ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
https://www.icf.ro/rrch/

Rev. Roum. Chim.,
2025, *70*(7–8), 395–402
DOI: 10.33224/rrch.2025.70.7-8.03

This work is dedicated to the memory of
Acad. Bogdan C. Simionescu, whose contributions to science will continue to inspire and endure

1D COORDINATION POLYMERS OF Zn(II), Cu(II) AND Co(II) WITH 1,3-BIS(CYANOPROPYL)TETRAMETHYLDISILOXANE: SYNTHESIS, STRUCTURE AND MOISTURE BEHAVIOR

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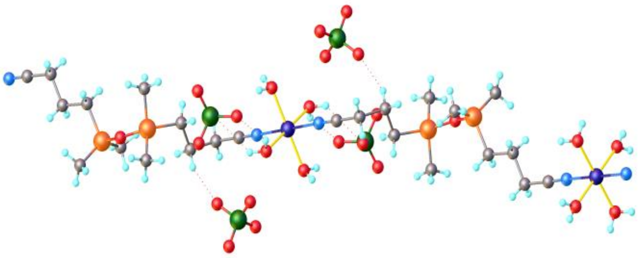
Received January 28, 2025



1,3-Bis(cyanopropyl)tetramethyldisiloxane (***Cy***) was used as a rare ligand for complexing the ions of Zn^{2+}, Cu^{2+}, and Co^{2+} from perchlorate salts in the melt. Single crystal X-ray diffraction (SC-XRD) analysis revealed in the three cases the formation of one-dimensional coordination polymers, $\{[CyZn(H_2O)_4](ClO_4)_2\}_n$ (**CP-1**), $[CuCy(H_2O)_2(ClO_4)_2]_n$ (**CP-2**), $\{\{[Cy_2Co(H_2O)_2](ClO_4)_2\}\{[Cy_2Co(H_2O)_2](ClO_4)_2\}\}_n$ (**CP-3**), with metal centers having octahedral or pseudo-octahedral coordination environments, supramolecularly stabilized by hydrogen bonding networks involving perchlorate counterions and water molecules. Experimental Fourier transform infrared (FTIR) spectra, supported by theoretically calculated ones, confirm the structure of the polymers. Despite the presence of the highly hydrophobic bis(propyl)tetramethyldisiloxane moiety in the structure, dynamic water vapor sorption (DVS) analysis revealed a strongly hydrophilic behavior, conferred by the extensive hydrogen bond networks. Although the compounds absorb water up to dissolution, the chemical structure is fully restored after desorption.

INTRODUCTION

An important family of coordination polymers is that of covalently extended one-way (1D) polymers, which are usually formed by the assembly of simple ligands, such as nitrogen heterocycles or aromatic carboxylic acids, with metal ions. Although partly eclipsed by the huge interest captured by three-dimensional analogues (3D MOFs), considered more robust and useful from a practical point of view, one-dimensional coordination polymers (1D CPs) are a class of materials with interesting specific properties. The linear chains of 1D CPs can assemble in 3D through weak supramolecular interactions, which allows easy access and orientation of various types of guest molecules, such as solvents, anions, cations, metal oxide clusters, etc. into the void spaces.[1,2] The most common structural motif in the dynamic packing of 1D CPs consists of the parallel alignment of linear chains, with the packing mode being influenced by their ability to structurally

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complement one another through close and orderly arrangements. Side groups, perpendicular to the direction of chain propagation, in combination with the possibly included solvent, determine the extent of interactions between chains.[1] Thus, depending on the strength of the supramolecular interactions and the packing density, 1D CPs could be useful as sensor and catalytic materials or as dynamic/selective sorbents, but also for the separation of molecules, larger than common gaseous species (N_2, CO_2, etc.), such as dyes or ions from aqueous solutions. This is due to their intrinsic flexibility and specific adsorption, which is an advantage over 3D MOFs.[3] In addition, 1D CPs have been shown to be more efficient in terms of electrical conductivity, finding applications in light-emitting diodes (LEDs), photovoltaic cells, field-effect transistors (FETs), etc. Noncovalent interactions between chains, such as π···π, C-H···π, or H bonds, play a significant role in facilitating hopping charge transport, which, together with band transport through chemical bonds, allows 1D CPs to be placed in the semiconductor domain.[4] It has been shown that a crystalline 1D CP shows selective adsorption of CO_2, while exhibiting dielectric switching behavior in a mixed N_2/CO_2 gas environment. Thus, the selective adsorption of gases in the mixture can be correlated with the physical properties.[5]

Although the formation of coordination polymers with 1D architecture is facilitated by the presence of rigid linkers in the ligand structure,[6,7] in this work three such polymers are obtained using 1,3-bis(cyanopropyl)tetramethyldisiloxane (***Cy***), an uncommon ligand with a high flexible spacer, for the complexation of 3d metals (Zn, Cu, and Co). This ligand has the capacity to coordinate to the metal ions through nitrogen atom (N-end) of the cyanopropyl groups, while their highly flexible and hydrophobic tetramethyldisiloxane core creates premises for unique structural and functional properties, which could be of interest for certain applications. The isolated compounds were characterized structurally and in terms of their moisture behavior.

RESULTS AND DISCUSSION

A siloxane-spaced biscyanide, 1,3-bis(cyanopropyl)tetramethyldisiloxane, was used for the complexation of Zn^{2+}, Cu^{2+}, and Co^{2+} ions, by using molten perchlorates as metal precursors, and subsequent crystallization of the products from methanol. The reaction products were isolated in crystalline state with yields of 79.9–93.8%. Considering the high flexibility and hydrophobicity of the ligand spacer, the crystallization of the complexes formed is an achievement. The use of the perchlorate counterion made this possible through stable supramolecular interactions.

Studies have shown[8-10] that, depending on the aliphatic or aromatic nature of the spacer and its length, bis(cyano) ligands can coordinate either with two different metal ions or form chelated complexes with a single metal ion. α,ω-Bis(2-cyanophenoxy) propane and -butane are the first examples of dicyanides capable of chelating a single metal center through their nitrogen lone pairs.[8,9] Ligands possessing six or fewer methylene units have been found to be sterically unable to chelate and therefore join two metal centers to give cationic dimers.[9] In our case, although the spacer, 1,3-bis(cyanopropyl) tetramethyldisiloxane, is longer, consisting of nine atoms, the two nitriles coordinate to different metal centers forming 1D coordination polymers, as shown by the structural analysis (see below). Table 1 provides the main crystallographic data and refining details, while Table 2 lists the hydrogen bonds. SC XRD analysis revealed that, for Cy-Zn (**CP-1**), the asymmetric unit is composed of one ***Cy*** molecule, one metal ion, four coordinated H_2O molecules and two perchlorate counter anions, $\{[CyZn(H_2O)_4](ClO_4)_2\}_n$. The zinc atoms occupy special position at the inversion center. Each metal ion exhibits a coordination number of six, adopting a slightly distorted N_2O_4 octahedral geometry provided by four O atoms from four water molecules and two N atoms from ***Cy*** ligand (Fig. 1a).

Selected interatomic distances (Å): Zn1-O1*w*: 2.094(4), Zn1-O2*w*: 2.065(4), Zn1-N1^1: 2.115(5), Zn1-N1: 2.115(5), Zn2-O3*w*: 2.078(5), Zn2-O4*w*: 2.095(4), Zn2-N2^2: 2.106(6), Zn2-N2: 2.106(6). Selected valence angles (°): ∠O1*w*Zn1O1*w*^{1}: 180, ∠O1*w*Zn1N1^1: 91.0(2), ∠O1*w*Zn1N1: 89.0(2), ∠O2*w*Zn1O1*w*: 89.2(3), ∠O2*w*Zn1O1*w*^{1}: 90.8(3), ∠O2*w*Zn1O2*w*^{1}: 180, ∠O2*w*Zn1N1: 90.2(2), ∠O2*w*Zn1N1^1: 89.8(2), ∠N1Zn1N1^1: 180, ∠O3*w*Zn2O4*w*^{2}: 90.9(3), ∠O3*w*Zn2O4*w*: 89.1(3), ∠O3*w*Zn2N2: 88.4(3), ∠O3*w*Zn2N2^2: 91.6(3), ∠O4*w*Zn2N2: 91.1(2), ∠O4*w*Zn2N2^2: 88.9(2), ∠N2Zn2N2^2: 180.0(3). Symmetry codes: ^{1} $-x, -y, -z$; ^{2} $2-x, 1-y, 2-z$.

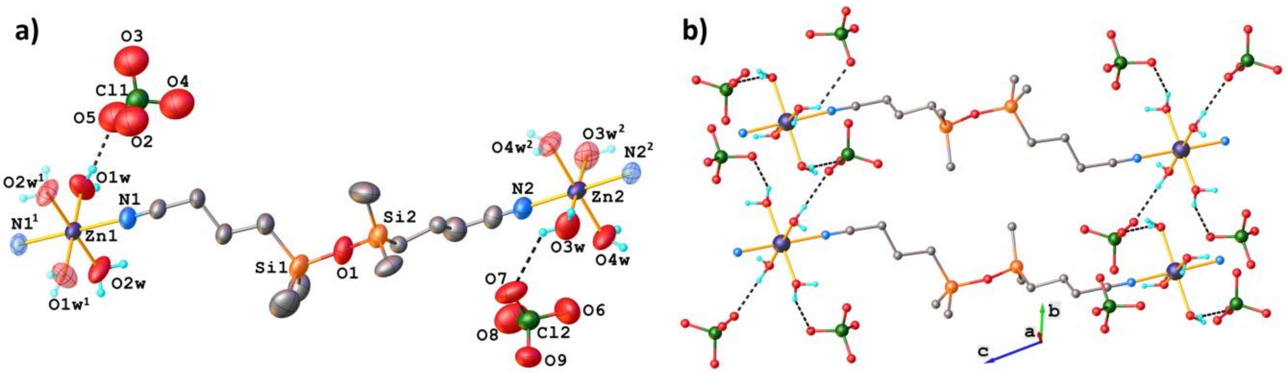

Fig. 1 – a) View of the asymmetric unit in the crystal **CP-1** with selected atom labeling and thermal ellipsoids at 50% level. Non-relevant H atoms have been omitted for clarity; b) Partial view of the crystal packing for **CP-1**.

Table 1

Crystal data and data collection details for coordination polymers **CP-1÷3**

Compound	CP-1 (Cy-Zn)	CP-2 (Cy-Cu)	CP-3 (Cy-Co)
Emp. formula	$C_{12}H_{32}Cl_2N_2O_{13}Si_2Zn$	$C_{12}H_{28}Cl_2CuN_2O_{11}Si_2$	$C_{24}H_{52}Cl_2CoN_4O_{12}Si_4$
Fw	604.84	566.98	830.88
Space group	*P*–*1*	*P*2₁/*c*	*P*–*1*
a[Å], b[Å], c[Å]	6.5142(4), 12.3902(8), 18.4314(11)	11.6159(8), 6.5597(4), 33.342(2)	8.8665(14), 13.857(2), 18.937(2)
α[°], β[°], γ[°]	107.016(5), 98.539(5), 98.595(5)	90, 95.510(6), 90	69.303(13), 6.310(11), 88.619(13)
V[Å^3], Z	1377.17(15), 2	2528.8(3), 4	2171.9(6), 2
ρ_{calc}[g/cm^3], μ[mm^{-1}]	1.459, 1.228	1.489, 1.219	1.271, 0.680
Crystal size [mm^3]	0.25 × 0.20 × 0.10	0.30 × 0.15 × 0.05	0.20 × 0.18 × 0.08
2Θ range	3.512 to 50.046	3.522 to 50.052	3.142 to 50.05
Refl. Collected/Indep. refl./R_{int}	11434/4820/0.0329	15101/ 4417/0.0314	17759/17759/0.079
Data/restraints/par.	4820/94/242	4417/26/243	17759/322/395
GOF, R_1, wR_2	1.040, 0.0796, 0.2424	1.047, 0.0883, 0.2845	1.019, 0.0782, 0.1950
CCDC No.	2223045	2418557	2418558

Table 2

Hydrogen bond's parameters for **CP-1÷3**

D-H···A	d(D-H)/Å	d(H···A)/Å	d(D-A)/Å	D-H···A/°	Symmetry code
CP-1					
O1*w*–H···O8	0.86	1.91	2.669(7)	146.4	$1-x, 1-y, 1-z$
O1*w*–H···O2	0.86	2.31	3.114(6)	155.4	$1-x, -y, 1-z$
O1*w*–H···O5	0.86	1.92	2.683(5)	146.8	$1-x, -y, 1-z$
O2*w*–H···O9	0.87	2.34	2.824(5)	115.6	$2-x, 1-y, 1-z$
O3*w*–H···O2	0.88	2.39	3.143(7)	143.5	
O3*w*–H···O3	0.89	2.63	3.235(6)	126.6	
O4*w*–H···O4	0.89	2.46	3.308(5)	159.3	$3-x, 1-y, 2-z$
O4*w*–H···O2	0.89	2.43	3.167(7)	140.8	$3-x, 1-y, 2-z$
C2–H···O4	0.97	2.53	3.429(8)	155.0	$2-x, -y, 1-z$
C11–H···O9	0.97	2.58	3.297(8)	130.7	$-1+x, +y, +z$
CP-2					
O1*w*–H···O9	0.86	2.49	3.217(6)	142.0	$+x, -1+y, +z$
O1*w*–H···O8	0.86	2.19	2.664(6)	114.9	$2-x, 1-y, 1-z$
O2*w*–H···O2	0.85	1.90	2.703(17)	157.1	$+x, 1+y, +z$
O2*w*–H···O3	0.85	2.15	2.661(15)	118.1	$1-x, 1-y, 1-z$
O2*w*–H···O5	0.85	2.66	3.472(19)	160.2	$1-x, 1-y, 1-z$
CP-3					
O1A*w*–H···O2	0.92	2.07	2.879(7)	145.7	
O1B*w*–H···O5	0.85	2.26	2.963(7)	139.7	
O1B*w*–H···O6	0.85	2.81	3.300(8)	118.6	

The self-assembly of the asymmetric unit leads to the formation of cationic polymer chains $\{[ZnCy(H_2O)_4]\}^{2n+}$, the positive charges being neutralized by the negative perchlorate anions. The supramolecular structure is supported by the presence of hydrogen bonds formed by the participation of coordination water molecules and the perchlorate counteranions. It is noted that ***Cy*** adopts a transoidal conformation (Fig. 1b).

In the complex $[CuCy(H_2O)_2(ClO_4)_2]_n$ (**CP-2**), the metal ion presents a distorted pseudo-octahedral environment of type 4+2. The perchlorate anion pseudo-coordinates to the Cu atom (Cu-O 2.48(16) – 2.5(16)) in the apical position, while two coordination water molecules and two N atoms are in the equatorial position (Fig. 2a). The supramolecular structure is built by the O-H···O hydrogen bonds, established between water molecules as donors and adjacent perchlorate anions as proton acceptors (Fig. 2b).

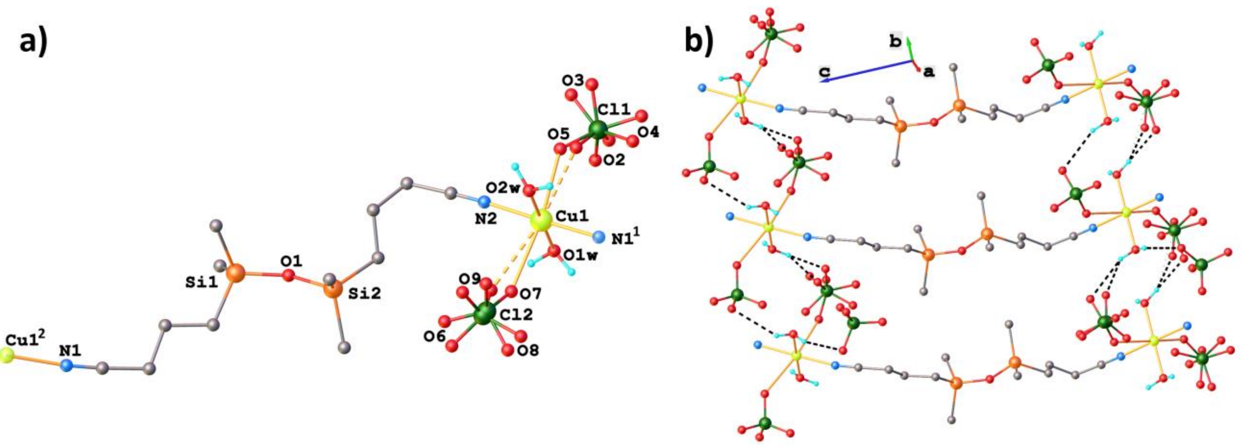

Fig. 2 – a) View of the asymmetric unit in the crystal **CP-2**; b) Crystal structure of **CP-2** showing the hydrogen bonds established between coordination water molecules and perchlorate anions.

Selected interatomic distances (Å): Cu1-O1*w*: 1.935(5), Cu1-O2*w*: 1.939(5), Cu1-N1^1: 1.952(6), Cu1-N2: 1.960(6), Cu1-O5: 2.483(17), Cu1-O7: 2.557(11); Selected valence angles (°): ∠O1*w*Cu1O2*w*: 178.8(2), ∠O1*w*Cu1N1^1: 89.1(2), ∠O1*w*Cu1N2: 90.7(2), ∠O1*w*Cu1O5: 99.5(4), ∠O1*w*Cu1O7: 82.8(3), ∠O2*w*Cu1N1^1: 89.9(2), ∠O2*w*Cu1N2: 90.4(2), ∠O2*w*Cu1O5: 81.0(5), ∠O2*w*Cu1O7: 96.8(3), ∠N2Cu1N1^1: 178.5(2), ∠O5Cu1N1^1: 85.0(4), ∠O7Cu1N1^1: 99.3(3), ∠N2Cu1O5: 93.6(4), ∠N2Cu1O7: 82.2(3), ∠O5Cu1O7: 175.2(4), ∠C1N1Cu1^2: 171.0(6), ∠C12N2Cu1 : 176.8(6), ∠Cl1O5Cu1: 135.8(10), ∠Cl2O7Cu1: 139.0(8); Symmetry codes: ^{1} + *x*, 3/2 – *y*, – ½ + *z*; ^{2} + *x*, 3/2 – *y*, ½ + *z*.

The **CP-3** structure is formed by the molecular cationic complex $[Cy_2Co(H_2O)_2]^{2+}$ (Fig. 3aI), coordination polymer $[Cy_2Co(H_2O)_2]_n^{2+}$ (Fig. 3aII), and perchlorate anions in a 1:1:4 ratio, with two crystallographically independent cobalt (Co1A and Co1B) sites. The coordination environment of the cobalt centers is slightly distorted octahedral and consists of two O atoms from coordination water molecules occupying the axial positions and four N atoms occupying the equatorial positions. The crystal arrangement of the components is driven by the presence of intermolecular hydrogen bonds with the participation of water molecules and perchlorate anions, which determines the formation of a dense supramolecular structure, as shown in Fig. 3b. The components are arranged in alternating layers (Fig. 3c).

Selected interatomic distances (Å): Co1A-O1A*w*^{1}: 2.058(5), Co1A-O1A*w*: 2.058(5), Co1A-N1A^2: 2.084(9), Co1A-N1A^3: 2.084(9), Co1A-N2A: 2.105(7), Co1B-O1B*w*: 2.060(8), Co1B-O1B*w*^{4}: 2.060(8), Co1B-N1B: 2.109(9), Co1B-N2B:2.099(11). Selected valence angles (°): ∠O1A*w*Co1AO1A*w*^{1}: 180, ∠O1A*w*^{1}Co1AN1A^2: 90.3(3), ∠O1A*w*Co1AN1A^2: 89.7(3), ∠O1A*w*Co1AN2A: 90.6(3), ∠O1A*w*Co1AN2A^1: 89.4(3), ∠N1A^{2}Co1AN1A^3: 180.00(16), ∠N2Aco1AN1A^3: 89.9(3), ∠N2Aco1AN2A^1: 180, ∠O1B*w*Co1BO1B*w*^{5}: 180, ∠O1B*w*Co1BN1B: 90.0(4), ∠O1B*w*Co1BN2B: 91.3(4), ∠O1B*w*Co1BN2B^5: 88.7(4), ∠N2Bco1BN1B: 88.9(4), ∠N2Bco1BN1B^5: 91.1(4), ∠N2B^{5}Co1BN2B: 180.0(6). Symmetry codes: ^{1} 1 – *x*, –*y*, 1 – *z*; ^{2} 2 – *x*, –*y*, 1 – *z*; ^{3} –1 + *x*, +*y*, +*z*; ^{4} 1 + *x*, +*y*, +*z*; ^{5}–*x*, 1 – *y*, 1 – *z*.

IR spectrum of the free ligand, 1,3-bis(cyanopropyl)tetramethyldisiloxane, exhibits absorption bands associated with the nitrile stretching vibration (–C≡N) at 2245 cm^{-1}, Si–CH_3 symmetric bending at 1256 cm^{-1}, the Si−O−Si asymmetric stretching vibration at 1061 cm^{-1}, Si–CH$_3$ symmetric rocking at 835 cm^{-1}, and the C−H asymmetric and symmetric stretching vibrations of the methyl groups in the region of 2882–2957 cm^{-1}, partially overlapping with the C−H stretching vibrations of the aliphatic −CH$_2$− groups.[11] The coordination compounds formed display similar profiles, with slight shifts to higher wavenumbers (1088, 1086, and 1069 cm^{-1} for **CP-1**, **CP-2**, and **CP-3**, respectively, compared to 1061 cm^{-1} for ***Cy***) and an increase in the intensity of the Si−O−Si stretching band. Structural analysis reveals that the ligand adopts a transoidal conformation in the obtained polymers. This conformational change may influence the strain within the Si−O−Si bond, thereby altering the vibration energy and the position of the corresponding band in the IR spectra. The change in the position of the nitrile stretching band (–C≡N) due to complexation is negligible, with a shift of about 2 cm^{-1}, from 2245 cm^{-1} in ***Cy***, which can be attributed to the instrumental precision limits. The theoretical IR spectrum of the 1D **CP-1** complex, calculated using Gaussian 16 software with the B3LYP method and the 6-311G(d,p) basis set, aligns well with the experimental one, with no significant change observed in the CN absorption band due to complexation (Fig. 4). In the case of **CP-3**, a new signal is observed at 2289 cm^{-1}, attributed to the CN group in the small molecular fragment, labeled as B in the X-ray structure showed in Fig. 3a. The presence of coordination water molecules in the complexes, in a molar ratio M^{II}:H$_2$O of 1:4 in **CP-1** and 1:2 in **CP-2** and **CP-3**, is supported by the presence in the IR spectra of the absorption band around 3500 cm^{-1}.

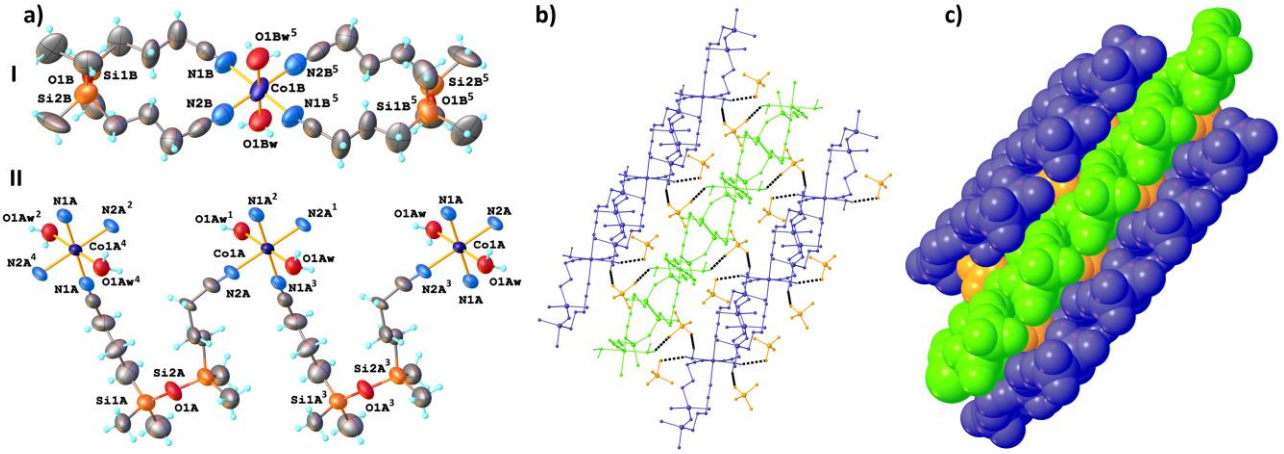

Fig. 3 – a) X-ray molecular structure of $[Cy_2Co(H_2O)_2]^{2+}$ (I); 1D polymer chain $[Cy_2Co(H_2O)_2]_n^{2+}$ (II); b) Hydrogen bonds in the supramolecular structure of **CP-3** complexes; c) Space filling representation of the crystal structure (the layer formed by $[Cy_2Co(H_2O)_2]^{2+}$ is represented in blue, $[Cy_2Co(H_2O)_2]_n^{2+}$ is represented in green, and the perchlorate anion in orange).

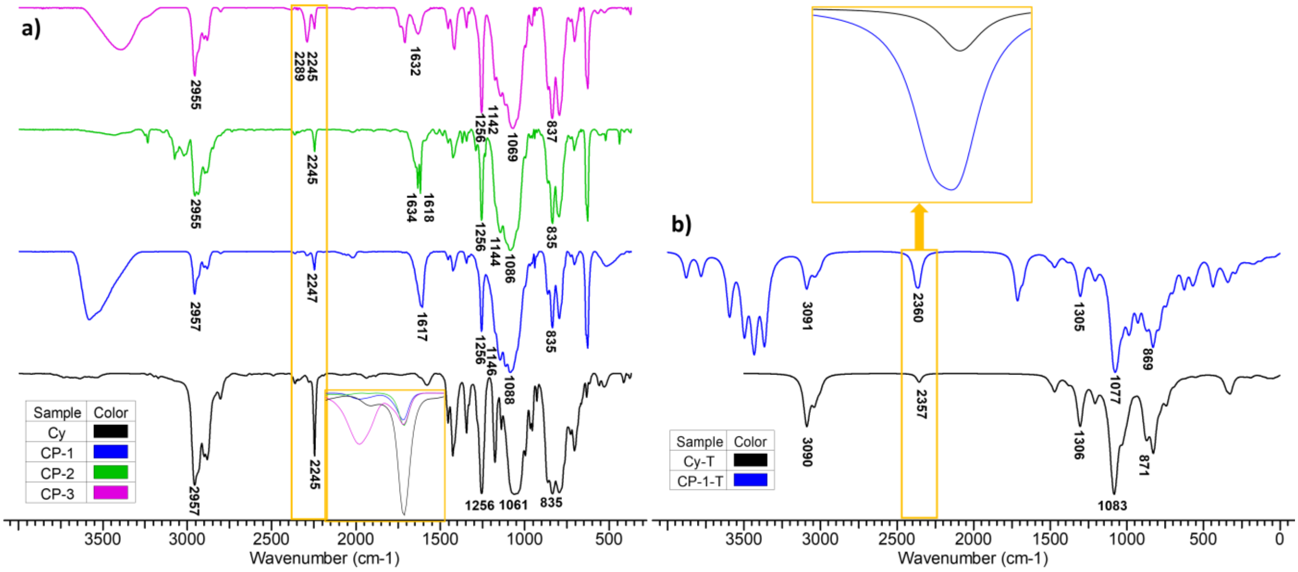

Fig. 4 – a) Experimental *vs* b) theoretical FTIR spectra of the studied compounds.

The analysis of water vapor sorption capacity under dynamic conditions (DVS) (Fig. 5) demonstrates that, despite the hydrophobicity of the ***Cy*** ligand (1.71 wt% water sorption at RH=90%), conferred by the presence of the tetramethyldisiloxane fragment in the structure, the resulting complexes exhibit hydrophilic behavior (63–64 wt% water sorption). Moreover, it was observed that, at the maximum sorption point, the compounds become liquid, a characteristic behavior of crystalline hydrates,[12] of application interest in various fields, such as pharmacology, food, electronics, construction, energy, etc.[13,14] It can also be observed in all cases that the first point of the absorption isotherm does not coincide with the last point of the desorption (Fig. 5a), the polymer gaining mass (Fig. 5b right). This phenomenon can be explained by the possibility of water molecules remaining within the hydrogen bond network. The larger amount of water absorbed and retained by the **CP-1** complex could be attributed to the smaller ionic radius and the higher charge density of zinc, in the homologous series, which facilitates the establishment of covalent coordination bonds with water molecules.[15,16]

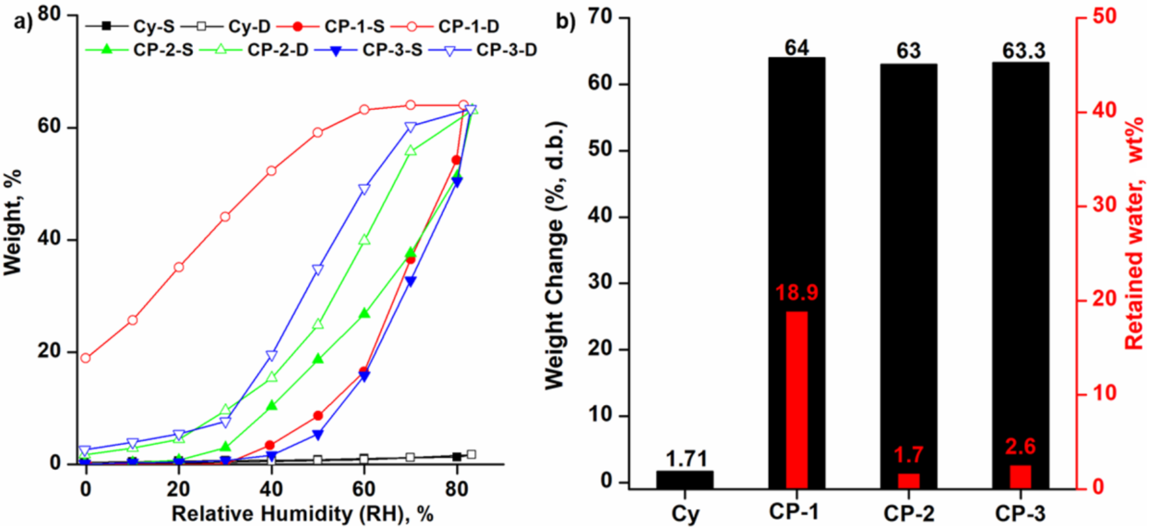

Fig. 5– DVS analysis results: a) Water vapor sorption/desorption isotherms recorded in dynamic mode for ***Cy*** and 1D coordination polymers **CP-1÷3** (S-sorption, D-desorption); b) left, black – maximum percentage of absorbed water; right, red – percentage of residual water retained after desorption.

Since the moisture sorption was performed on single crystals, the X-ray diffraction analysis of the water-vapor-saturated samples revealed much lower diffraction, with weaker intensity, than that of the initial sample, which was attributed to the advanced physical degradation of the crystal. However, the FTIR spectra of the samples subjected to the DVS sorption-desorption cycle do not differ significantly from those of the initial crystalline samples, with only slight increases in the intensity of the characteristic bands for the water molecule being visible (Fig. 6). This is in agreement with the final points on the desorption curves (Fig. 5a), which indicate water retention. Although the crystalline integrity decreases, the compounds remain chemically stable, making them suitable for repeated use in applications where chemical structure is more important than mrphology.

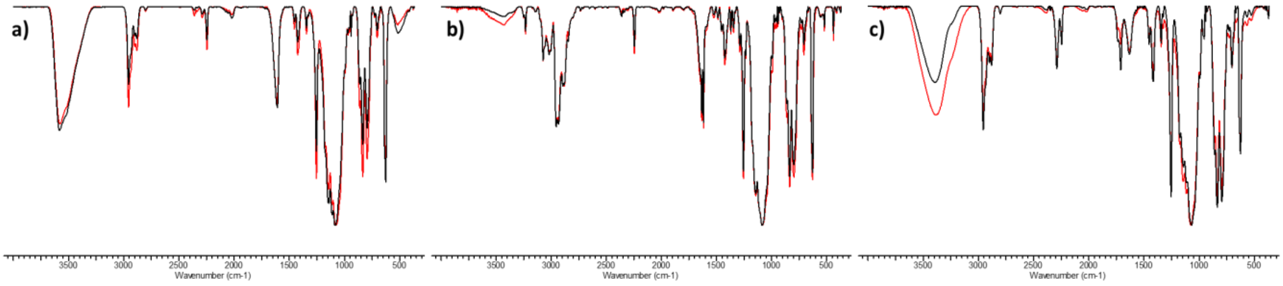

Fig. 6 – Comparative FTIR spectra: initial (black) and after (red) DVS analysis, highlighting the hydrolytic stability of 1D CPs: a) **CP-1**; b) **CP-2**; c) **CP-3**.

EXPERIMENTAL

Materials used

1,3-Bis(3-cyanopropyl)tetramethyldisiloxane, ***Cy***, $C_{12}H_{24}N_2OSi_2$, M = 268.51 g/mol (Gelest), $Zn(ClO_4)_2 \times 6H_2O$, (Aldrich), $Cu(ClO_4)_2 \times 6H_2O$, (Aldrich) and $Co(ClO_4)_2 \times 6H_2O$, (Aldrich) were used as received.

Synthesis of ***CP-1÷3***

A predetermined amount of metal salt (186.1 mg $Zn(ClO_4)_2 \times 6H_2O$, 185.2 mg $Cu(ClO_4)_2 \times 6H_2O$, or 182.9 mg $Co(ClO_4)_2 \times 6H_2O$) was melted in an aluminum crucible, after which, 143.7 μL ***Cy*** was added, and it was mixed vigorously with a glass rod. A solid immediately formed, crystallizing on the walls of the crucible. After complete crystallization, 2 mL of MeOH was added, resulting in a homogeneous solution that was left to stand at room temperature. Within 2–3 days, crystals in the form of rectangular plates were obtained. 1D **CP-1**: Yield, 0.283 g, 93.86%; Anal. Calcd. for $C_{12}H_{32}Cl_2N_2O_{13}Si_2Zn$ (M = 604.84 g/mol), %: C 23.83; H 5.33; N 4.63; Found: C 23.87; H 5.43; N 4.78. 1D **CP-2**: Yield, 0.225 g, 79.95%; Anal. Calcd. for $C_{12}H_{28}Cl_2N_2O_{11}Si_2Cu$ (M = 566.98 g/mol), %: C 25.42; H 4.97; N 4.94; Found: C 24.91; H 4.83; N 4.65. 1D **CP-3**: Yield, 0.36 g, 87.67%. Anal. Calcd. for $C_{24}H_{52}Cl_2CoN_4O_{12}Si_4$ (M = 830.88 g/mol), %: C 34.69; H 6.31; N 6.74; Found: C 34.85; H 5.90; N 6.12.

Caution: Perchlorates are potentially explosive when handled improperly. All procedures involving molten perchlorates were carried out using small quantities under appropriate safety protocols to minimize risks.

Investigation methods

Fourier transform infrared (FTIR) spectra in transmission mode (400–4000 cm^{-1} spectral range, 2 cm^{-1} resolution, with the accumulation of 32 scans, room temperature) were recorded on a Bruker Vertex 70 FT-IR spectrometer. Dynamic water vapor sorption (DVS) measurements were conducted using a Hiden Analytical IGASorp analyzer with an ultrasensitive microbalance to monitor the changes in sample mass with humidity change at constant temperature. Samples were dried at 25 °C under a nitrogen flow (250 mL/min) until equilibrium was reached at RH < 1%. Adsorption isotherms were then recorded by increasing RH from 0 to 90% in 10% increments, allowing 20–40 minutes at each step to reach equilibrium before monitoring. The frequencies (IR spectrum) were calculated by modeling the structures in the GausView6 software, and the structure was optimized using the Gaussian16 with the B3LYP method and the 6-311G(d,p) basis set. The IR spectrum was scaled using the value 0.966 in the Molden6 software.

The crystallographic analysis (SC-XRD) was performed using an Oxford Diffraction CCD diffractometer, XCALIBUR E, with graphite-monochromated Mo-Kα radiation at 293 K. The CrysAlis package from Oxford Diffraction was used for unit cell determination and data integration.[17] The structures were solved by Intrinsic Phasing using Olex2[18] software with the SHELXT[19] structure solution program and refined by full-matrix least-squares on F_2 with SHELXL-2015[20] applying an anisotropic model for non-hydrogen atoms. All H atoms were introduced in idealized positions (d_{CH} = 0.96 Å).

CONCLUSIONS

This study consisted in the synthesis of 1D coordination polymers based on the flexible and hydrophobic ligand 1,3-bis(cyanopropyl) tetramethyldisiloxane with Zn^{2+}, Cu^{2+} and Co^{2+} ions. Structural analysis revealed the formation of one-dimensional coordination structures, supramolecularly assembled by hydrogen bonding networks established between perchlorate anions and coordination water molecules. This supramolecular arrangement accounts for the unexpected hydrophilic behavior and the high water retention capacity of these crystalline compounds, as revealed by dynamic water vapor sorption analysis. Moreover, FTIR spectroscopy demonstrated that the chemical structure of the compounds is preserved after desorption, making them suitable for repeated use in applications exploiting their moisture absorption capacity, such as humidity sensors, drying agents, latent thermal energy storage, or controlled release systems..

Acknowledgements. The paper was supported by a grant of the Roumanian National Authority for Research, project no. PNRRIII-C9-2023-I8-99/31.07.2023 within the National Recovery and Resilience Plan (Roumania).

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