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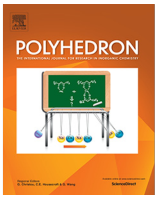

1-(4-Carboxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid – A versatile ligand for the preparation of coordination polymers and mononuclear complexes

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ABSTRACT

The straightforward and facile synthetic approaches towards four coordination polymers, $\{[CdL(H_2O)]\cdot 0.5H_2O\}_n$, $\{[Cd_2L_2(H_2O)_2(4,4'\text{-bipy})]\cdot 4H_2O\}_n$, $\{[Cd_2L_2(H_2O)_2(4,4'\text{-azpy})]\cdot 3H_2O\}_n$ and $\{[CoL(H_2O)_3]\cdot 2.5H_2O\}_n$ (4,4′-bipy = 4,4′-bipyridine; 4,4′-azpy = 4,4′-azopyridine), based on the polydentate ligand 1-(4-carboxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid (LH_2) and Cd(II) and Co(II) ions are reported. In addition, two mononuclear complexes, $[Cu(HL)_2(DMA)]$ and $[Cu(HL)_2(H_2O)_2]$, derived from the same ligand and the Cu(II) ion have been prepared. The coordination compounds have been characterized by infrared spectroscopy, thermogravimetry, powder X-ray diffraction and elemental analysis. Single crystal X-ray structures for each of these coordination compounds have been established. The specific surface of the 3D Cd(II)- and Co(II)-derived coordination polymers, determined through nitrogen adsorption, is negligible ($S_{BET} < 25\ m^2/g$).

1. Introduction

Owing to the interesting properties, considerable potential and practical applications of coordination polymers, significant effort has been devoted by many research groups to the preparation of novel metal–ligand coordination entities in recent years. The combination of structurally different ligands with various metal ions can theoretically lead to a virtually infinite number of coordination polymers. Within this vast category of coordination polymers, coordination polymers generically known as metal–organic frameworks (MOFs) have gradually become a privileged subclass because of their frequent porosity, which makes these materials valuable for the storage of gases [1,2], gas separation and purification [3,4], or catalysis [5,6]. In addition, MOFs have been designed to incorporate fluorogenic chemical functionalities (either the ligand, or the metal ion, or both) with the view to render them useful for various sensing applications, *i.e.* the detection of biomolecules, environmental toxins, explosives, etc. [7,8]. Recently, several coordination polymers derived from 1-(4-carboxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid and incorporating either common transition metal ions [9] or lanthanides [10,11] have been shown to be luminescent and exhibit sensing properties towards xanthine, colchicine, simple phenols, bicromate and metal ions. As an extension of these investigations, the present study explores the versatility of the same rigid, triazole-based dicarboxylate ligand in the generation of new coordination polymers and complexes, whose structure and properties were subsequently examined.

2. Experimental

2.1. Materials and methods

Methyl 4-aminobenzoate, $NaNO_2$, NaN_3, 36.5% aq. HCl, sodium, NaOH, LiOH, $Cd(NO_3)_2\cdot 4H_2O$, $Co(NO_3)_2\cdot 6H_2O$ and 4,4′-bipyridine (**10**) (4,4′-bipy) were obtained from Alfa Aesar (Ward Hill, MA, USA), while ethyl acetoacetate (**2**), 4,4′-azopyridine (**11**) (4,4′-azpy) and $Cu(NO_3)_2\cdot 3H_2O$ were provided by Merck–Sigma–Aldrich (Darmstadt, Germany). These chemical reagents were used without further purification. The solvents (abs. ethanol, *N.N*-dimethylformamide (DMF), *N.N*-dimethylacetamide (DMA),

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dimethylsulfoxide (DMSO), methanol) were purchased from VWR International (Radnor, PA, USA). The melting point was taken on a MEL-TEMP capillary melting point apparatus and is uncorrected. NMR spectra were recorded in DMSO d_6 on a Bruker Avance III 400 instrument operating at 400.1 and 100.6 MHz for ^{1}H and ^{13}C nuclei, respectively. Chemical shifts are reported in ppm relative to the residual solvent peak (^{1}H: 2.512 ppm, and ^{13}C: 39.48 ppm). Fourier Transform-Infrared (FT-IR) spectra were taken on a FT-IR Bruker Vertex 70 spectrophotometer in the transmission mode using KBr pellets. The intensity of the absorption bands is given as very strong (vs), strong (s), medium (m), weak (w) and very weak (vw). Elemental analysis was performed on a Vario EL III CHNS analyzer. Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku MiniFlex 600 diffractometer using monochromated CuKα-radiation (λ = 1.541874 Å) in the angular range 5–50° (2θ) with a scanning step of 0.01° and a recording rate of 1 deg min^{-1}, at room temperature. Diffractograms were plotted using Match! software from Crystal Impact (Bonn, Germany). Mercury software was used to generate the simulated PXRD patterns. Thermogravimetric (TG) measurements were performed with a STA 449F1 Jupiter instrument. Sensitivity calibrations in the temperature range 30–700 °C were carried out with indium. Approximately 20 mg of the solid samples were weighed and placed in aluminum pans and the TG experiments were run within a temperature range of 30 to 700 °C, with a heating rate of 5 °C/min, under an atmosphere of dry nitrogen at a flow rate of 50 mL/min. The data was processed with Netzsch Protens 4.2 software. Nitrogen adsorption experiments were carried out with a Quantachrome NOVA 3200e surface area and pore size analyzer. Prior to the N_2 isotherm measurements at 77 K, the samples were activated by solvent exchange and degassed at 100 °C under high vacuum for 3 h. For the adsorption measurements, an amount in the range of 50–80 mg of the samples was weighed before and after the degassing procedure to confirm the removal of any retained solvent.

2.2. Synthesis

2.2.1. Synthesis of 1-(4-carboxyphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylic acid (H_2L) (3)

To a solution of sodium ethoxide (freshly prepared from sodium (460 mg, 20 mmol) and 50 mL of abs. ethanol), ethyl acetoacetate (**2**) (2.6 g, 20 mmol) was added, followed by a solution of methyl 4-azidobenzoate (**1**) [12] (3.54 g, 20 mmol) in abs. ethanol (25 mL). The mixture was heated at reflux temperature for 2 h, then allowed to reach room temperature. The solid was filtered, washed with abs. ethanol (2 × 25 mL) and air-dried at room temperature. The material was then added to 0.2 M NaOH (200 mL) and the solution was heated at reflux temperature for 5 h. After the cold reaction mixture had been filtered, the solution was brought to pH 5–6 by the dropwise addition of acetic acid under efficient stirring. The resulting solid was filtered, washed thoroughly with distilled water and air-dried at room temperature to afford the title compound as colorless microcrystals (3.4 g, 69%); Mp: 229–230 °C (dec.). FT-IR (ν, cm^{-1}): 3411 m, 2868w, 2640w, 2530w, 1694vs, 1608 m, 1593w, 1516w, 1473 m, 1447w, 1313w, 1287 s, 1234w, 1121 m, 989 m, 864w, 806 m, 776 m. ^{1}H NMR (400.1 MHz, DMSO d_6) δ, ppm: 2.51 (s, 3H), 7.80 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 2H), 13.30 (br s, 2H). ^{13}C NMR (100.6 MHz, DMSO d_6) δ, ppm: 9.8, 125.4, 130.6, 132.0, 136.8, 138.6, 139.2, 162.5, 166.3. *Anal.* Calcd. for $C_{11}H_9N_3O_4$ (%): C, 53.44; H, 3.67; N, 17.00. Found: C, 53.72; H, 3.49; N, 16.73.

2.2.2. Synthesis of catena-poly[[(aqua-κO)cadmium(II)-μ3-((1-(4-carboxylatophenyl-κ^{2}O,O′)-5-methyl-1H-1,2,3-triazole-κN^3-(4-μ-carboxylato-κ^{3}O,O:O′)(2-))] hemihydrate] {[CdL(H2O)]·0.5H2O}n (4)

To a solution of 1-(4-carboxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid (H_2L) (**3**) (74.2 mg, 0.3 mmol, 1 equiv.) in DMF (12 mL) contained in a 20 mL Duran™ glass vial with a PTFE-coated PBT screw cap, a solution of $Cd(NO_3)_2{\cdot}4H_2O$ (370.2 mg, 1.2 mmol, 4 equiv.) in water (3 mL), followed by 65% HNO_3 (3 drops) were added. The vial was heated at 80 °C for 72 h and then allowed to slowly reach room temperature. The resulting solid was filtered, washed sequentially with DMF (2 × 5 mL) and methanol (3 × 10 mL), then air-dried to afford colorless block crystals that were suitable for single crystal X-ray diffraction. Yield 106 mg (91.6% based on H_2L). FT-IR (ν, cm^{-1}): 3585 m, 3279 m, 3159 m, 2928w, 1680 s, 1588vs, 1544vs, 1399vs, 1312 s, 1242 s, 1136 m, 1098 m, 1011 m, 866 s, 847 s, 787 s, 707 m, 673w, 543w, 458 m. *Anal.* Calcd. for $C_{33}H_{30}Cd_3N_9O_{16.5}$ (%): C, 34.22; H, 2.59; N, 10.89. Found: C, 34.54; H, 2.37; N, 11.15.

2.2.3. Synthesis of catena-poly[[(aqua-κO)cadmium(II)-hemi-μ-(4,4′-bipyridine-κN)-μ3-(1-(4-carboxylatophenyl-κ^{2}O,O′)-5-methyl-1H-1,2,3-triazole-κN^3-(4-μ-carboxylato-κ^{3}O,O:O′)(2-))] dihydrate] {[Cd2L2(H2O)2(4,4′-bipy)]·4H2O}n (5)

The ligand H_2L **3** (37.1 mg, 0.15 mmol, 1 equiv.) was dissolved in DMF (6 mL) in a 20 mL Duran™ glass vial with a PTFE-coated PBT screw cap. Separately, 4,4′-bipyridine (**10**) (11.7 mg, 0.075 mmol, 0.5 equiv.) was dissolved in 96% ethanol (2 mL) and $Cd(NO_3)_2{\cdot}4H_2O$ (185.1 mg, 0.6 mmol, 4 equiv.) was dissolved in water (4 mL). The solution of the neutral ligand was layered over the solution of the dicarboxylic ligand, followed by the solution of the Cd(II) salt. The vial was heated at 80 °C for 72 h and then allowed to slowly reach room temperature. The resulting solid was filtered, washed sequentially with DMF (2 × 5 mL) and methanol (3 × 10 mL), then air-dried to yield colorless acicular crystals. Yield 59 mg (80.3% based on H_2L). FT-IR (ν, cm^{-1}): 3413 s, 3099w, 2927w, 1605vs, 1562vs, 1448 s, 1381vs, 1308 m, 1283 m, 1230w, 1134w, 1065w, 1009 m, 876 m, 844 m, 789 s, 708 m, 631 m, 546 m, 510 m, 456 m. *Anal.* Calcd. for $C_{16}H_{17}CdN_4O_7$ (%): C, 39.20; H, 3.47; N, 11.43. Found: C, 39.51; H, 3.72; N, 11.74.

2.2.4. Synthesis of catena-poly[[(aqua-κO)cadmium(II)-hemi-μ-(4,4′-azopyridine-κN)-μ3-(1-(4-carboxylatophenyl-κ^{2}O,O′)-5-methyl-1H-1,2,3-triazole-κN^3-(4-μ-carboxylato-κ^{3}O,O:O′)(2-))] sesquihydrate] {[Cd2L2(H2O)2(4,4′-azpy)]·3H2O}n (6)

1-(4-Carboxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid (**3**) (37.1 mg, 0.15 mmol, 1 equiv.) was dissolved in DMF (6 mL) in a 20 mL Duran™ glass vial with a PTFE-coated PBT screw cap. Separately, 4,4′-azopyridine (**11**) (27.6 mg, 0.15 mmol, 1 equiv.) was dissolved in DMF (2 mL) and $Cd(NO_3)_2{\cdot}4H_2O$ (185.1 mg, 0.6 mmol, 4 equiv.) was dissolved in water (4 mL). The solution of the neutral ligand was layered over the solution of the dicarboxylic ligand, followed by the solution of the Cd(II) salt. The vial was heated at 80 °C for 72 h, and then allowed to slowly reach room temperature. The resulting solid was filtered, washed sequentially with DMF (2 × 5 mL) and methanol (3 × 10 mL), then air-dried to afford dark orange crystals. Yield 64 mg (86.3% based on H_2L). FT-IR (ν, cm^{-1}): 3369 m, 3065w, 2929vw, 1665 m, 1606vs, 1562vs, 1444 s, 1383vs, 1305 m, 1282 m, 1011 m, 873 m, 856 m, 840 s, 788 m, 705 m, 579 m, 546 m. *Anal.* Calcd. for $C_{16}H_{15.95}CdN_5O_{6.4}$ (%): C, 38.84; H, 3.22; N, 14.16. Found: C, 39.09; H, 2.98; N, 14.27.

2.2.5. Synthesis of [dimethylacetamido-κO-bis(1-(4-carboxyphenyl)-5-methyl-1H-1,2,3-triazole-(4-carboxylato-κ^{2}N^3,O)(1-))copper(II)] [Cu(HL)2(DMA)] (7)

Separately, the ligand H_2L **3** (37.1 mg, 0.15 mmol, 1 equiv.) was dissolved in DMA (4 mL), and $Cu(NO_3)_2{\cdot}3H_2O$ (145 mg, 0.6 mmol, 4 equiv.) was also dissolved in DMA (2 mL). The clear mixture obtained by combining the two solutions in a 10 mL glass vial with a PTFE-coated PP screw cap was heated at 80 °C for 72 h and then allowed to reach room temperature over several hours. The solid that formed during the heating stage was filtered and sequentially washed with DMA (2 × 5 mL) and methanol (3 × 10 mL), then air-dried to afford blue crystals. Yield 21 mg (43.5% based on H_2L). FT-IR (ν, cm^{-1}): 3416w, 2936w, 2870w, 2771w, 2571w, 2435w, 1935w, 1712 s, 1628 s, 1597vs, 1509 m, 1422 s, 1378 s, 1322 m, 1269 s, 1251 s, 1170 m, 1116 m, 1041 m, 1015 s, 864 m, 828 s, 804 s, 776 s, 696 m, 684w, 601w, 511 m, 440 m. *Anal.* Calcd. for $C_{26}H_{25}CuN_7O_9$ (%): C, 48.51; H, 3.88; N, 15.23. Found: C, 48.23; H, 3.59; N, 14.94.

2.2.6. Synthesis of [di(aqua-κO) bis(1-(4-carboxyphenyl)-5-methyl-1H-1,2,3-triazole-(4-carboxylato-κ^{2}N^3,O)(1-))copper(II)] [Cu(HL)$_2$(H$_2$O)$_2$] (8)

(1-(4-Carboxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid (**3**) (37.1 mg, 0.15 mmol, 1 equiv.) was dissolved in DMSO (6 mL) in a 20 mL Duran^{TM} glass vial with a PTFE-coated PBT screw cap. Separately, $Cu(NO_3)_2 \cdot 3H_2O$ (145 mg, 0.6 mmol, 4 equiv.) was dissolved in water (4 mL). The clear mixture produced by combining these two solutions was heated at 80 °C for 72 h, and then allowed to slowly reach room temperature. The material that separated was filtered and sequentially washed with DMSO (2 × 5 mL) and methanol (3 × 10 mL), then air-dried to afford light blue crystals. Yield 23 mg (51.8% based on H_2L). FT-IR (ν, cm^{-1}): 3512 s, 3445 m, 2944w, 2871w, 2785w, 2614w, 2487w, 1702 s, 1661vs, 1595 s, 1419 s, 1377vs, 1311 s, 1246vs, 1139 m, 1122 s, 1015 m, 858 m, 801 m, 774 s, 695 m, 685 m, 531 m, 494 m, 442 m. *Anal.* Calcd. for $C_{22}H_{20}CuN_6O_{10}$ (%): C, 44.59; H, 3.37; N, 14.18. Found: C, 44.82; H, 3.66; N, 13.91.

2.2.7. Synthesis of catena-poly[[tri(aqua-κO)cobalt(II)-μ$_3$-((1-(4-carboxylatophenyl-κ^{2}O,Ó)-5-methyl-1H-1,2,3-triazole-κN^3-(4-μ-carboxylato-κ^{3}O,O:Ó)(2-))]-hydrate(5/2)]{[CoL(H$_2$O)$_3$]·2.5H$_2$O}$_n$ (9)

Ligand **3** (37.1 mg, 0.15 mmol, 1 equiv.) was dissolved in a mixture of water (6 mL) and aqueous 0.1 M LiOH (3 mL) in a 20 mL Duran^{TM} glass vial with a PTFE-coated PBT screw cap under efficient stirring at 40–50 °C. Separately, $Co(NO_3)_2 \cdot 6H_2O$ (174.6 mg, 0.6 mmol, 4 equiv.) was dissolved in water (6 mL). The aqueous solution of the metal salt was added to the solution of the ligand, and the mixture was warmed to 80 °C over 1 h. The mixture was kept at 80 °C for 72 h, and then gradually cooled to room temperature over 14 h. The solid was filtered, washed thoroughly with water and air-dried to afford large red block crystals that were suitable for single crystal X-ray diffraction. Yield 45 mg (74.4% based on H_2L). FT-IR (ν, cm^{-1}): 3400 s, 3187 m, 2926w, 1615vs, 1553 s, 1425 s, 1400vs, 1381 s, 1310 s, 1244 m, 1137 m, 1016 m, 781 m. *Anal.* Calcd. for $C_{11}H_{18}CoN_3O_{9.5}$ (%): C, 32.73; H, 4.46; N, 10.41. Found: C, 32.39; H, 4.69; N, 10.11.

2.3. X-ray crystallographic measurements

Intensity data for coordination polymer **4** were collected with an Oxford Diffraction SuperNova diffractometer using hi-flux micro-focus Mo Kα radiation and for compounds **5**–**9** on an Oxford-Diffraction XCALIBUR E CCD device equipped with Mo Kα radiation. The unit cell determination and data integration were carried out using the CrysAlisPro package from Oxford Diffraction [13]. Multi-scan absorption corrections for all the crystals were applied. The structures were solved using the intrinsic phasing methods of SHELXT [14] and refined by full-matrix least-squares minimization on F^2 with SHELXL [15] in the graphical interface of Olex2 program [16]. Hydrogen atoms were placed at calculated positions and refined in the riding model, except those attached to oxygen atoms, which were located from Fourier maps and refined accordingly to the intermolecular interactions. The positional parameters of disordered non-hydrogen atoms were refined by applying combined anisotropic/isotropic refinement in combination with imposed restrains on positional and displacement parameters. The molecular plots were obtained using the Olex2 program. Crystallographic data are listed in Table 1, whilst bond lengths and angles can be found in Table S1 in the Supplementary Information (SI). CCDC: 2,024,571 (**4**), 2,024,577 (**5**), 2,024,578 (**6**), 2,024,579 (**7**) and 2,024,580 (**8**).

3. Results and discussion

3.1. Synthesis and characterization of ligand 3, coordination polymers 4–6 and 9, and complexes 7 and 8

Ligand **3** has been obtained previously through a base-catalyzed triazole ring closure reaction that employed 4-azidobenzoic acid as the azide reagent [9,10]. Ligand **3** was prepared through a similar Dimroth cyclization in the present study, only this synthetic variant employed methyl 4-azidobenzoate (**1**) as the azide reagent instead of 4-azidobenzoic acid (Scheme 1). Methyl 4-azidobenzoate (**1**) required for this synthetic variant was prepared from methyl 4-aminobenzoate according to a reported procedure [12]. The crude product isolated from the Dimroth ring closure was a mixture of esters that consisted primarily of ethyl 1-(4-(ethoxycarbonyl)phenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylate (resulted via transesterification of the normal reaction product) and ethyl 1-(4-(methoxycarbonyl)phenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylate (the normal reaction product) as a minor component, according to NMR spectra. The mixture of esters was subsequently hydrolyzed under basic conditions to afford the ligand with moderate yield and excellent purity.

The structure of the key ligand **3** has been confirmed by NMR spectroscopy. The ^1H NMR spectrum of this compound (Fig. S1 in the SI) shows a sharp singlet at δ 2.56 ppm corresponding to the protons of the methyl group, two doublets appearing as an AA′BB′ spin system in the aromatic region of the spectrum, which are associated with the protons of the phenyl ring, and a broad offset signal integrating for two protons, which are attributed to the protons of the carboxyl groups. The aliphatic region of the carbon spectrum of ligand **3** (Fig. S2 in the SI) features the peak associated with the carbon atom of the methyl group at δ 9.77 ppm, whereas the two signals δ 166.32 and 162.47 ppm are attributed to the carbon atoms of the two distinct carboxyl groups. In addition, the correct number of six aromatic carbon atoms, belonging to the benzene and triazole rings, has also been identified in the carbon spectrum of compound **3**.

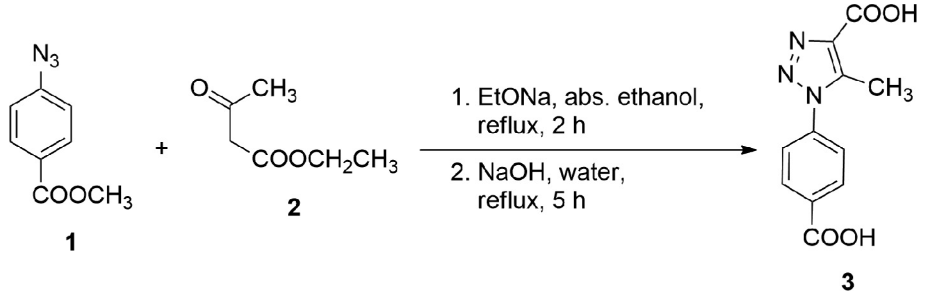
In order to obtain coordination polymers from this ligand that have topologies that are distinct from the ones already reported, numerous different experimental conditions have been tried for the solvothermal synthesis of novel crystalline complexes derived from ligand **3**. This approach led to the isolation of crystals that were appropriate for structure determination by single crystal X-ray diffraction for a new cadmium-based coordination polymer (**4**) when the reaction was performed in DMF in the presence of HNO_3 (Scheme 2).

In addition, nitrogen-containing neutral ligands, such as 4,4′-bipyridine (4,4′-bipy) and 4,4′-azopyridine (4,4′-azpy), which are able to function as pillars between the planes of a 2D coordination polymer and presumably yield porous MOFs, have been employed in the complexation experiments between ligand **3** and Cd(II) ions. To the best of our knowledge, no coordination polymers derived from ligand **3** and containing auxiliary ligands in their structure have been reported until now. Again, several reaction conditions were tried with the view to obtain crystalline coordination polymers that could be structurally characterized by single crystal X-ray diffraction. The use of 4,4′-bipyridine (**10**) as an ancillary ligand in the reaction between ligand **3** and Cd(II) ions led to crystals

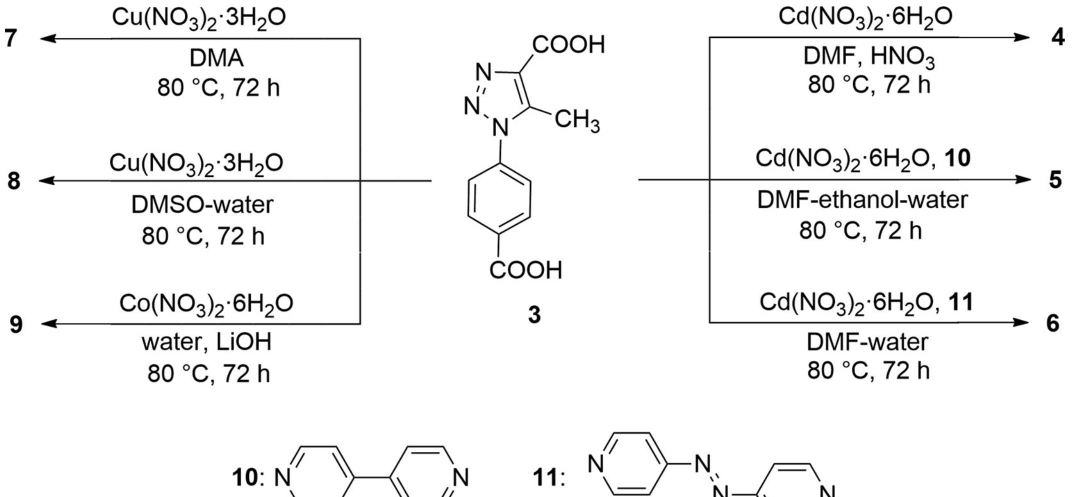
Table 1
Crystal data and details of the data collection for compounds **4–8**.

Compound	4	5	6	7	8
Empirical formula	$C_{33}H_{30}Cd_3N_9O_{16.5}$	$C_{16}H_{17}CdN_4O_7$	$C_{16}H_{15.95}CdN_5O_{6.4}$	$C_{26}H_{25}CuN_7O_9$	$C_{22}H_{20}CuN_6O_{10}$
Fw	1156.88	489.73	494.29	643.07	591.98
space group	*R*3	*Pccn*	*Pccn*	*Cm*	*P*-1
a [Å]	20.9672(8)	20.932(2)	21.3152(8)	8.0696(4)	6.8575(3)
b [Å]	20.9672(8)	19.6383(19)	19.0391(8)	22.9695(8)	7.2928(4)
c [Å]	8.5333(3)	8.7394(12)	9.2720(4)	7.7440(3)	12.9599(7)
a[°]	90	90	90	90	103.954(5)
b [°]	90	90	90	112.074(5)	98.412(4)
g [°]	120	90	90	90	104.290(4)
V [$Å^3$]	3248.8(3)	3592.5(7)	3762.8(3)	1330.16(10)	594.77(6)
Z	3	8	8	2	1
r_{calcd} [g cm^{-3}]	1.774	1.811	1.745	1.606	1.653
Crystal size [mm]	0.3 × 0.1 × 0.1	0.15 × 0.05 × 0.03	0.8 × 0.1 × 0.05	0.3 × 0.1 × 0.02	0.25 × 0.15 × 0.05
T [K]	293	293	180	180	180
m [mm^{-1}]	1.538	1.265	1.208	0.891	0.990
2 Θ range	7.62 to 49.988	4.148 to 50.054	4.278 to 50.054	3.546 to 58.918	3.318 to 50.052
Reflections collected	4990	11,191	8691	10,952	5846
Independent reflections	2532[R_{int} = 0.0236]	2532[R_{int} = 0.1069]	3321[R_{int} = 0.0240]	3229[R_{int} = 0.0327]	2108[R_{int} = 0.0381]
Data/restraints/parameters	2532/70/208	3167/6/255	3321/0/272	3229/2/207	2108/0/180
R_1[a]	0.0256	0.0598	0.0328	0.0285	0.0393
wR_2[b]	0.0549	0.0806	0.0747	0.0544	0.0771
GOF[c]	1.067	0.983	1.066	1.045	1.072
Largest diff. peak/hole / e $Å^{-3}$	0.26/-0.24	0.66/-0.65	0.89/-0.41	0.58/-0.30	0.33/-0.40
Flack parameter	0.00(2)	–	–	0.007(5)	–

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $GOF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.



Scheme 1. Synthesis of H_2L **3** through the Dimroth cycloaddition.



Scheme 2. Synthesis of coordination compounds **4–9** from the ligand H_2L (**3**).

under a few sets of reaction conditions, but the needle-like shape of these crystals and their modest size, which was the consequence of the massive separation of the crystalline solid in the initial hours of the heating stage, precluded any definitive structure determination. Finally, the use of a ternary reaction solvent (DMF–water–ethanol) afforded larger crystals, and coordination polymer **5** could be isolated as crystals suitable for X-ray diffraction in 80% yield (Scheme 2). When 4,4′-azopyridine (**11**) was employed as an auxiliary ligand, coordination polymer **6** was obtained as large orange crystals by employing a mixture of DMF and water as the solvent (Scheme 2).

Until now, the only coordination compound based on ligand **3** and copper ions has been a polymer that was obtained under harsh reaction conditions in low yields [9]. Therefore, several different sets of solvothermal reaction conditions have been evaluated for the synthesis of other copper-derived coordination polymers based on ligand **3**. By heating a mixture of the ligand and copper(II) nitrate trihydrate in DMA at 80 °C for 72 h, blue crystals suitable for X-ray diffraction separated gradually during the heating stage (Scheme 2). Unfortunately, structural investigation by XRD showed that the compound $[Cu(HL)_2DMA]$ (**7**) obtained under these experimental conditions was a discrete mononuclear complex. Furthermore, when the same reaction was attempted in a mixture of DMSO and water, another mononuclear complex, $[Cu(HL)_2(H_2O)_2]$ (**8**), was isolated from the reaction mixture (Scheme 2). Use of auxiliary ligands such as 4,4′-bipyridine (**10**), 4,4′-azopyridine (**11**) or 1,2-di(4-pyridyl)ethylene in experiments aiming at preparing coordination polymers from H_2L and either copper(II) nitrate or copper(II) acetate under various conditions did not produce materials whose structure could be properly established by single crystal X-ray diffraction. Despite our efforts, the desired copper-containing coordination polymers based on ligand **3** remained elusive.

Out of the several cobalt-containing solid materials that could be isolated from the reaction of ligand **3** with cobalt(II) nitrate under various experimental conditions, only the coordination network $\{[Co(L)(H_2O)_3]\cdot 2\cdot 5H_2O\}_n$ (**9**) separated out as large block crystals that were suitable for characterization by single crystal X-ray diffraction. A comparison between the crystallographic data for coordination polymer **9** (available in the SI) and the data that has been already reported in the literature [9] proved conclusively the chemical and crystallographic identity of the two compounds. Therefore, although the reaction conditions employed for the preparation of compound **9** (using $Co(NO_3)_2\cdot 6H_2O$ as the source of Co(II) ions, water as the solvent, in the presence of LiOH, at 80 °C for 2 days) are quite different from the ones previously reported, the isolated crystals have the same structure as those obtained from $CoCl_2\cdot 6H_2O$ in a mixture of methanol–water at 100 °C for 2 days. Our synthetic approach provides a slightly higher yield (74% based on H_2L) than the one previously reported for the same compound (29% based on Co, that is 58% based on H_2L) [9].

The IR spectrum of ligand **3** (Fig. S3 in the SI) was examined and the IR bands of complexes **4**–**9** (Fig. S4–S9 in the SI) have been assigned relative to those identified for ligand **3**. The IR spectrum of the diacid **3** is similar to that given in a previous publication [9] and shows the characteristic absorption bands for carboxylate groups. Thus, the strong peak at 1694 cm^{-1} has been attributed to the $\nu_{as(C=O)}$ stretching vibration of the carboxylate groups, while the band at 1473 cm^{-1} was assigned to $\nu_{s(C=O)}$ in the same groups. The absorption bands corresponding to other bonds in the structure of the diacid **3** are detailed in Table 2.

In the IR spectra of complexes **4**–**9**, the broad bands between 3584 and 3279 cm^{-1} correspond to asymmetric and symmetric O—H stretching vibrations of water molecules within the structure of these complexes. Weak absorption bands observed immediately below 3000 cm^{-1} are characteristic for the $\nu_{(C—H)}$ vibration modes of the methyl group. The strong absorption peaks at 1680–1605 cm^{-1} can be associated with asymmetric vibrations of the carboxylate groups, while peaks at 1448–1399 cm^{-1} can be assigned to symmetric vibrations of the same groups [17]. The bands in the range 1597–1509 cm^{-1} are attributed to the characteristic stretching vibrations of the phenyl rings. Various absorption bands appearing between 1386 and 1136 cm^{-1} in the IR spectra of complexes **4**–**9** are indicative for the triazole ring. Because of the partial overlap of the stretching vibrations for the carboxylate groups and the characteristic stretching vibrations of the triazole and phenyl rings (range of 1100–1680 cm^{-1}), the absorption bands characteristic for DMA in complex **7** are difficult to identify unequivocally. Absorption bands observed between 876 and 776 cm^{-1} could be tentatively attributed to the bending vibration of a *para*-substituted benzene ring.

3.2. Crystal structures of the coordination polymers and complexes 4–9

The X-ray diffraction study has demonstrated that compound **4** is a three-dimensional coordination polymer with the molecular formula $\{[CdL(H_2O)]\cdot 0.5H_2O\}_n$, which crystallizes as a pure enantiomer in the Sohnke *R*3 space group of the trigonal system. As shown in Fig. 1, the asymmetric part of the structure is formed by one Cd atom, one double-deprotonated linker (L^{2-}) and a fractional number of water molecules distributed in disordered positions. The Cd atom is seven-coordinated by O_6N, supplied by the ligand L^{2-} and one molecule of water. Its irregular coordination polyhedron approaches a strongly distorted pentagonal bi-pyramidal geometry. The double deprotonated L^{2-} linker behaves as hexadentate ligand, being coordinated through both carboxylate groups and a nitrogen atom in the triazole ring. One of the carboxylate group functions as a κ^2O,O' bidentate-chelating group, while the second one is coordinated in a μ_2-$\kappa^3O,O':O$ tridentate-bridging mode, and links two Cd atoms at a distance of 4.6650(5) Å. The crystal packing results via the self-assembly of the asymmetric entities, constituting a three-dimensional coordination polymer, which exhibits parallel channels along the 001 direction (Fig. 2), filled by co-crystallized water molecules with fractional occupancy. The total solvent accessible volume after removing the water molecules, calculated using the tool available in the Olex2 program, is 452.6 Å^3 (13.9% of the unit cell volume).

The crystal structures of coordination polymers **5** and **6** are closely related, despite the presence of two different ancillary ligands (4,4′-bipyridyl in **5** and 4,4′-azopyridine in **6**). Both structures were solved in the *Pccn* space group and had similar unit cell parameters (see Table 1). A view of the asymmetric part for polymers **5** and **6** are shown in Fig. 3a and Fig. 3b, respectively. In both polymers, the Cd atom exhibits an O_4N_2 coordination in a strongly distorted octahedral environment. The sums of the deviations from 90° for all 12 *cis* bond angles for **5** and **6** are 81.8 and 79.41°, respectively. Unlike its coordination mode in the network of **4**, the L^{2-} linker in **5** and **6** acts as a tridentate ligand, with a set of O_3N donor atoms. Thus, the two carboxylate groups have different coordination functions: one carboxylate has a bridging bidentate form in a *syn*–*anti* arrangement, while the second one is coordinated as a monodentate group, the non-coordinated oxygen atom being involved as an acceptor in hydrogen bonds with coordinated and solvate water molecules as donors of protons (Fig. 3, a and b). As expected, the crystal packings for these two compounds are also very similar, and they feature a three-dimensional network with ~ 6 × 6 Å one-dimensional rectangular channels, as shown in Fig. 4 (a and b). The total volume of the empty channels calculated by Olex2 program represents ~ 12% relative to the total volume of the unit cell.

According to the X-ray diffraction analysis, compound **7** has a molecular crystal structure built up from the neutral mononuclear complex $[Cu(HL)_2(DMA)]$, which is shown in Fig. 5. No co-crystallized solvent molecules have been found in the crystal. The copper atom exhibits a slightly distorted O_3N_2 square-pyramidal coordination generated by two bidentate mono-deprotonated HL^- ligands in the equatorial plane and the DMA

Table 2
IR absorption bands (cm^{-1}) of ligand **3** and complexes **4–9**.

	3	**4**	**5**	**6**	**7**	**8**	**9**
$\nu_{(O—H)}$	3411	3584,3279	3413	3369	–	3512,3445	3400
$\nu_{(-CH3)}$	2868	2928	2927	2929	2936	2944	2926
$\nu_{as(COO^{-})}$	1694	1680	1605	1606	1628	1661	1615
$\nu_{s(COO^{-})}$	1473	1399	1448	1444	1422	1419	1426
$\nu_{(phenyl)}$	1516	1588,1544	1562	1562	1597,1509	1595, 1513	1553
$\nu_{(triazole)}$	1313,1287,1234	1312,1242,1136	1308,1283,1230	1383,1305, 1282	1378,1322,1269	1377,1311,1246	1381,1311, 1244
$\nu_{(Ar-H)}$	864,806	847	876, 844	856, 840	864, 828	858,829	781

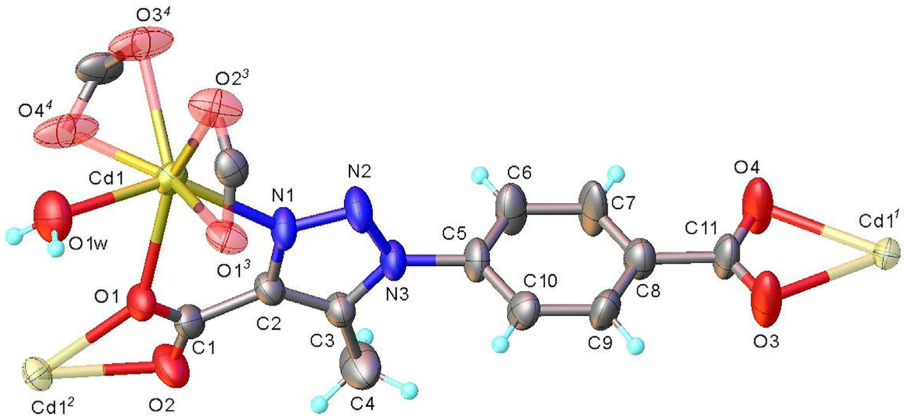


Fig. 1. View of the asymmetric part in the crystal structure of **4**, along with labelling of the atoms. Thermal ellipsoids are shown at the 50% probability level. Only the major component of the distorted fragment is shown. Co-crystallized water molecules are omitted for clarity. Symmetry generated fragments are shown with faded colors.

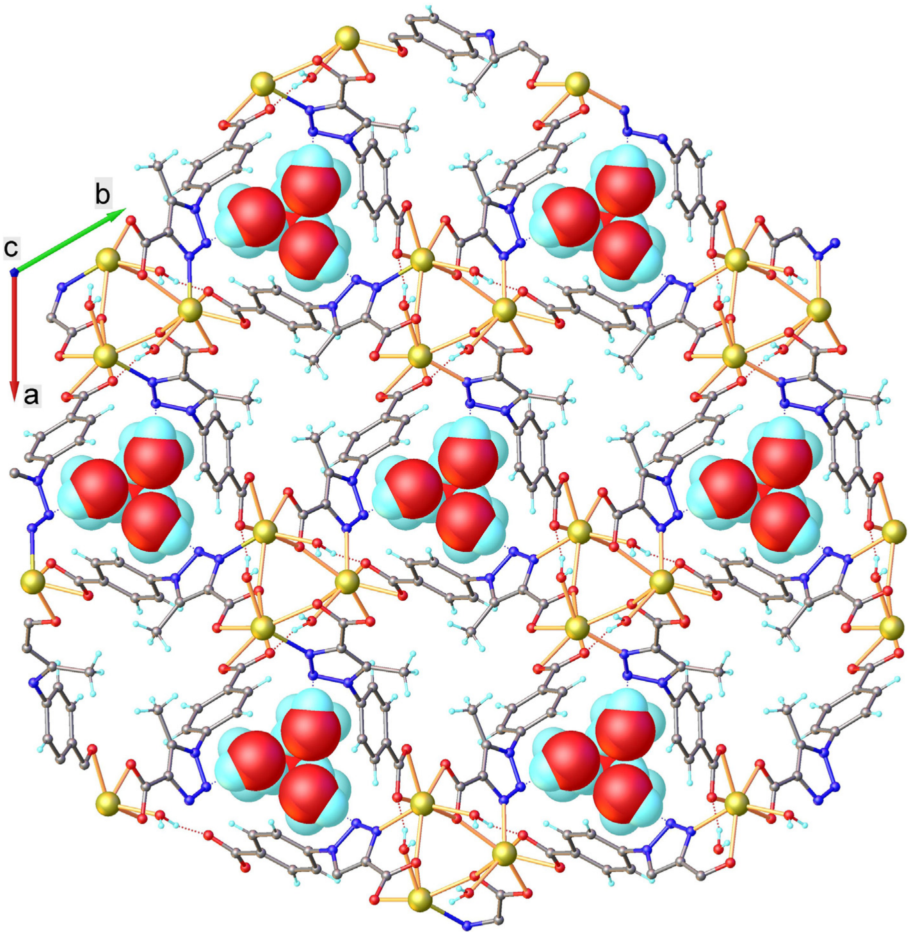


Fig. 2. Partial crystal structure packing of **4** viewed along the *c* axis. Co-crystallized water molecules located in the channels are drawn in the space filling mode.

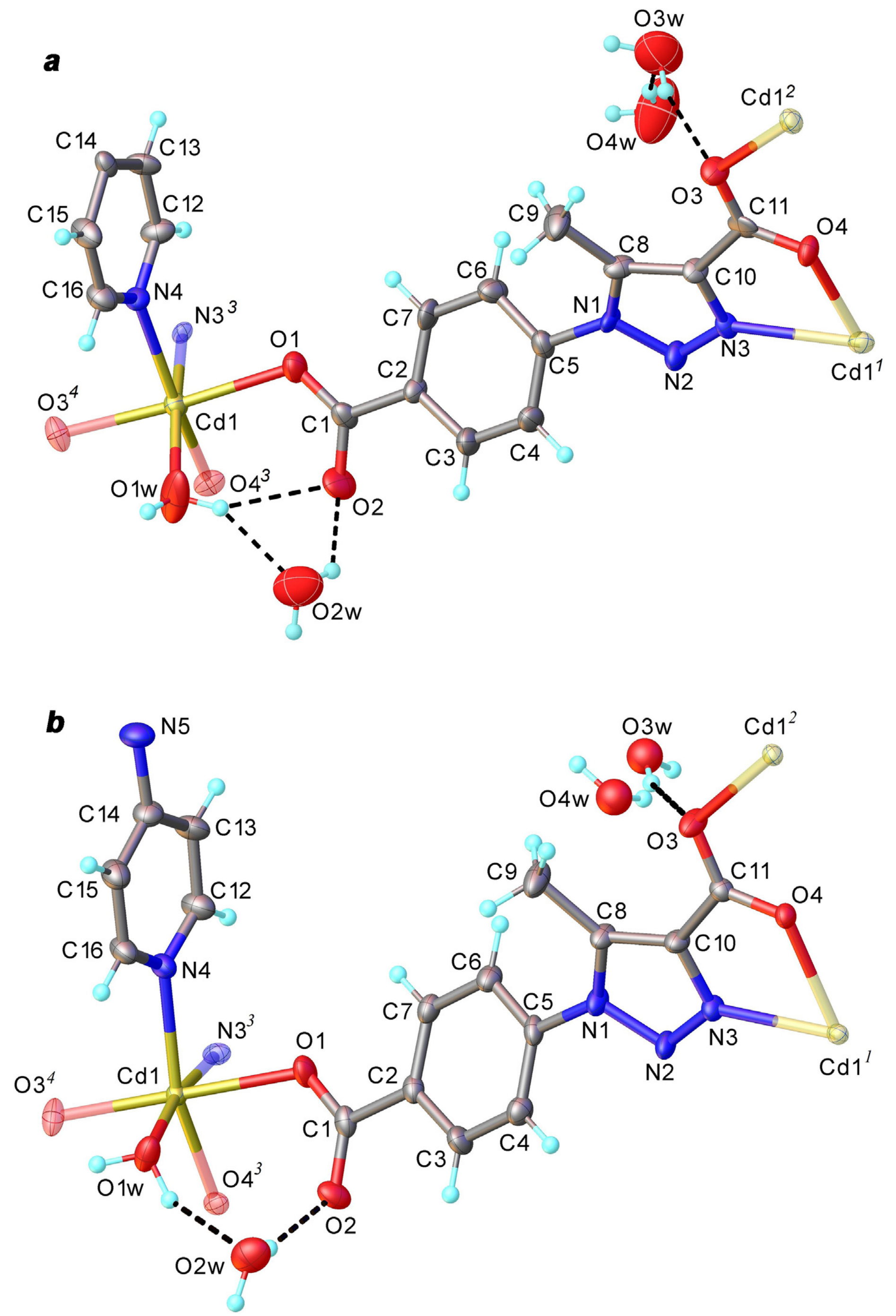


Fig. 3. View of the asymmetric part in the crystal structures of **5** (a) and **6** (b), along with their atom labelling. Thermal ellipsoids are shown at the 50% probability level. Symmetry generated fragments are shown with faded colors.

molecule in the apical position. The Cu atom is displaced from the mean N_2O_2 basal plane by 0.184(2) Å towards oxygen atom O5. The organic ligand HL^- behaves as a bidentate ligand that coordinates through one nitrogen atom of the triazole ring and one monodentate carboxylate group. Notably, the second carboxylic group of the ligand is not coordinated to any metal atom. The non-coordinated carboxylic moiety participates in the formation of hydrogen bonds with one oxygen atom of the coordinated carboxylate that acts as acceptor of a proton. In turn, these hydrogen bonds determine the formation of stripe-like 1D supramolecular aggregates, as shown in Fig. 6.

The attempt to synthesise a copper coordination compound based on the ligand H_2L in a 1:1 DMSO–water reaction mixture afforded compound **8** as another mononuclear complex. The crystal structure of this compound consists of the neutral complex $[Cu(HL)_2(H_2O)_2]$ (Fig. 7), in which the copper(II) atom occupies a special position on the inversion center. When compared to complex **7**, it is noteworthy that two bidentate HL^- ligands in compound **8** fulfill the same coordination function, but are coordinated in a *trans* configuration. On the other hand, the copper atom adopts a slightly distorted N_2O_4 octahedral polyhedron (see Table S1). The analysis of the packing of the $[Cu(HL)_2(H_2O)_2]$ molecules revealed

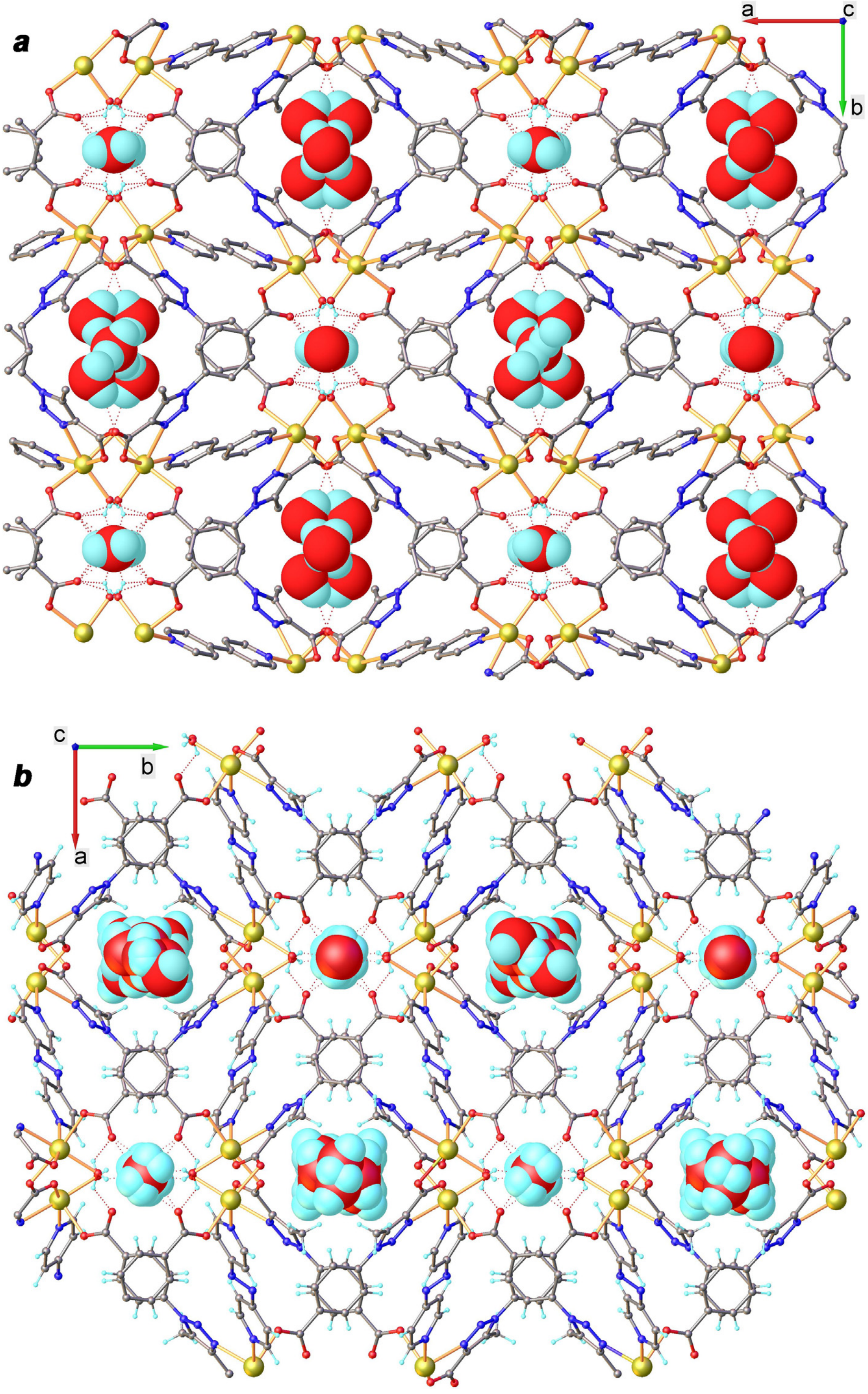


Fig. 4. Partial crystal structure packing viewed along the *c* axis for **5** (a) and for **6** (b). Co-crystallized water molecules located in the channels are drawn in the space filling mode.

that all the possibilities for hydrogen bond formation are completely realized in the crystal. Consequently, the crystal structure, which is shown in Fig. 8, essentially results from the parallel packing of two-dimensional supramolecular networks.

The crystal structure of network **9** is identical to the one reported previously for a coordination polymer of ligand **3** with Co(II) ions that was obtained under different reaction conditions [9]. The crystal data and details of the data collection for compound **9** are presented in the SI.

3.3. Thermogravimetric, PXRD analysis and adsorption studies

In order to assess the robustness of the coordination architecture of the compounds, thermogravimetric analysis was performed on the crystalline materials. The curves recorded for the coordination polymers and complexes **4**–**9** can be found in the SI associated with this article (Figs. S10–S15). For coordination polymer **4**, the results suggest that the initial weight loss of 7.98% which occurs before 315 °C is associated with the complete release of water from

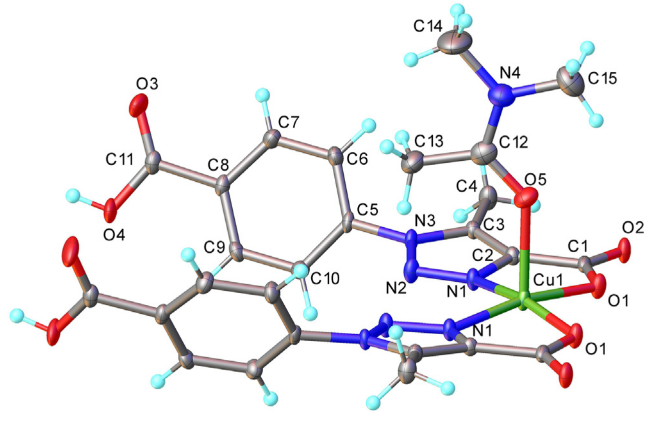


Fig. 5. X-ray molecular structure of complex **7** with the atom labelling and thermal ellipsoids at 50% probability.

the structure of the compound (one coordinated water molecule and a half lattice water molecule, calcd. 7.00%). Interestingly, the residue left at the end of the experiment (17.62%) does not account for the amount of cadmium in the sample subjected to thermal decomposition (calcd. 29.15%). As the metal in organic–inorganic hybrid samples is usually converted into the corresponding metal oxide under the experimental conditions of thermogravimetric analysis, the difference between the experimental results and theoretical calculations in this case is even more striking; thus, the calculated percentage of the residue is 33.30%, considering that the residue is composed solely of cadmium oxide. A similar behavior was observed for another Cd-derived coordination polymer synthesized by our group [18]. Moreover, it was found that for several Cd-based coordination polymers reported by different research groups, the percentage of the solid residue resulting at the end of thermogravimetric experiments was also lower than the calculated content for cadmium in the respective compounds [19–22]. Therefore, we hypothesize that, at least in these cases, cadmium is partially removed as organic or inorganic derivatives that are volatile at high temperatures. For coordination polymer **5**, the complete removal of the water molecules (calcd. 11.02%) in its structure corresponds to weight loss of 10.73% which is observed at 277 °C as two gentle, continuous stages. A more significant weight loss (18.41%) has been recorded for temperatures between 277 and 350 °C, and this loss could be tentatively assigned to the elimination of the auxiliary ligand (calcd. 15.93%). For the higher temperatures in the 277–350 °C range, the end of auxiliary ligand loss from polymer **5** is presumably laid over the beginning of the decomposition of the organic linker L^{2-}. Again, the percentage recorded for the residue at the end of the thermal decomposition experiment for coordination polymer **5** (16.22%) is lower even than the theoretical cadmium content of the sample (22.95%). A succession of gentle stages, that account for a total weight loss of 8.35% due to the release of two coordinated water molecules and three lattice water molecules (calcd. 9.10%) from the structure of coordination polymer **6**, can be noticed in the corresponding thermogravimetric curve up to 202 °C. Next, removal of the auxiliary ligand (calcd. 18.61%) that takes place in the temperature range 202–369 °C is most likely to correspond at least in part to the experimental weight loss of 23.22%; the beginning of the thermal decomposition of the ligand L^{2-}, or even the elimination of cadmium as volatile derivatives, might account for the difference of more than 4% between the experimental and calculated values. The percentage for the residue recovered at the end of the thermal decomposition of coordination polymer **6** (21.95%) is noticeably higher than those recorded for networks **4** or **5**, but is still lower that the theoretical percentage (25.97%, calcd. for CdO). Mononuclear complex **7** is very stable up to 239 °C owing to the absence of any volatile solvent molecules. Afterwards, a sudden weight loss of 41.28% in a very narrow temperature range (239–269 °C) occurs, when the breaking of the complex presumably takes place. For the mononuclear complex **8**, the thermogravimetric data shows a first stage of 5.24% weight loss before 197 °C, owing to the elimination of two coordinated water molecules (calcd. 6.08%). A second stage is observed in a narrow temperature range (238 to 270 °C) and this stage can be ascribed to the decomposition of the complex and the release of the ligand from the material, in a manner similar to the one recorded for complex **7** in the same temperature range. The results obtained from the thermogravimetric analysis of coordination polymer **9** are similar to those previously reported [9] for the same compound, *i.e.* a weight loss of 24.82% before 290 °C, which is equivalent to the release of three coordinated water molecules and 2.5 lattice water molecules from the structure of this compound (calcd. 24.57%).

The experimental PXRD patterns of coordination polymers **4**, **5**, **6** and **9** (Fig. S16–S19 in SI) closely match the diffractograms that were generated using the single crystal X-ray diffraction data, which suggest that all five complexes are phase pure. In order to ascertain the preservation of their structural integrity, a second experimental PXRD pattern was recorded for these compounds after their activation prior to determination of the specific surface area. According to the results, Cd-based networks **4**–**6** appear to be stable, and removal of their lattice water does not result in the collapse of the network. However, removal of lattice water in coordination polymer **9** led to structural changes, as suggested by the heavily modified PXRD pattern recorded for the sample after solvent exchange. Moreover, the structural integrity of coordination polymer **9** was definitely compromised during the thermal activation stage in the initial stage of the adsorption experiment, as gleaned from the PXRD pattern appearing as a broad envelope of peaks that was recorded for this particular sample at the end of the adsorption experiment (data not shown).

Samples of coordination polymers **4**, **5**, **6** and **9** were activated using the solvent exchange technique, during which the water molecules that were trapped in the pores of the coordination polymers were replaced by ethanol. Specifically, samples consisting of large crystals and having a weight in the range of 60–80 mg were stirred at room temperature with 5 mL of ethanol for 6 h, then the sample was centrifuged at 6,000 rpm for 15 min, and the super-

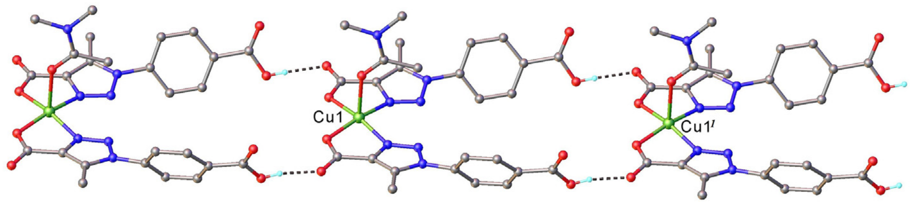


Fig. 6. View of the 1D supramolecular unit in the crystal structure of **7**. H-bond parameters: O4-H···O2 [O4-H 0.820 Å, H···O2 1.790 Å, O4···O2(1 + *x*, *y*, −1 + *z*) 2.599(4) Å, ∠O4HO2 168.7°].

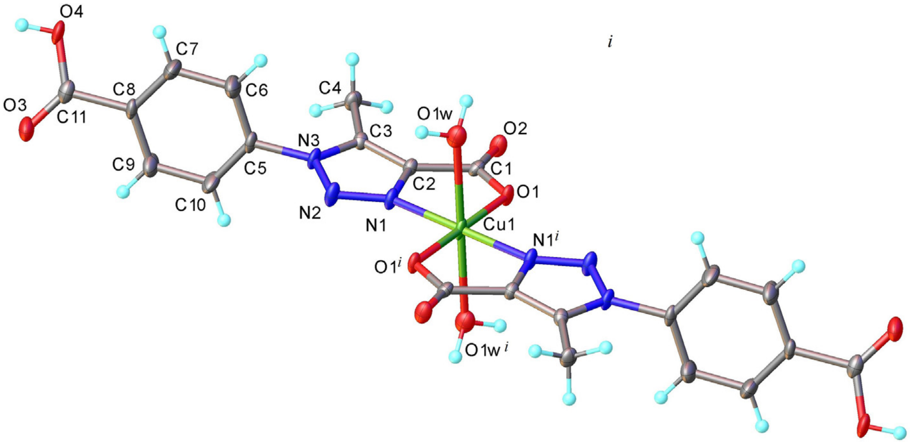


Fig. 7. X-ray molecular structure of complex **8** with the atom labelling and thermal ellipsoids at 50% probability.

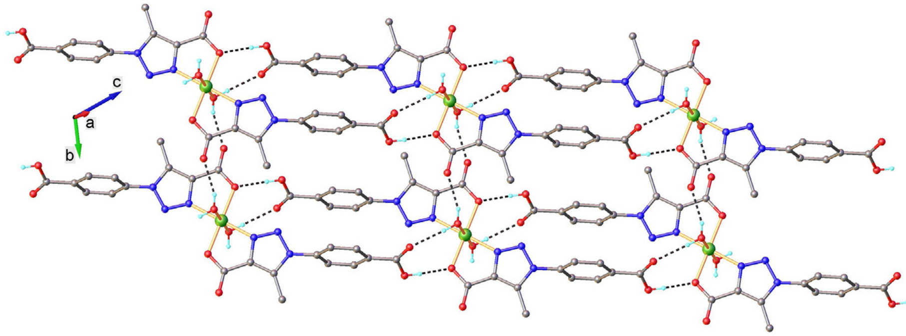


Fig. 8. View of the 1D supramolecular layer in the crystal structure of complex **8**. Non-relevant H-atoms are omitted for clarity. H-bonds are drawn in dashed-black lines. H-bonds parameters: O1*w*-H···O2 [O1*w*-H 0.86 Å, H···O2 2.02 Å, O1*w*···O2(1 -*x*, -*y*, 1 -*z*) 2.768(3) Å, ∠O1*w*HO2 144.5°]; O1*w*-H···O3 [O1*w*-H 0.87 Å, H···O3 2.04 Å, O1*w*···O3(-*x*, -*y*, -*z*) 2.900(3) Å, ∠O1*w*HO3 166.9°]; O4-H···O1 [O4-H 0.82 Å, H···O1 1.80 Å, O4···O1(-1 + *x*, −1 + *y*, −1 + *z*) 2.613(2) Å, ∠O4HO1 169.4°].

natant was removed. Fresh ethanol (5 mL) was added to the sample, which was then stirred for 22 h and centrifuged again. Removal of the solvent afforded powder-like materials, which were allowed to dry in the centrifugation tubes, first at room temperature for 24 h, then in a vacuum oven at 50 °C and 0.02 MPa for 4 h. The determined Brunauer-Emmett-Teller (BET) surface areas for the activated coordination polymers were small (2.8 m^2/g for **4**, 1.4 m^2/g for **5**, 2.2 m^2/g for **6** and 22.4 m^2/g for **9**). These low specific surface areas, in conjunction with limited pore volume available for adsorption processes in the micropores, suggest that adsorption for these coordination polymers mainly occurs on the external surface of the material as a fine powder, in the diffusion region.

4. Conclusions

A 1,2,3-triazole-containing dicarboxylate ligand was employed for the synthesis of three hitherto unreported coordination polymers containing Cd(II) ions and two new mononuclear complexes based on the Cu(II) ion. In addition, a previously known Co(II)-containing coordination polymer derived from the same ligand was obtained with improved yields under different experimental conditions. Single crystal X-ray analysis showed that this organic linker behaves as a tridentate ligand in these polymers, as both carboxylate groups and N-3 in the 1,2,3-triazole ring coordinate to the metal center. One of the Cd(II)-based coordination polymers was obtained as a pure enantiomer in the Sohnke *R*3 space group of the trigonal system. The remaining two Cd(II)-based coordination polymers included either 4,4′-bipyridine or 4,4′-azopyridine as ancillary ligand in their structures, making them the first coordination polymers derived from 1-(4-carboxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid to present co-ligands in their structures. They were both solved in the *Pccn* space group and their unit cell parameters are similar despite featuring different bipyridine co-ligands. The use of different solvents in the reaction of the 1,2,3-triazole-containing dicarboxylate ligand with Cu(II) ions led to distinct neutral complexes, which form 1D or 2D supramolecular arrangements. Evaluation of the specific surface of the Cd(II)- and Co(II))-based coordination polymers produced poor results, which indicate that the 3D networks are not useful as materials for gas storage.

CRediT authorship contribution statement

Bogdan-Ionel Bratanovici: Investigation, Methodology, Formal analysis, Data curation. **Sergiu Shova:** Investigation, Formal analysis, Writing - original draft. **Vasile Lozan:** Formal analysis, Writing - original draft. **Ioan-Andrei Dascălu:** Investigation, Formal analysis, Data curation. **Rodinel Ardeleanu:** Investigation, Data curation. **Gheorghe Roman:** Conceptualization, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary information to this article (^{1}H and ^{13}C NMR spectra of ligand **3**, IR spectra of ligand **3** and coordination compounds **4**–**9**, thermogravimetric curves for coordination compounds **4**–**9**, PXRD patterns for coordination compounds **4**, **5**, **6** and **9**, crystal data for compound **9**, tabled bond length and angles in coordination compounds **4**–**9**) can be found online. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115115.

References

[1] H.W. Langmi, J. Ren, B. North, M. Mathe, D. Bessarabov, Electrochim. Acta 128 (2014) 368–392.
[2] Y. Lin, C. Kong, Q. Zhang, L. Chen, Adv. Energy Mater. 7 (2017) 1601296.
[3] H. Li, K. Wang, Y. Sun, C.T. Lollar, J. Li, H.-C. Zhou, Mater. Today 21 (2018) 108–121.
[4] X. Yang, Q. Xu, Cryst. Growth Des. 17 (2017) 1450–1455.
[5] Y.-B. Huang, J. Liang, X.-S. Wang, R. Cao, Chem. Soc. Rev. 46 (2017) 126–157.
[6] L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, Chem. Rev. 117 (2017) 8129–8176.
[7] W.P. Lustig, S. Mukherjee, N.D. Rudd, A.V. Desai, J. Li, S.K. Ghosh, Chem. Soc. Rev. 46 (2017) 3242–3285.
[8] Y. Cui, Y. Yue, G. Qian, B. Chen, Chem. Rev. 112 (2012) 1126–1162.
[9] D. Shang, J. Ni, X. Gao, C. Li, X. Lin, Z. Wang, N. Du, S. Li, Y. Xing, New J. Chem. 40 (2016) 8100–8109.
[10] Y. Wang, S.-H. Xing, F.-Y. Bai, Y.-H. Xing, L.-X. Sun, Inorg. Chem. 57 (2018) 12850–12859.
[11] J.X. Li, Q.L. Guan, Y. Wang, Z.X. You, Y.H. Xing, F.Y. Bai, L.X. Sun, New J. Chem. 44 (2020) 1446–1454.
[12] F.R. Bou-Hamdan, F. Lévesque, A.G. O'Brien, P.H. Seeberger, Beilstein J. Org. Chem. 7 (2011) 1124–1129.
[13] CrysAlis RED, Oxford Diffraction Ltd.,Version 1.171.40.53, 2003).
[14] G.M. Sheldrick, Acta Crystallogr. C Struct. Chem. C71 (2015) 3–8.
[15] G.M. Sheldrick, Acta Crystallogr. A Found. Crystallogr. A64 (2008) 112–122.
[16] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339–341.
[17] K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, Wiley, New York, 1997.
[18] I.-A. Dascalu, S. Shova, D.G. Dumitrescu, G. Roman, B.-I. Bratanovici, R. Ardeleanu, V. Lozan, Polyhedron 170 (2019) 463–470.
[19] H.-Y. Yu, X. Fang, K.-K. Zhang, M.-J. Lin, D. Gao, M.-D. Huang, J.-D. Wang, CrystEngComm 15 (2013) 343–348.
[20] Q. Zhao, C. Ding, Y. Feng, J. Coord. Chem. 71 (2018) 1250–1257.
[21] M. Barsukova, T. Goncharova, D. Samsonenko, D. Dybtsev, A. Potapov, Crystals 6 (2016) 132.
[22] P. Vishnoi, R. Murugavel, Z. Anorg. Allg. Chem. 640 (2014) 1075–1080.