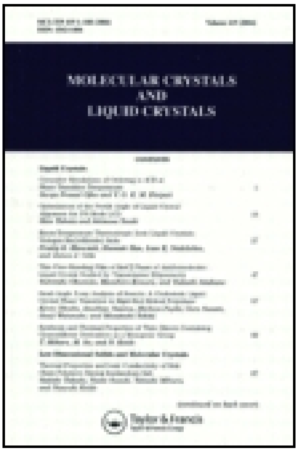

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Synthesis, Characterization and Supramolecular Structure of Two New Isotypic Coordination Polymers: Poly-Bis(μ_2-ethane-1,2-diyl bis(pyridine-3-carboxylate)κ^2N,N′-Bis(aquo)-Copper(II)X_2 ($X = ClO_4^-$; NO_3^-)

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Synthesis, Characterization and Supramolecular Structure of Two New Isotypic Coordination Polymers: Poly-Bis(μ_2-ethane-1,2-diyl bis(pyridine-3-carboxylate)κ^2N,N′–Bis(aquo)-Copper(II)X_2 ($X = ClO_4^-$; NO_3^-)

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Two novel coordination polymers, $\{[CuL_2(H_2O)_2]X_2\}_n$, with L = ethane-1,2-diyl bis(pyridine-3-carboxylate) and $X = ClO_4^-$; NO_3^- have been prepared by self-assembly of Cu(II) salts with L in THF/H_2O system. The IR, TGA, and the reflectance spectra in the solid state have been recorded, and both complexes were structurally characterized by X-ray crystallography confirming that the complexes are one-dimensional coordination isotypic polymers, and L acts in a μ_2-N,N′-bidentate fashion to link Cu(II) cations to form a double-stranded chain along [001]. The main structural motifs difference between both compounds is related to supramolecular self-assembly.

Keywords Copper(II) coordination polymers synthesis; crystal structure; thermal and spectroscopic properties

Introduction

The rational design and construct of functional coordination polymers have recently witnessed explosive growth in the areas of inorganic chemistry, coordination chemistry, crystal engineering, and materials science, not only due to their intrinsic aesthetic value but also their potential applications in catalysis, gas storage, molecular adsorption, optical and magnetic materials [1–5]. In general, the construction of these polymers is influenced by many factors such as the coordination geometry of metal center, the ligand nature, solvent,

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template, counter anions, temperature, and other factors. Among these, the judicious selection of appropriate ligands plays a key role in the manipulation of the structures of coordination polymers [6,7]. Although the overall structure is predominantly controlled by the coordination preferences of the transition metal and the ligand building blocks, more subtle effects such as anion control [8] and π–π stacking interactions [9] have been seen to have a profound effect upon network topology. Here, we report on the syntheses of two copper complexes, by reaction of the ditopic flexible ethane-1,2-diyl bis(pyridine-3-carboxylate) ligand, and copper salts with perchlorate and nitrate anions. Considering the different conformations exhibited by this type of ligand, its capability of forming hydrogen bonds with the anions and solvent molecules, as well as the potential π–π stacking interactions between fragments pyridine-3-carboxylate, we think that the products should present interesting structural features. Only a few compounds with this ligand have been reported [10].

Experimental

All chemicals used in this work were analytical reagent grade and employed as supplied, without further purification, except the ligand, which was synthesized by us [11]. Single crystals suitable for X-ray diffraction study for the compounds 1 and 2 were obtained after slow diffusion of 27.1 mg (0.1 mmol) of ethane-1,2-diyl bis(pyridine-3-carboxylate) dissolved in THF (5 ml), through a mixture water: THF 1:5, until getting in contact with a solution of water (5 ml) containing 36.9 mg (0.1 mmol) of metal salts, $Cu(ClO_4)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$, respectively. The FT–IR (KBr) ν cm^{-1} for compounds 1 and 2: 3521 br, 3125 w, 2987 w, 1733 m, 1651 w, 1612 m, 1444 m, 1370 m, 1103 m, 845 w, 745 m, 521 m and 3473 s, 3080 w, 3047 w, 2960 w, 1726 s 1612 m, 1441 s, respectively.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-893340 and CCDC-893341 for compounds 1 and 2, respectively (data copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44–1223-336–033; e-mail: deposit@ccdc.cam.ac.uk).

For compound 1, diffraction data were collected on Bruker-Nonius KappaCCD diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Frames were collected with the COLLECT program [12], indexed, processed and the files scaled together using the DENZO-SMN program [13].

For compound 2, diffraction data were collected on TOE IPDS II two-circle-diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Frames were collected, indexed, processed and the files scaled together using the X-area program [14]. In both compounds, the absorption correlation was applied using a MULABS method based on multiple scanned reflections on PLATON program [15]. The structure solution and refinement process were made using the SHELXS97 program [16]. In both compounds, all non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least squares procedures on F^2. Hydrogen atoms were treated by mixed refinement and refined allowing to ride on their parent atoms with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. Relevant crystal data, experimental conditions, and the final refined parameters are listed in Table 1. Infrared spectra were obtained as KBr pellets with a Thermo-Nicolet Avatar 330 FT–IR spectrometer.

Results and Discussion

Flexible ligands containing N-donor groups have attracted considerable interest for their wide-ranging properties and are usually the typical building elements in coodination

Table 1. Structure determination summary for $C_{28}H_{28}CuN_6O_{16}$ (compound 2) and $C_{28}H_{28}Cl_2CuN_4O_{18}$ (compound 1)

Empirical formula	$C_{28}H_{28}CuN_6O_{16}$	$C_{28}H_{28}Cl_2CuN_4O_{18}$		
Formula weight	768.10	842.98		
Temperature	173(2) K	293(2) K		
Wavelength	0.71073 Å	0.71073 Å		
Crystal system	Triclinic	Triclinic		
Space group	P –1	P –1		
Unit cell dimensions	$a = 7.3118(7)$ Å	$\alpha = 92.109(7)^\circ$	$a = 7.7740(16)$ Å	$\alpha = 89.34(3)^\circ$
	$b = 10.0597(8)$ Å	$\beta = 105.804(7)^\circ$	$b = 10.092(2)$ Å	$\beta = 70.69(3)^\circ$
	$c = 11.2579(10)$ Å	$\gamma = 98.416(7)^\circ$	$c = 11.627(2)$ Å	$\gamma = 80.40(3)^\circ$
Exptl. crystal description	Plate	Block		
Exptl. crystal color	Light blue	Blue		
Volume	785.63(12) Å^3	847.9(3) Å^3		
Z	1	1		
Density (calculated)	1.624 mg/m^3	1.651 mg/m^3		
Absorption coefficient	0.784 mm^{-1}	0.889 mm^{-1}		
F(000)	395	431		
Crystal size	0.25 × 0.19 × 0.09 mm^3	0.40 × 0.25 × 0.20 mm^3		
Theta range for data collection	3.46° to 25.62°	2.81° to 27.49°		
Index ranges	$-8 < = h < = 8, -12 < = k < = 12, -11 < = l < = 13$	$-10 < = h < = 9, -10 < = k < = 13, -14 < = l < = 15$		
Diffrn. measurement device type	TOE IPDS II two-circle-diffractometer	Nonius KappaCCD area-detector diffractometer		
Diffrn. measurement method	ω	ω		

(*Continued on next page*)

Table 1. Structure determination summary for $C_{28}H_{28}CuN_6O_{16}$ (compound 2) and $C_{28}H_{28}Cl_2CuN_4O_{18}$ (compound 1) (*Continued*).

Empirical formula	$C_{28}H_{28}CuN_6O_{16}$	$C_{28}H_{28}Cl_2CuN_4O_{18}$
Reflections collected	8041	8176
Independent reflections	2918 [R(int) = 0.0655]	3811 [R(int) = 0.0442]
Completeness to theta = 25.00°	99.4%	99.1%
Absorption correction	MULABS [13]	MULABS [13]
Max. and min. transmission	0.9328 and 0.8282	0.8422 and 0.7175
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2918/1/235	3811/0/249
Goodness-of-fit on F^2	0.936	1.084
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0419$, $wR_2 = 0.0905$	$R_1 = 0.0566$, $wR_2 = 0.1027$
R indices (all data)	$R_1 = 0.0601$, $wR_2 = 0.0954$	$R_1 = 0.0767$, $wR_2 = 0.1108$
Largest diff. peak and hole	0.566 and −0.424 e.Å^{-3}	0.382 and −0.348 e.Å^{-3}
Refine ls. hydrogen treatment	Treated by mixed refinement	Treated by mixed refinement
Computing structure solution	SHELXS97 [14]	SHELXS97 [14]
Computing structure refinement	SHELXL97 [14]	SHELXL97[14]

R indices: $R_1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$; $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (0.0450P)^2 + 0.0000P]$, where $P = [(F_o{}^2) + 2F_c{}^2)]/3$ for $C_{28}H_{28}CuN_6O_{16}$;

$w = 1/[\sigma^2(F_o{}^2) + (0.0268P)^2 + 0.8560P]$, where $P = [(F_o{}^2) + 2F_c{}^2)]/3$ for $C_{28}H_{28}Cl_2CuN_4O_{18}$; Goodness-of-fit $= \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(N_{obs} - N_{parameters})\}^{1/2}$.

networks, since they can adopt various coordination modes and geometries. The flexible ligand ethane-1,2-diyl bis(pyridine-3-carboxylate), L, can adopt either *trans* or *gauche* conformations [11]. To understand the coordination chemistry of this flexible L ligand, and the counter ion effect upon network topology, we have employed this ligand in the reaction with Cu(II) salts under diffusion conditions and we have obtained two isotypic one-dimensional coordination polymer, $\{[Cu(C_{14}H_{12}N_2O_4)_2(H_2O)_2(ClO_4)_2]\}_n$, (compound 1) and $\{[Cu(C_{14}H_{12}N_2O_4)_2(H_2O)_2(NO_3)_2]\}_n$ (compound 2), (Fig. 1). Both compounds are stable in air and insoluble in water and most organic solvents. As a result of that, no additional measurements in solution could be performed. An FT–IR spectroscopic study for compounds 1 and 2 shows a increased stretching frequency for the C=N group (1612 cm^{-1}) compared with the free ligand (1589 cm^{-1}) due to coordination of the Cu(II) ion through the nitrogen atom of the pyridine ring [11]. A broad band at about 1100 cm^{-1} and 1441 cm^{-1} can be ascribed to the uncoordinated perchlorate and nitrate anion, respectively. The reflectance spectra in the solid state (Fig. 2) were recorded in the range 200–1000 nm. The visible reflectance spectra for compounds 1 and 2 contain only one band at 579 and 584 nm, respectively, characteristic of a d^9 electronic configuration.

Copper(II) $dx_2–y_2 \rightarrow$ dxz dyz transition via ($2B_{1g} \rightarrow 2E_g$) in a square-planar geometry (or elongated octahedron), with the unpaired electrons mainly located in the $dx_2–y_2$ orbital [17]. When in a complex of octahedral symmetry, the aqua ligands are in transposition with respect to the metal, suffer a tetragonal distortion, the orbital of these ligands interact more weakly on the z-axis, those z-components orbitals (dz^2, dxz, dyz) will be stabilized and those without z component will be destabilized (Jahn–Teller effect), causing a splitting of the orbital T_{2g} and E_g. For compounds 1 and 2, there are one band to 325 and 318 nm, respectively, and two bands to 236, 283 and 231, 278 nm, respectively, corresponding to the intraligand transfer-charge $\pi \rightarrow \pi^*$ transitions.

The thermal stability for compound 2 was studied using thermal gravimetric analysis (TGA) from 25°C to 800°C under flowing nitrogen at a heating rate of 10°C min^{-1} (Fig. 3). In Fig. 3, the right vertical scale is the first derivative of loss sample weight respect to time. The decomposition thermal process is produced on three stages. The first step weight loss occurs from 60°C to 230°C and corresponds to the loss of two coordination water molecules (calcd. 4.65%; found 4.69%). The IR spectrum of 1 shows a broad vibration band at ~3080 cm^{-1} assigned to stretching O–H of the water molecules. The second step weight loss occurs from 230°C to 290°C that is attributable to the complete removal of two ligand molecules (calcd. 69.8%; found 70.87%). The third step weight loss occurs from 290°C to 430°C that is attributable to the decomposition of two nitrate anions (calcd. 15.5%; found 16.15%). The final residue is attributable to copper compound of unknown composition. The thermal stability for compound 1 cannot be studied due to the explosive properties of perchlorate anion.

The asymmetric unit for compounds 1 and 2 contains one ligand molecule, one water molecule, one Cu(II) ion, which lies on an inversion center, one perchlorate and nitrate anion, respectively. In both compounds, the Cu(II) ion is six coordinated by four N atoms symmetry-related from ethane-1,2-diyl bis(pyridine-3-carboxylate) ligand in the equatorial plane (for compound 1: Cu–N1 = 2.052(2) and Cu–N2 = 2.062(2) Å; for compound 2: Cu–N1 = 2.030(2) and Cu–N2 = 2.066(2) Å) and two aqua ligands in the apical positions (Cu–O9 = 2.516(3) Å; Cu–O9 = 2.566(4) Å) for 1 and 2, respectively. The *cis* N–Cu–N bond angles are 91.15(10)° and 88.85(10)° for 1 and 91.09(9)° and 88.41(9)° for 2, displaying a distorted octahedral coordination environment. The Cu–N distances are typical for copper(II) aqua-complexes with pyridine ligands [18–20]. Conversely, the Cu–O distances are longer than the sum of covalent radii in both compounds. It is of interest

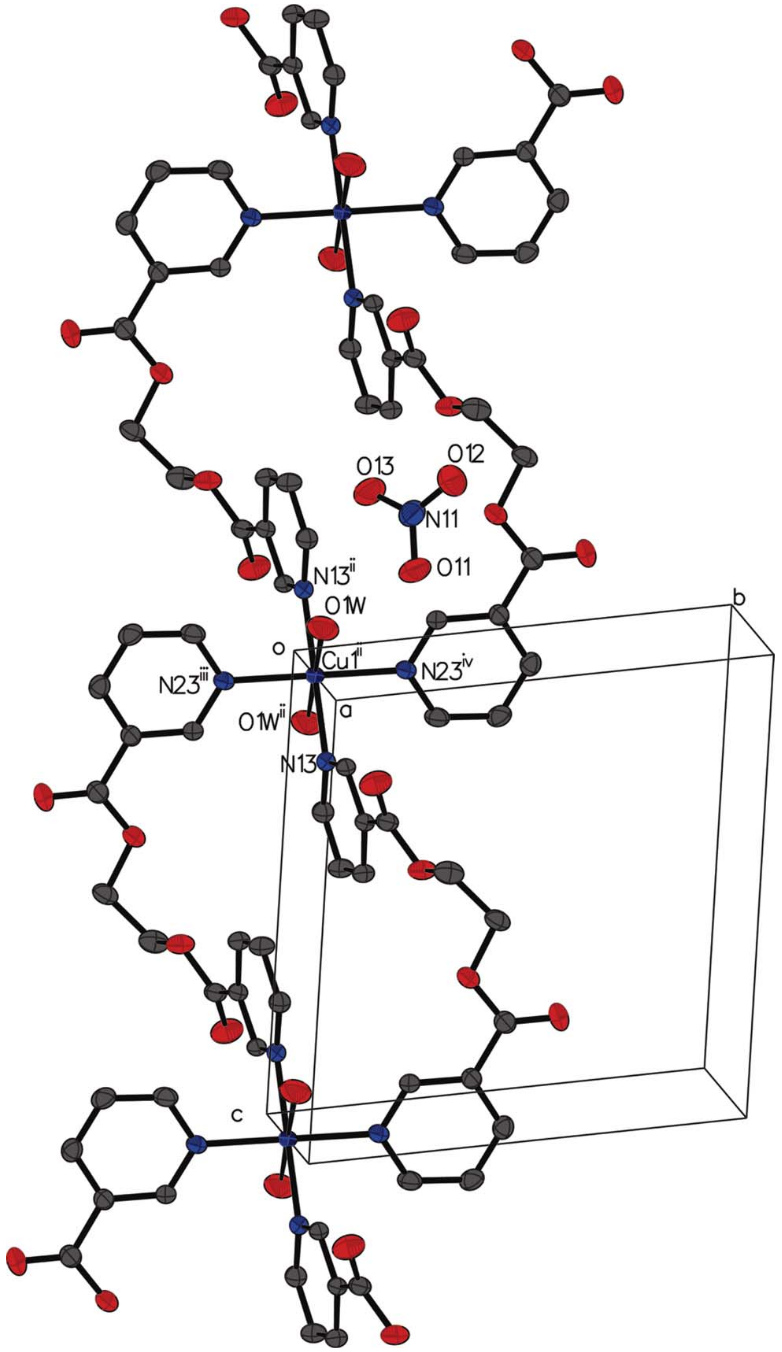

Figure 1. Part of the polymeric structures for compounds 1 and 2 showing a double-stranded chain, along c axis, and the metallacycle formed by two copper atoms and two ligands. Symmetry code for compound 1: i: (1−x, 1−y, 1−z). Symmetry code for compound 2: ii: (1−x, −y, −z); iii: (1−x, −y, 1−z); iv: (x, y, −1+z).

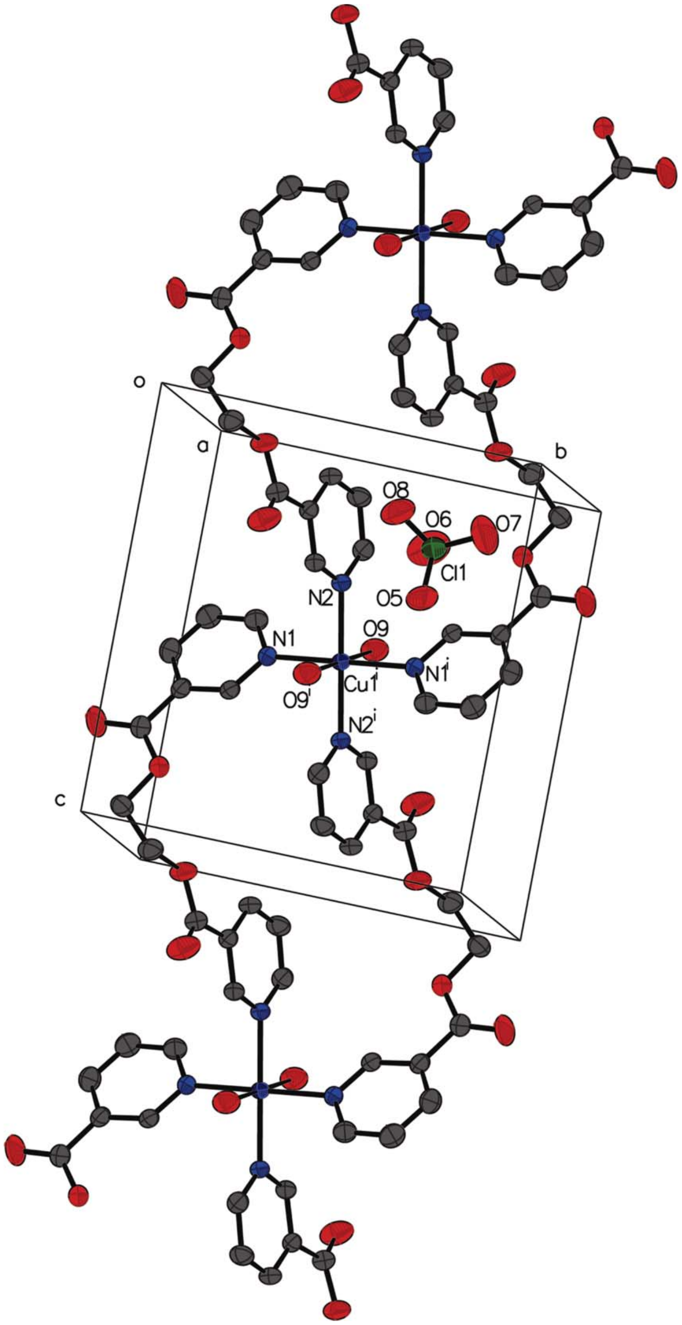

Figure 1. (Continued)

to note that the CuN_4O_2 chromophore provides strong corroboration of the Jahn–Teller predictions of elongation along the axial direction [21,22]. A search of the Cambridge Structural Database (CSD; Version 5.33) [23], for similar CuN_4O_2 chromophore yielded six structures with distances (Cu–O) ranging from 2.515(5) to 2.638(6) Å [24–28].

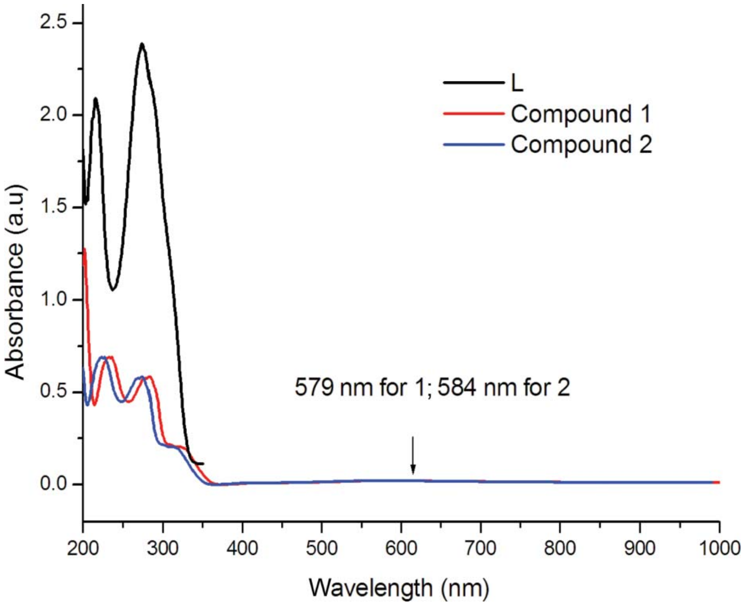

Figure 2. The reflectance spectra in the solid state.

In both compounds, the ligand, (L) acts in a μ_2-N,N′-bidentate fashion to link Cu(II) cations to form a double-stranded chain along [001]. The ethylene moiety of L retains the gauche conformation [11]. The dihedral angles between the two pyridyl rings are 81.14(15)° and 77.08(15)° for 1 and 2, respectively. An entirely similar pattern of angles and distances is observed for L in both compounds. Each copper center is bridged by two ligands to form

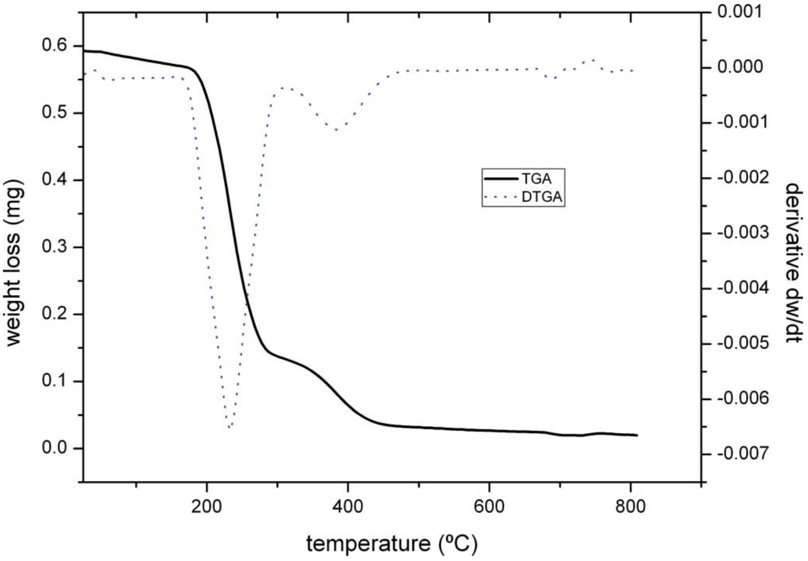

Figure 3. TGA curve for compound 2.

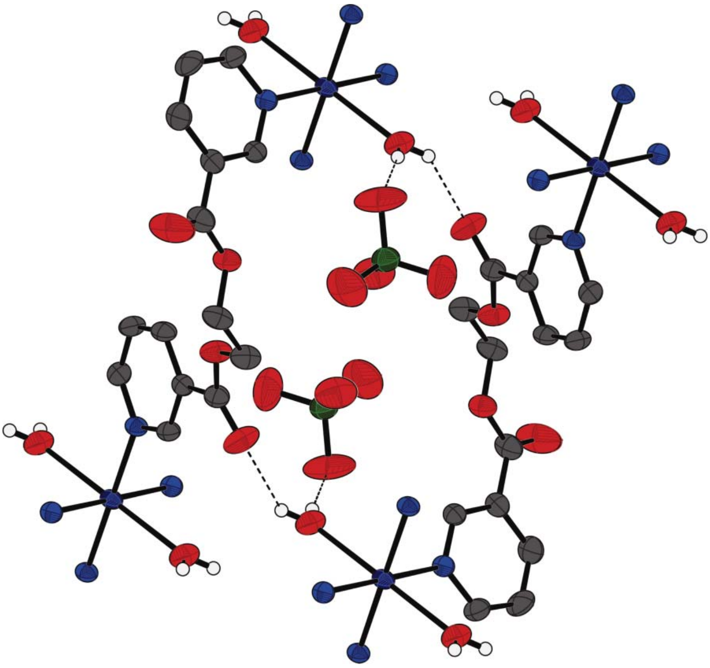

Figure 4. Part of the crystal structure of compound 1, showing the formation of a $R^2_2(26)$ rings. For the sake of clarity, H atoms not participating in the motif shown have been omitted.

a double-stranded chain, along c axis for both compounds. As in other double-stranded chain complexes, two copper atoms and two ligands form a metallacycle (Fig. 1). The main structural motifs difference between both compounds is related to supramolecular self-assembled, in the compound 1, the aqua ligands link neighboring chains by weak O–H···O^i (carbonyl groups, H9A···O4^i: 2.38(5) Å, O9···O4^i: 3.008(4) Å, O9–H9A···O4^i: 140(5)°; H9B···O5^i: 2.03(6) Å, O9···O5^i: 2.862(5) Å, O9–H9B···O5^i: 168(6)°; symmetry code: (i) x+1, y, z) hydrogen bonds forming $R^2_2(26)$ rings [29] generating a two-dimensional supramolecular aggregate (Fig. 4). One strong hydrogen bond is observed between the perchlorate anion and one aqua ligand. In the compound 2, the aqua ligands are linked by two strong intermolecular O–H···O (H1WA···O1: 1.852(1) Å, O1W···O1: 2.708(4) Å, O1W–H1WA···O1: 171(4)°; H1WB···O1W^{ii}: 2.10 Å, O1W···O1W^{ii}: 2.961(6) Å, O1W–H1WB···O1W^{ii}: 155.1°; symmetry code: (ii) −x, −y, −z) hydrogen bonds with graph-set motif $R^2_2(4)$ [29] and link neighboring chains by weak O–H···O hydrogen bonds forming $R^2_2(34)$ rings generating a two-dimensional supramolecular aggregate in the (1 1 0) plane (Fig. 5). One strong hydrogen bond is observed between the nitrate anion and one aqua ligand.

The use of different anions to generate diversity in solid state has been well documented in the literature, and the size of counter ions affects the overall supramolecular interactions in the crystalline state of the polymers [30,31], so the observed difference in supramolecular self-assembled of the compounds 1 and 2 could be related to size of the counter anions (ClO_4^- (82 Å^3); NO_3^- (64 Å^3)), which are located between the polymeric chains (Figs. 4 and 5).

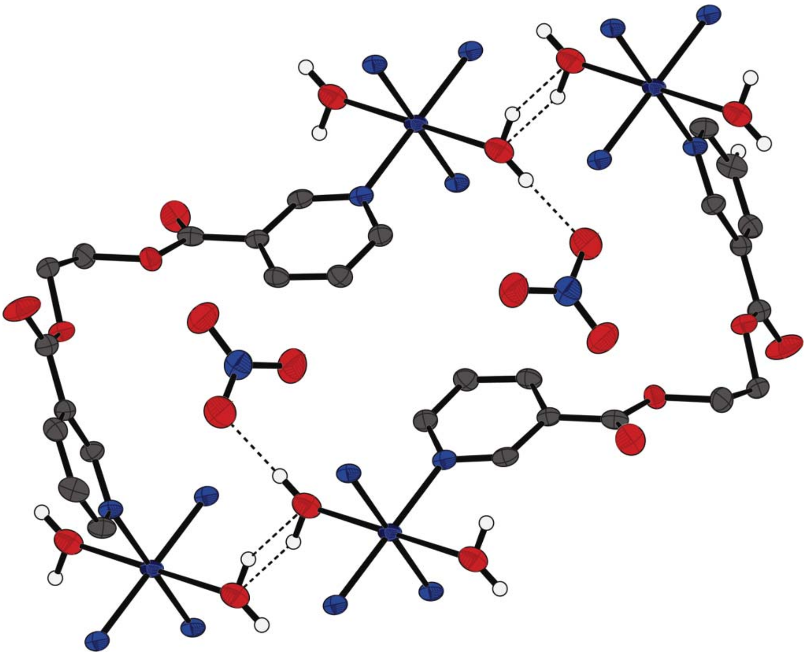

Figure 5. Part of the crystal structure of compound 2, showing the formation of a $R^2_2(4)$ and $R^2_2(34)$ rings. For the sake of clarity, H atoms not participating in the motif shown have been omitted.

Conclusion

The use of different anions to generate diversity in solid state has been well documented in the literature, so in this paper, we have shown the main differences between both isotypic compounds are related to subtle effects of the anions control upon network topology.

Acknowledgments

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