# Synthesis and Characterisation of Coordination Polymers of $Cu^{II}$ and $Zn^{II}$ with 1,3-Bis(1,2,3,4-tetrazol-2-yl)propane − Rotational Freedom of the Donor Group Favours Structural Diversification

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The novel bidentate ligand 1,3-bis(1,2,3,4-tetrazol-2-yl)propane (pbtz), which possesses a flexible spacer, was synthesised in order to investigate the influence of the flexibility of ligand molecules on the architecture of coordination polymers. For that purpose the reactions between pbtz and $M(ClO_4)_2·6H_2O$ salts (M = $Cu^{II}$ and $Zn^{II}$) were performed. The complexes $[\{Cu(pbtz)_3\}(ClO_4)_2]_\infty$ and $[\{Zn(pbtz)_3\}(ClO_4)_2·2EtOH]_\infty$ were characterised by IR and UV/Vis spectroscopy and their crystal structures were determined by single-crystal X-ray diffraction measurements. In both compounds the pbtz ligand molecules act as N4,N4′ connectors bridging the central atoms, and the 2-substituted tetrazole rings coordinate in a monodentate fashion to the central atoms forming M(tetrazole)$_6$ cores. $[\{Cu(pbtz)_3\}(ClO_4)_2]_\infty$ was isolated as a 1D coordination polymer. The copper(II) ions are triply bridged by ligand molecules, leading to the formation of infinite 1D chains. A highly unusual manner of bridging, with the tethering of two neighbouring central atoms by the same kind of ligand molecules, although possessing different conformations, is observed. In $[\{Zn(pbtz)_3\}(ClO_4)_2·2EtOH]_\infty$ the six-coordinate zinc(II) ions, which are bridged by single ligand molecules, serve as topological nodes, leading to the formation of a 3D α-polonium-type network. The crystal structure of the $Zn^{II}$ complex contains only one such net solvated by ethanol molecules. A conformational analysis of the ligand molecules in both compounds demonstrates that the flexibility of the pbtz and the ability of the tetrazole rings in particular to adopt various, relative orientations is responsible for the diversity of the architectures of the obtained complexes.

## Introduction

The schematic method created by Wells[1] and developed further by Robson[2] for the description of coordination polymers characterises such materials as a self-repeating system of nodes (central atoms) and rods (ligand molecules). This approach assumes the presence of a coordination bond, which is much stronger than other contacts such as hydrogen bonds or π−π interactions, and points to the importance of the coordination geometry of the central atom. In effect, the presence of coordination bonds means that the coordination geometry of the central atom can be propagated throughout the network. This indicates the possibility of a more reasoned approach to the synthesis of new materials with a desired topology and dimensionality, especially in the case of the application of rigid rod-like molecules as ligands.[3,4] In reality, however, this simple way of forecasting the architecture of the coordination networks is strongly perturbed both by the ability of the metal ions to form complexes with heteroleptic surrounded central atoms and by the influence of the angularity of the rigid ligand molecules,[5−10] *cis*/*trans* isomerism,[11] and the conformational freedom of ligands possessing a flexible spacer.[12−16] The flexibility of the ligand molecules usually leads to great structural diversification of the products, including the formation of supramolecular isomers.[17]

The length of the ligand molecule affects the distance between the bridged central atoms. This separation implies either the formation of voids, which can be filled by solvent molecules, or interpenetrated structures.[18−20] In bis(4-pyridyl)alkanes the position of the nitrogen donor atom means that although various configurations can be adopted by the pyridyl rings in relation to the alkyl spacer, the intraligand N···N′ distance depends only on the conformation of the alkyl spacer.[14] A more complicated situation arises in the case of five-membered polyazole rings as the donor groups. Conjugated bis(polyazoles) can act as linear or angular connectors, and in such a situation the distance between the central atoms bridged by common ligand molecules depends on the relative orientation of the polyazole rings.[21−29] The incorporation of an alkyl spacer tethering imidazole,[30−34] pyrazole,[35] benzimidazole,[36,37] triazole,[38−45] benzotriazole,[37,46,47] or tetrazole[48−57] moieties causes a significant increase of the flexibility of the ligand molecule, thus allowing the formation of a wide range of coordination polymer architectures.

Among the five-membered polyazoles, the coordination chemistry of 2-substituted tetrazoles is very much under-

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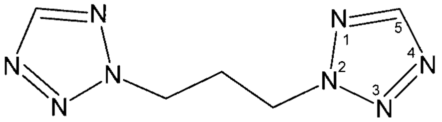
developed, especially in relation to their 1-substituted isomers.[47–54,58–63] In the majority of 2-substituted tetrazole complexes the polyazole ring coordinates to the metal ion in a monodentate fashion through the N4 nitrogen atom.[55,56,64,65] This ability to form a coordination bond through the *exo*-nitrogen atom of the tetrazole ring enables the use of this donor group for the preparation of nonchelating bi- and polypodal ligands appropriate for the construction of coordination polymers. Indeed, the results of recently started investigations of a new family of ligands, namely 1,ω-bis(1,2,3,4-tetrazol-2-yl)alkanes, point to their usefulness in the preparation of coordination networks with various dimensionalities and topologies. Thus, 1,2-bis(1,2,3,4-tetrazol-2-yl)ethane (ebtz) reacts with $Zn^{II}$ to form a triple-stranded 1D linear chain,[55] whereas the complexes obtained from the reaction of $Cu^{II}$ with 1,4-bis(1,2,3,4-tetrazol-2-yl)butane (bbtz) were isolated, depending on the reaction conditions, as either 2D or 3D networks.[56] Naturally, in such a situation an intriguing question arises concerning the architecture of the coordination polymers in the case of the application of an intermediate-length spacer tethering the tetrazole rings, namely 1,3-propylene; therefore a new flexible ligand 1,3-bis(1,2,3,4-tetrazol-2-yl)propane (pbtz; Scheme 1) was synthesised.



Scheme 1

Taking into account the tendency to structural diversification of the products in the case of the application of flexible ligand molecules, the investigation of the coordination abilities of pbtz was focused first of all on octahedrally coordinating metal ions, aiming especially at complexes with a homoleptic ligand environment. In this paper the synthesis of the pbtz ligand and the coordination polymers obtained from the reaction of pbtz with perchlorate salts of $Cu^{II}$ and $Zn^{II}$ is reported in detail. The results of spectroscopic investigations and single-crystal X-ray diffraction studies of 1D and 3D polynuclear complexes are also presented.

## Results and Discussion

### Synthesis, Properties and Spectroscopic Characterisation

The new flexible ligand 1,3-bis(1,2,3,4-tetrazol-2-yl)propane (**1**) was synthesised by alkylation of sodium tetrazolate with 1,3-dibromopropane, according to the method described previously for other members of this family of ligands.[55,56] Because of the competitive process of formation of 1-substituted tetrazoles in this synthetic route[66–68] a low yield of pbtz was also obtained in this case due to the formation of other bis(tetrazole) ligands, namely 1,3-bis(1,2,3,4-tetrazol-1-yl)propane and 1-(1,2,3,4-tetrazol-1-yl)-3-(1,2,3,4-tetrazol-2-yl)propane.[54] The pbtz ligand was isolated as a colourless liquid. It is completely miscible in polar solvents such as methanol, acetonitrile, and dichloromethane, although it is significantly less soluble in $CCl_4$ and is completely insoluble in aliphatic hydrocarbons; it is stable during storage at room temperature.

The results of elemental analysis indicated that the reactions between pbtz and $M(ClO_4)_2\cdot 6H_2O$ salts (M = $Cu^{II}$, $Zn^{II}$), performed in a 3:1 ligand/metal stoichiometry, afforded complexes with formula $[\{Cu(pbtz)_3\}(ClO_4)_2]_\infty$ (**2**) and $[\{Zn(pbtz)_3\}(ClO_4)_2\cdot 2EtOH]_\infty$ (**3**).

The synthesis of **2** leads first of all to the formation of small amounts of a light-blue polycrystalline solid. After about 10 d, crystals of **2** started to grow accompanied by the partial disappearance of the products precipitated during the first stage of the synthesis. Because only very small amounts of these polycrystalline products were formed, and due to their lack of homogeneity, it was not possible to characterise them. Therefore, only the light-blue crystals of complex **2** were isolated and characterised. The synthesis of the $Cu^{II}$ complex depends strongly on the ethanol volume, the presence of water in the solvent, and the growing time of the crystals, and therefore this influences both the yield of product **2** and amount of the polycrystalline mixture formed.

The preparation of the zinc(II) complex was successful only in absolute ethanol; the addition of water prevents formation of the product. Under these reaction conditions only the formation of complex **3** was observed. In contrast to **2**, the zinc(II) complex is unstable during storage in air, and a few days after removal from the mother liquor crystals of **3** become cloudy.

The IR spectrum of pbtz is characteristic of 2-alkyltetrazoles.[69] The formation of a coordination bond through the N4 nitrogen atom of the tetrazole ring involves changes in the bands that are composed from combinations of the vibrations of the tetrazole ring components. The characteristic narrow band located at 3141 $cm^{-1}$ and assigned to $\nu(C_{ring}-H)$ stretching vibrations in **1** is shifted to higher frequencies by 10 $cm^{-1}$ and 6 $cm^{-1}$ for complexes **2** and **3**, respectively. The bands attributed to the stretching vibrations of the N=N (1450 $cm^{-1}$), C=N (1360 $cm^{-1}$) and N–N (1290 $cm^{-1}$) bonds in the IR spectrum of the free pbtz ligand are also shifted to higher wavenumbers after complexation. These changes are in agreement with those observed for $[Cu(2\text{-alkyltetrazole})_2X_2]$ (X = $Cl^-$, $SCN^-$)[70] and complexes of $Zn^{II}$ and $Cu^{II}$ with ebtz[55] and bbtz[56] ligands. In contrast to **2**, the broad, intense band located at 3393 $cm^{-1}$ observed for compound **3** confirms the presence of alcohol molecules in the crystal lattice of the $Zn^{II}$ complex. The presence of nonsplit, strong absorption bands at 1094 and 624 $cm^{-1}$ for **2** and 1090 and 626 $cm^{-1}$ for **3** points to a lack of strong deviation of the perchlorate anions from tetrahedral symmetry.[71]

The electronic spectrum of complex **2** shows a d-d transition at 15400 $cm^{-1}$ with a shoulder at 9800 $cm^{-1}$. These values are characteristic of square-planar $CuN_4$ or distorted octahedral $CuN_4X_2$ (X = N, O) chromophores[72] and are similar to those found for mononuclear complexes of 1-alkyltetrazoles, such as [Cu(1-alkyltetrazole)$_6$](BF$_4$)$_2$.[73]

## Structural Studies

### Description of the Crystal Structure of 2

The structure of **2** is depicted in Figure 1 together with the labelling scheme of the atoms. The Cu$^{II}$ ion environment is formed by six 2-substituted tetrazole rings coordinating monodentately through their N4 nitrogen atoms. The four nitrogen atoms forming an equatorial plane are placed at distances of 1.993(2) and 2.061(2) Å. The distance to both axially located nitrogen atoms is equal to 2.414(2) Å. The N−Cu−N angles are close to 90°, ranging from 88.36(6) to 91.64(6)°. This coordination geometry of the elongated octahedron is typical for CuN$_6$ chromophores distorted by the Jahn−Teller effect and is similar to those found for other complexes of both 2-substituted[56] and 1-substituted tetrazoles.[47,60]

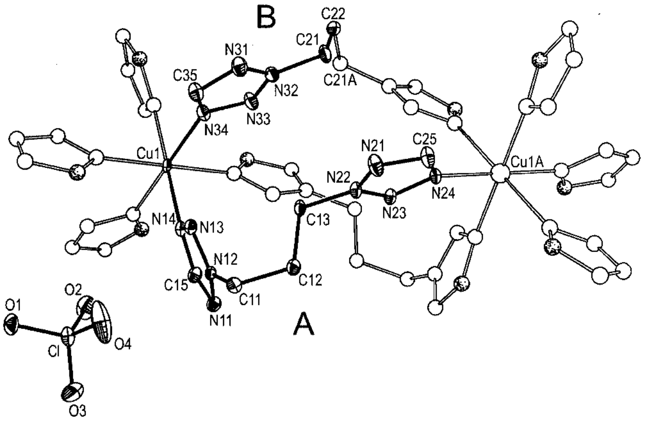


Figure 1. Coordination geometry around Cu$^{II}$ in **2** and labelling scheme of atoms (50% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected torsion angles [°] for ligand molecule **A**: N11−N12−C11−C12 86.0(2), N12−C11−C12−C13 54.2(2), C11−C12−C13−N22 172.6(2), N21−N22−C13−C12 −91.2(2) (*TG* conformation); for ligand molecule **B**: N31−N32−C21−C22 −132.6(2), N32−C21−C22−C21a −75.9(2) (*GG′* conformation); atom C21A generated by symmetry operation −*x*, *y*, −*z* + 3/2

Each molecule of pbtz acts as an N4,N4′ bridging ligand and three molecules of pbtz simultaneously link two neighbouring copper(II) ions. This bridging propagates along the *c* axis and leads to the formation of an infinite chain (Figure 2a). In the case of 1,3-bis(polyazolyl)propane ligands a similar motif of a triple-stranded infinite chain has been found for complexes of Fe$^{II}$ and Cu$^{II}$ with 1,3-bis(1,2,3,4-tetrazol-1-yl)propane.[54] Among polynuclear complexes based on 1,ω-bis(polyazolyl) ligands possessing an alkyl spacer other than 1,3-propylene, this type of bridging of the metal atoms has been observed for complexes of 1,1-bis(1,2,3,4-tetrazol-2-yl)methane,[74] 1,2-bis(1,2,3,4-tetrazol-2-yl)ethane,[55] 1,2-bis(1,2,3,4-tetrazol-1-yl)ethane[47,49] and 1,2-bis(1,2,3,4-tetrazol-1-yl)propane.[50] In **2** the copper atoms linked by common ligand molecules are separated by a distance of 9.001(1) Å while the shortest distance between the copper atoms from neighbouring chains is 8.950(1) Å. These data clearly show that in relation to 1D coordination polymers based on bis(tetrazolyl)ethane ligands[47,49,50,55] an elongation of the spacer in pbtz results in an increase of the metal−metal separation within the polymeric unit of **2** by 1.6−2.3 Å.

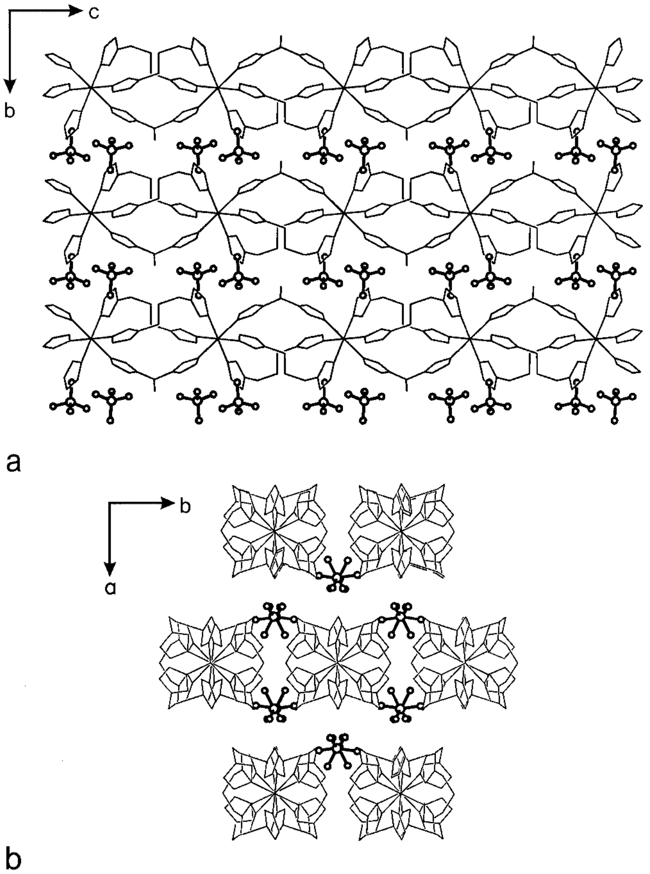


Figure 2. Projection of the structure of **2** (a) along the *a* axis and (b) along the *c* axis; hydrogen atoms are omitted for clarity

An unusual feature of the triple-stranded bridge in **2** is the presence of ligand molecules with two different conformations that simultaneously tether the same two central atoms. In this compound two crystallographically related ligand molecules adopt *TG* conformations whereas the third molecule of pbtz adopts a *GG′* conformation. A comparison of the torsion angles for both types of pbtz ligands shows that a change of the spacer conformation in ligand **A** is accompanied by rotation of the tetrazole ring, which leads to an adjustment of the intramolecular N4···N4′ distance relative to that in ligand **B**. Hence, despite differences between the conformations of the pbtz molecules the N4···N4′ distances are similar and are equal to 7.015(2) Å and 6.827(3) Å for molecules adopting the *TG* and *GG′* conformations, respectively. This behaviour, observed here for the first time for complexes based on alkylbis(polyazole) ligands, demonstrates a fundamental difference of the properties of the pbtz ligand in relation to those of 1,3-

bis(pyridyl-4-yl)propane — the distance between the metal centers depends only on the alkyl spacer conformation.[14]

The architecture of **2** enforces a localisation of the perchlorate ions in the channels between the polymeric chains (Figure 2b). The perchlorate ions do not form any coordination bonds with the copper(II) ions. However, they are engaged in the formation of C15−H15···O2(Cl) ($-x$, $-y + 1$, $-z + 2$) and C25−H25···O4(Cl) ($-x + 1/2$, $y + 1/2$, $-z + 3/2$) contacts. Direct C25−H25···N13 ($x$, $-y + 2$, $z - 1/2$) contacts are also observed between the polymeric chains. As a result no voids are accessible for the incorporation of solvent molecules.

### Description of the Crystal Structure of 3

In **3** there are two crystallographically independent zinc(II) ions. The coordination environments of both central atoms are similar and consist of six nitrogen atoms from monodentate 2-substituted tetrazole moieties (Figure 3). There are two sets of metal−ligand bond lengths for Zn1−N [2.150(3) and 2.172(3) Å], whereas for the second crystallographically independent zinc atom the Zn2−N distances are practically the same, ranging from 2.163(3) to 2.166(3) Å. The values of the N−Zn−N angles vary from 87.0(1) to 92.2(1)° for Zn1 and from 88.8(1) to 90.9(1)° for Zn2, indicating a significantly larger rhombic distortion of the coordination environment in the case of the Zn1 atom, consisting in this case of a compression of the coordination octahedron along the threefold axis in the *c* direction. The coordination geometry, especially in the case of the Zn1 atom, is similar to that found for $Zn^{II}$ in the 1D coordination polymer $[\{Zn(ebtz)_3\}(ClO_4)_2]_\infty$.[55]

The pbtz molecule acts as an N4,N4′ bridging ligand. In this case, contrary to **2**, six pbtz molecules are coordinated to one central atom and two central atoms are bridged only by a single ligand molecule. This bridging fashion of the adjacent zinc atoms spreads in the three noncoplanar directions, leading to the formation of a 3D coordination polymer. In this way an octahedral network composed of distorted rhombohedral "boxes" is formed (Figure 4). The topology of the network in **3** originates from the coordination symmetry of the zinc atoms. However, differences in the relative orientations of the neighbouring octahedra mean that the coordination bond directions do not determine the direction of the propagation of the network. In spite of this the flexibility of the pbtz molecules enables a bridging of the central atoms, which are separated by distances of 10.666(1) and 10.706(1) Å. In comparison with octahedral networks based on butylbis(polyazole) ligands, this fitting of the geometry of the pbtz molecules to the localisation of the coordination sites of the neighbouring central atoms involves a significant shortening of the appropriate M···M distances by about 2.4−3.6 Å.[33,34,52,54] As a consequence, such a large decrease of the distances between the central atoms causes a lack of free space accessible for the interpenetration, leading, in the case of the 1,3-propylene spacer, to the formation of a coordination polymer composed from only one octahedral network. Known α-

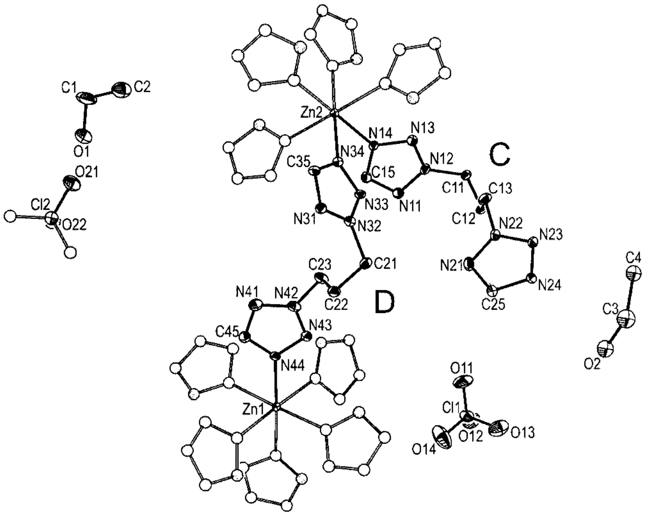


Figure 3. Coordination geometry around $Zn^{II}$ in **3** and labelling scheme of atoms (30% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected torsion angles [°] for ligand molecule **C**: N13−N12−C11−C12 104.6(4), N12−C11−C12−C13 −69.4(5), C11−C12−C13−N22 172.0(4), N21−N22−C13−C12 −76.4(5) (*TG* conformation); for ligand molecule **D**: N31−N32−C21−C22 70.4(5), N32−C21−C22−C23 57.9(5), C21−C22−C23−N42 176.2(4), N41−N42−C23−C22 87.0(5) (*TG* conformation)

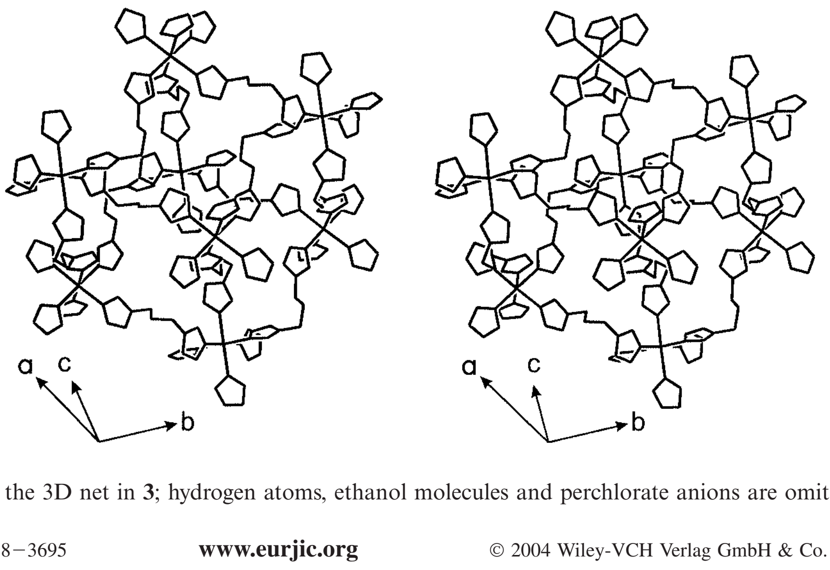


Figure 4. A stereoview of the 3D net in **3**; hydrogen atoms, ethanol molecules and perchlorate anions are omitted for clarity

polonium-type 3D systems based on alkylbis(polyazole) ligands contain four or more methylene groups in the alkyl spacer and they are composed from two[33,34,51] or three[52,54] 3D interpenetrated nets. Compound **3** therefore represents the first example of a non-interpenetrated 3D α-polonium-type system based on a flexible bis(polyazole) ligand.

The transition from compound **2** (1D net) to compound **3** (3D net) involves an increase of the number of pbtz molecules possessing the opposite localisation of the nitrogen donor atoms. This is expressed by an increase of the angles between the nitrogen−metal bonds (for central atoms bridged by common ligand molecule) from about 60 to 110°. This corresponds to the change of character of the pbtz molecules from angular (in **2**) to more linear (in **3**) connectors. In consequence, the distances between the zinc atoms separated by common ligand molecules in **3** are about 1.7 Å greater than the analogous Cu···Cu distance in **2**. Naturally, this large separation of the metal atoms in **3** explains the lack of bridging ligand molecules possessing a *GG′* conformation. The differences between ligand molecules possessing a *TG* conformation of the spacers suggests that the increase of the intramolecular N4···N4′ distances in **3** relative to **2** is achieved in two ways. A comparison of ligands **A** (inverted structure) in **2** and **C** in **3** indicates that a combined effect both of the change of the spacer conformation and the relative orientation of the rings is responsible for the increase of the N4···N4′ distance. Surprisingly, the torsion angles for ligand **A** (compound **2**) and ligand **D** (compound **3**) suggest that the increase of the metal···metal separations in this case results from the change of the relative orientation of the tetrazole rings; the conformation of the alkyl spacers remains unchanged (see Figure 5). In contrast to ligands possessing axially symmetrical donor groups, (e.g. 4-pyridyl), a noncolinear orientation of the metal−nitrogen bond and the ring−alkyl bond (here N−C) enables the bridging of metal atoms separated by different distances despite the retention of the same conformation of the alkyl spacer. The conformational flexibility of the spacer observed in complexes **2** and **3**, and especially the rotational freedom of the tetrazole ring, is responsible for the adoption of various relative orientations by the donor groups and therefore by the N4 donor atoms, which leads to the difference in the metal−metal distances and the topology of the networks as well.

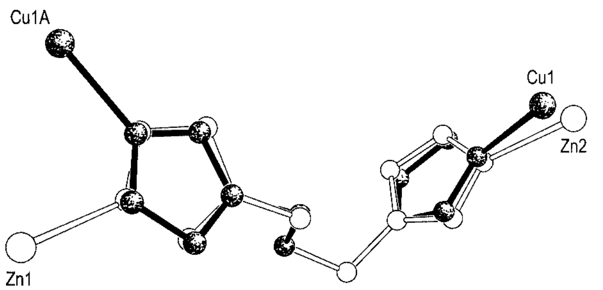


Figure 5. A superposition of the ligand molecules **A** (compound **2**) and **D** (compound **3**); hydrogen atoms are omitted for clarity; atom Cu1A generated by symmetry operation: $-x, y, -z + 3/2$

The perchlorates are noncoordinated and are gathered around the Zn(tetrazole)$_6$ cores. The remaining free space (943 Å$^3$; 17.1% of the unit cell volume) is composed of two kinds of voids with approximate volumes of 82 and 68 Å$^3$. The ethanol molecules that occupy the larger voids are arranged in pillars positioned parallel to the *c* axis (Figure 6). The space situated in the void of the rhombohedral boxes is occupied by ethanol molecules disordered about the threefold axis. The perchlorates are engaged in the formation of hydrogen bonds O2−H2···O21(Cl) ($-y + 2/3$, $x - y + 1/3$, $z + 1/3$) and O2−H2···O11(Cl) ($x + 1/3$, $y + 2/3$, $z + 2/3$) with both types of ethanol molecules.

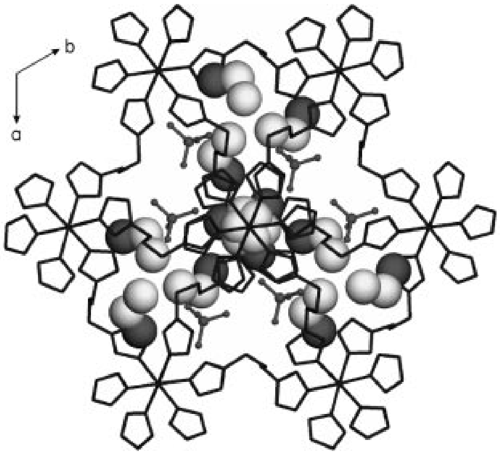


Figure 6. A view along the *c* axis showing channels filled by ethanol molecules in **3**; hydrogen atoms are omitted for clarity

## Concluding Remarks

The new flexible ligand 1,3-bis(1,2,3,4-tetrazol-2-yl)propane and two coordination polymers of Cu$^{II}$ and Zn$^{II}$ have been synthesised. They were characterised spectroscopically and the crystal structures of both complexes were determined. The bidentate and nonchelating nature of the pbtz ligand is reflected in the polymeric structure of the complexes: $[\{Cu(pbtz)_3\}(ClO_4)_2]_\infty$ crystallises as a 1D triple-stranded infinite chain, whereas $[\{Zn(pbtz)_3\}(ClO_4)_2\cdot 2EtOH]_\infty$ was isolated as a 3D network.

A strong influence of the spacer length on the architecture of the coordination polymers in this series of complexes based on 1,ω-bis(1,2,3,4-tetrazol-2-yl)alkanes is observed. Thus, use of pbtz rather than 1,2-bis(1,2,3,4-tetrazol-2-yl)ethane,[55] resulted not only in a 1D system but also in a coordination polymer of higher dimensionality (3D). In comparison with 1,4-bis(1,2,3,4-tetrazol-2-yl)butane,[56] a shortening of the alkyl spacer to 1,3-propylene resulted in the lowering of the degree of interpenetration and the formation of coordination polymers built up from only one octahedral network.

The coordination polymers described in this paper are based exclusively on octahedrally coordinated central atoms. Differences between the coordination properties of the $Cu^{II}$ and $Zn^{II}$ ions are reflected both in the course of the syntheses and in the diversification of the architectures of the isolated complexes. The flexibility of the ligand molecules, and especially the rotational freedom of the tetrazole rings, enable this structural diversification. The conformational analysis has shown that a rotation of the tetrazole rings around the ring−spacer bond ($C_{alkyl}-N2_{ring}$) can compensate a change of conformation of the alkyl spacer, leading to adjustment of the distances between the N4 and N4′ donor atoms. This peculiarity enables a bridging of the same two central atoms by the ligand molecules even though they possess different conformations. On the other hand the possibility of changing the relative orientation of the donor groups (tetrazole rings) by the simultaneous retention of the spacer conformation significantly influences the intrapolymer metal−metal distances. This leads, in consequence, to the formation of a coordination network with a different architecture. In summary, the rotational freedom of donor groups, especially their relative orientations, plays a similar role to the orientation effect of the donor group in the case of rigid ligands,[75,76] enabling here the formation of 1D and 3D networks.

## Experimental Section

**General Remarks:** The infrared spectra of pbtz and its complexes were recorded with a Bruker IFS66 IR FTIR spectrometer in the range 50−4000 $cm^{-1}$ as nujol mulls. $^1H$ and $^{13}C$ NMR spectra were obtained with an AMX Bruker NMR 300 MHz spectrometer at room temperature in $CD_3CN$ solutions. The ligand-field spectra were measured on powdered, pure samples with the diffuse-reflectance technique using a Cary 500 SCAN UV/Vis/NIR spectrometer. Elemental analyses for C, H, N were performed with a Perkin−Elmer 240C elemental analyser. Ethanol was dried by distilling from magnesium ethanolate. 1*H*-tetrazole was prepared by a previously described procedure.[55,77] The degree of hydration of the $Cu(ClO_4)_2{\cdot}6H_2O$ and $Zn(ClO_4)_2{\cdot}6H_2O$ salts was determined with an ICP spectrometer. The other commercially available reagents were used without further purification. ***Caution:*** Even though no problems were encountered it is worth mentioning that complexes containing perchlorates are potentially explosive and should be synthesised on a milligram scale and handled with care!

**Synthesis of 1,3-Bis(1,2,3,4-tetrazol-2-yl)propane (1):** A solution of NaOH (0.15 mol, 6.0 g) in water (20 mL) was added in a few portions to 1*H*-tetrazole (0.15 mol, 10.5 g) dissolved in water (20 mL). After cooling, the resulting clear solution was concentrated to dryness in a rotary evaporator. The remaining solid matter was finally dehydrated by an azeotropic distillation with three portions (100 mL each) of absolute ethanol. 1,3-Dibrompropane (0.07 mol, 7.15 mL) was then added to the obtained sodium tetrazolate suspended in MeCN (300 mL). The reaction mixture was stirred and refluxed for 4 d. The NaBr formed was filtered off and solvents were evaporated under reduced pressure. The resulting yellow oil was dissolved in water (150 mL). The aqueous solution was extracted with pentane (3 × 100 mL) and then with $CCl_4$ (10 × 100 mL). The crude product was isolated by removal of the solvent from the $CCl_4$ phase and purified by column chromatography on silica gel (230 mesh) using dichloromethane/acetone (100:5, v/v) as eluent ($R_f = 0.38$). Yield: 1.81 g (12.8%). $C_5H_8N_8$ (180.17): calcd. C 33.3, H 4.48, N 62.2; found C 33.8, H 4.60, N 61.9. ESI-MS: *m/z* calcd. for $C_5H_9N_8$ $[LH^+]$ 181.2; found 181.1. IR: $\tilde{\nu}$ = 3141 (m), 3012 (w), 2965 (w), 1773 (w), 1629 (w), 1450 (s), 1361 (s), 1284 (s), 1186 (m), 1167 (w, sh), 1135 (s), 1051 (w, sh), 1028 (s), 1009 (m), 986 (w), 887 (m), 803 (w), 757 (w), 727 (w), 709 (s), 689 (m), 661 (w), 640 (w), 475 (m), 370 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $CD_3CN$, 298 K): $\delta = 2.69$ (q, $^3J_{H,H} = 6.7$ Hz, 2 H, 2-H), 4.74 (t, $^3J_{H,H} = 6.7$ Hz, 4 H, 1-H, 3-H), 8.58 (s, 2 H, 5-H) ppm. $^{13}C$ NMR (300 MHz, $CD_3CN$, 298 K): $\delta = 29.09$, 50.83, 153.98 ppm.

**Synthesis of $[\{Cu(pbtz)_3\}(ClO_4)_2]_\infty$ (2):** A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.020 mmol, 7.4 mg) in EtOH (2.0 mL) was added to a solution of pbtz (0.060 mmol, 10.8 mg) in EtOH (2.0 mL). The reaction mixture was heated to 50 °C to give a clear solution. A few minutes after cooling, the solution became turbid and a small amount of precipitate appeared. The precipitate was left in the solution. The reaction mixture was kept in a closed tube at room temperature. Light-blue crystals were formed after 3 weeks. The crystals of **2** were separated manually under the microscope from the rest of the polycrystalline solids and then dried in air. Yield: 3.8 mg (24%). $C_{15}H_{24}Cl_2CuN_{24}O_8$ (802.95): calcd. C 22.4, H 3.01, N 41.9; found C 22.7, H 3.11, N 41.5. IR: $\tilde{\nu}$ = 3549 (w), 3151 (m), 3036 (w), 2980 (m, sh), 2923 (s), 2854 (s, sh), 1626 (w), 1468 (s, sh), 1460 (s), 1447 (sh), 1378 (m), 1367 (m), 1312 (m), 1292 (m), 1273 (w), 1211 (w), 1205 (w), 1185 (m), 1151 (s), 1139 (s), 1092 (vs), 1044 (w), 1044 (w), 1037 (w), 1029 (w), 1023 (w), 974 (w), 900 (w), 885 (m), 844 (m), 810 (w), 756 (w), 719 (w), 710 (w), 700 (m), 693 (m), 673 (w), 644 (w), 624 (s), 473 (w), 455 (w), 404 (m), 391 (w), 361 (w), 295 (w), 276 (w), 251 (w), 210 (w), 183 (w) $cm^{-1}$. UV/Vis: $\lambda_{max} = 15400$, 9800 $cm^{-1}$.

**Synthesis of $[\{Zn(pbtz)_3\}(ClO_4)_2{\cdot}2EtOH]_\infty$ (3):** A solution of pbtz (0.06 mmol, 11.6 mg) in absolute ethanol (0.4 mL) was added to a solution of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.02 mmol, 7.4 mg) in ethanol (0.4 mL). The resulting clear solution was allowed to stand in a closed tube at room temperature for 1 week. After this time, colorless crystals were collected and dried in a stream of nitrogen. Yield: 10.3 mg (57.4%). $C_{15}H_{24}Cl_2N_{24}O_8Zn{\cdot}2EtOH$ (896.92): calcd. C 25.4, H 4.04, N 37.5; found C 25.0, H 3.89, N 37.6. IR: $\tilde{\nu}$ = 3396 (br. s), 3169 (w), 3146 (m), 2953 (s, sh), 2925 (s), 2854 (m), 1650 (w, br), 1466 (m), 1455 (m), 1374 (m), 1364 (w, sh), 1304 (w), 1285 (m), 1204 (w), 1181 (w), 1151 (s, sh), 1140 (s, sh), 1109 (vs), 1090 (s, sh), 1029 (m, sh), 991 (w), 940 (w), 929 (w), 877 (w), 818 (w), 708 (w), 689 (m), 637 (m, sh), 626 (s), 475 (w), 388 (w), 191 (w) $cm^{-1}$.

**X-ray Crystallographic Study:** Single crystals of complexes **2** and **3** were obtained directly from the synthesis. The crystals were coated with a layer of inert oil, mounted on a glass fiber and transferred to the cold nitrogen stream of the diffractometer. Measurements of crystals of both compounds were performed with a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation, equipped with an Oxford Cryosystem device. Crystal data and refinement details for **2** and **3** are listed in Table 1. The data were corrected for Lorentz and polarisation effects. No absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) Sp. z o.o (formerly Kuma Diffraction Wroclaw, Poland) programs. The structures were solved by direct methods (program SHELXS-97[78]) and refined by the full-matrix least-squares method on all $F^2$ data using the SHELXL-97[79] programs. An analysis of the holes was performed using the Platon program.[80] The visualisation of the extended structure depicted in Figure 6 was prepared using the OLEX[81] program. For **2** all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located from the Fourier difference map and were refined with isotropic displacement parameters. For **3** the zinc atoms, the atoms of the

Table 1. Crystal data and structure refinement parameters for **2** and **3**

| | **2** | **3** |
|---|---|---|
| Empirical formula | $C_{15}H_{24}Cl_2CuN_{24}O_8$ | $C_{15}H_{24}Cl_2ZnN_{24}O_8{\cdot}1.92C_2H_6O$ |
| Formula mass | 803.02 | 893.15 |
| $T$ [K] | 293(2) | 100(2) |
| λ [Å] | 0.71073 | 0.71073 |
| Crystal system | monoclinic | trigonal |
| Space group | $C2/c$ | $R3$ |
| $a$ [Å] | 18.5212(11) | 17.5080(9) |
| $b$ [Å] | 8.9503(5) | 17.5080(9) |
| $c$ [Å] | 18.0019(9) | 20.7888(16) |
| $\alpha$ [°] | 90 | 90 |
| $\beta$ [°] | 90.566(7) | 90 |
| $\gamma$ [°] | 90 | 120 |
| $V$ [Å$^3$] | 2984.0(3) | 5.518.7(6) |
| $Z$ | 4 | 6 |
| $D_c$ [Mg·m$^{-3}$] | 1.787 | 1.612 |
| μ [mm$^{-1}$] | 0.999 | 0.894 |
| $F$(000) | 1636 | 2694 |
| Crystal size [mm] | 0.10 × 0.12 × 0.17 | 0.12 × 0.12 × 0.15 |
| θ range for data collection [°] | 3.39 to 28.47 | 3.69 to 28.43 |
| Ranges of $h,k,l$ | $-24 \le h \le 24$<br>$-11 \le k \le 11$<br>$-24 \le l \le 20$ | $-22 \le h \le 22$<br>$-23 \le k \le 19$<br>$-27 \le l \le 27$ |
| Reflections collected | 14322 | 12692 |
| Independent reflections | 3552 | 5313 |
| $R_{int}$ | 0.0429 | 0.0331 |
| Data/restraints/parameters | 3552/0/276 | 5313/4/341 |
| GOF($F^2$) | 1.101 | 1.078 |
| Final $R_1/wR_2$ indices [$I > 2\sigma(I)$] | 0.0374/0.0868 | 0.0435/0.1161 |
| Largest diff. peak/hole [e·Å$^{-3}$] | 0.405/−0.999 | 0.798/−0.605 |

ligands, the perchlorate anions and one of the two ethanol molecules were refined with anisotropic displacement parameters. Hydrogen atoms were included from the geometry of the molecules and were then refined isotropically. The three residual density peaks positioned about a threefold axis were modelled as the second ethanol molecule. For refinement of the respective position of this EtOH molecule three distance restraints — C−C = 1.44(1), C−O = 1.42(1) and C···O = 2.38(1) Å — were applied.[82] The oxygen and carbon atoms were refined isotropically. A refinement with a freely established occupancy factor showed the partial occupation of this position. A consideration of the presence of these additional small amounts of ethanol molecules (ca. 0.4 ethanol molecules per formula unit) solvating the crystal lattice of **3** leads to agreement with the results of the elemental analysis. CCDC-232496 (**2**) and -232497 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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