, $M_t = 705.85$ g mol$^{-1}$, tetragonal, space group I4$_1$/a, $a = b = 10.7557(1)$, $c = 40.574(1)$ Å, $V = 4693.8(1)$ Å$^3$, $Z = 8$, $\rho = 1.998$ g cm$^{-3}$, $T = 100(2)$ K, $\mu$(Mo-K$\alpha$) = 1.204 mm$^{-1}$, reflections: 23,890 collected, 2243 unique, $R_{int} = 0.046$, $R_1$(all) = 0.0758, $wR_2$(all) = 0.201.

**Crystal data for III:** C$_4$H$_{10}$Cl$_2$CuN$_8$O, $M_t = 320.65$ g mol$^{-1}$, monoclinic, space group $P2_1$/a, $a = 7.303(3)$, $b = 13.838(5)$, $c = 11.019(4)$ Å, $\alpha = 101.67(2)^\circ$, $\beta = 109.06(7)$ Å$^3$, $Z = 4$, $\rho = 1.953$ g cm$^{-3}$, $T = 101(2)$ K, $\mu$(Mo-K$\alpha$) = 2.486 mm$^{-1}$, reflections: 28,160 collected, 2225 unique, $R_{int} = 0.055$, $R_1$(all) = 0.0316, $wR_2$(all) = 0.0915.

**Crystal data for IV:** C$_8$H$_{22}$Cl$_2$Cu$_2$F$_6$N$_{16}$O$_3$Si, $M_t = 730.51$ g mol$^{-1}$, triclinic, space group P$\overline{1}$, $a = 7.210(3)$, $b = 11.673(4)$, $c = 15.271(5)$ Å, $\alpha = 70.35(2)$, $\beta = 82.16(2)$, $\gamma = 79.55(2)^\circ$, $V = 1186.4(8)$ Å$^3$, $Z = 2$, $\rho = 2.045$ g cm$^{-3}$, $T = 105(2)$ K, $\mu$(Mo-K$\alpha$) = 2.167 mm$^{-1}$, reflections: 19,683 collected, 4296 unique, $R_{int} = 0.066$, $R_1$(all) = 0.0504, $wR_2$(all) = 0.1124.
CCDC 902803 (L), 902805 (II), 902804 (III) and 902806 (IV) contain the supplementary crystallographic data. 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, UK; Fax: (+44) 1223-336-033; or E-Mail: deposit@ccdc.cam.ac.uk.

4. Conclusions

In this work, two Cu(II) NH₂trz mononuclear complexes I and II have been isolated and structurally characterized, which is rather uncommon for a ligand routinely used in coordination chemistry to afford polynuclear complexes. Our work opens interesting perspectives because such materials are described as potential energy sources for ballistic applications [23,38,39]. We have also presented two novel examples of 1D NH₂trz chains, III and IV, where neighboring Cu(II) atoms are linked by two bridging bis-monodentate µ₂-N₁,N₂-NH₂trz and one bridging µ₂-chloride ligand, a configuration which was not yet explored for this family of coordination polymers. Their resulting strong antiferromagnetic coupling has been quantitatively evaluated after considering precise SQUID and EPR measurements.

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Conflicts of Interest

The authors declare no conflict of interest.

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