Crystal architectures of copper and zinc metal complexes containing 2-thiophenepropionate and 1,2-bis(4-pyridyl)ethane building blocks

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HIGHLIGHTS

- Three new complexes involving thiophenepropionate, 1,2-bis(4-pyridyl) ethane and Cu and Zn ions.
- The complexes present 2-D (Cu compound) and 3-D (Zn compounds) coordination polymers.
- The Zn compound **3** present supramolecular interactions involving π-stacking.
- Raman and infrared spectra confirm the geometries of coordination for the complexes.

GRAPHICAL ABSTRACT
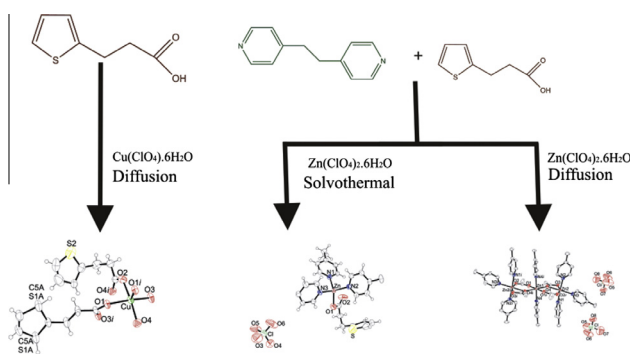
ABSTRACT

In this work the synthesis, spectroscopic properties (infrared and Raman) and crystal structures of three new coordination polymers named [Cu(2-TPA)$_2$]$_n$ (**1**), {[Zn(bpa)(bpa)$_{1/2}$(2-TPA)]·ClO$_4$}$_n$ (**2**) and {[Zn$_3$ (bpa)$_4$(2-TPA)$_4$]·(ClO$_4$)$_2$}$_n$ (**3**) are reported, where 2-TPA is 2-thiophenepropionate and bpa is 1,2-bis(4-pyridyl) ethane. Compounds **1** and **3** were synthesized by the diffusion method, using methanol/water as solvent for compound **1** and ethanol/water for compound **3**. Compound **2** was obtained using solvothermal synthesis, ethanol/water as solvent and with a maximum heating of 90 °C. Compounds **1** and **2** crystallize in monoclinic system and space group $P2_1/c$: for complex **1** was observed the presence of Cu—Cu*i* bond with distance of 2.587 (2) Å, whereas for compound **2** was observed the formation of cavities in the structure. Compound **3** crystallizes in a triclinic system and space group $P-1$, with two crystallographically distinct metallic centers named Zn1 and Zn2; the coordination sphere of Zn1 metal ion exhibits slightly distorted octahedral coordination geometry, whereas the other metal site (Zn2) appears in a slightly distorted square-based pyramid ($\tau = 0.34$). Another important point refers to the synthesis procedure adopted for obtaining different crystalline arrangements involving the same building blocks: by solvothermal or by diffusion, different compounds could be obtained. The vibrational spectra of all the compounds are very similar, and in agreement with the crystal data. The Raman and infrared spectra have shown important bands to confirm the compound formation, such as the coupled ν(CC)/ν(CN) mode at 1600–1620 cm^{-1} (in both Raman and infrared) and ν$_a$(COO) mode at *ca.* 1580 cm^{-1} (infrared).

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Introduction

The synthesis of polymeric coordination networks is a prominent branch of inorganic research in the field of supramolecular chemistry [1], due to their potential applications in catalysis [2], electrical conductivity [3], magnetism [4,5], photochemistry [6], non-linear optical (NLO) [7], gas storage [8], host–guest complexes [9] and drug delivery systems [10]. A macro structure of these compounds extends indefinitely through self-organization reactions between ligands and metal units, generating repeated units, which extend through interactions of the metal–ligand [1,11]. However, several supramolecular architectures are formed simply by the contribution of non-covalent intermolecular forces such as hydrogen-bonding, π-stacking, electrostatic and van der Waals [12]. In many cases such interactions can also be used to predict a possible complicated array, under the crystal engineering field point of view [13].

The use of different building blocks becomes interesting as an alternative to the formation of new supramolecular assemblies, with different physical and chemical properties [14]. One of the building blocks studied here is 2-thiophenepropionic acid, which contains several different coordination modes through the carboxylate group, such as monodentate, chelate, bridging ligands and monoatomic bridge [15]. Thiophene derivatives are known to show biological activities, being used as antiallergic, antimigraine and intestinal antibacterial agents, as well as for influenza treatment [16]. Thiophene carboxylates have also been used as potential antifungal and antitumor agents [17] in the treatment for osteoporosis [18]. It has also been described that thiophene derivatives present in complexes with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, are biologically more active than the free molecules [18].

Another ligand used in this study is 1,2-bis(4-pyridyl)ethane, which has two pyridyl donor groups; it represents an excellent alternative for structural research due to its flexible structure, exhibiting two lowest energy conformations, *gauche* and *anti* [19]. It is broadly used in coordination chemistry as a bidentate bridging ligand, as a terminal ligand or as a host molecule [20], and can also be further involved in hydrogen bonding and/or π-stacking interactions [21]. This kind of molecule has been used to assemble the inorganic building layers to provide porous coordination polymers with variable properties [22] and supramolecular motifs, including ladder (1D), brick wall (2D), molecular bi-layer (2D) and frame (3D), based on T-shaped coordination [23].

The main purpose of this investigation is to describe both the conventional and hydrothermal synthesis, as well as the spectroscopic and structural characterization of three new coordination compounds obtained from the interaction among the 1,2-bis(4-pyridyl)ethane (bpa) and 2-thiophenepropionate (2-TPA) building blocks with Cu^{2+} and Zn^{2+} ions.

Experimental

Materials and methods

All chemicals were of reagent grade and used without further purification. The compounds 1,2-bis(4-pyridyl)ethane (bpa), 2-thiophenepropionic acid (2-HTPA), $Zn(ClO_4)_2 \cdot 6H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$ were purchased from Sigma Aldrich®, whereas ethanol and methanol, used as solvents, were purchased from Vetec®.

The infrared spectra of all the samples were obtained in a Bomem FTIR spectrometer model MB102 in the 4000–400 cm^{-1} region; samples were prepared using KBr as support, with a resolution of 4 cm^{-1} and 64 scan accumulations.

The Raman spectra were performed using a SENTERRA dispersive Raman microscope instrument, using a Nd/YAG laser operating at 532 nm in the green region and a CCD as detector; good signal-to-noise ratios were obtained from 10 spectra of 10 s with a spectral resolution of 3 cm^{-1} and a laser power of 20 mW.

Single crystal X-ray data were collected using an Oxford GEMINI A Ultra diffractometer with Mo Kα (λ = 0.71073 Å) at room temperature. The data collection, reduction, and cell refinement were performed by CrysAlis RED Oxford Diffraction Ltd – Version 1.171.32.38 program [24]. The structures were solved and refined using SHELXL-97 [25] and a multiscan absorption correction was applied [26]. An empirical isotropic extinction parameter x was refined according to the method described by Larson [27]. All non-hydrogen atoms in the compound were anisotropically refined. The hydrogen atoms were positioned geometrically and refined using riding model with C—H = 0.93 Å and Uiso (H) = 1.2 Ueq (C) for aromatic C—H = 0.86 Å and Uiso (H) = 1.2 Ueq (C). The structures were drawn by ORTEP-3 for windows [28] and Mercury

Table 1
Crystal data for $[Cu(2-TPA)_2]_n$ (**1**), $\{[Zn(bpa)(bpa)_{1/2}(2-TPA)] \cdot ClO_4\}_n$ (**2**) and $\{Zn_3(bpa)_4(2-TPA)_4] \cdot (ClO_4)_2\}_n$ (**3**).

Compound	(**1**)	(**2**)	(**3**)
Formula	$C_{14}H_{14}CuO_4S_2$	$C_{25}H_{25}ZnClN_3O_6S$	$C_{76}H_{76}Cl_2N_8O_{16}S_4Zn_3$
Formula weight/g mol^{-1}	373.92	596.38	1752.70
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P-1$
a/Å	5.1961(2)	6.3501(13)	12.9024(6)
b/Å	24.3215(12)	27.177(5)	13.0771(7)
c/Å	11.8920(5)	15.125(3)	13.5708(6)
α	90.00	90.00	111.71
β	90.395(4)	101.75(3)	93.60
γ	90.00	90.00	109.77
V/Å^3	1502.84(11)	2555.7(9)	1955.16(16)
Z	4	4	1
Crystal size/mm	0.446 × 0.154 x 0.043	0.849 × 0.104 × 0.059	0.68 × 0.24 × 0.20
D_{calc}/g cm^{-3}	1.653	1.550	1.489
μ(Mo Kα)/cm^{-1}	1.742	1.194	1.159
Transmission factors (min/max)	0.732/0.928	0.862/0.932	0.723/0.793
Reflections measured/unique	10,195/3078	18,623/5204	15,636/9144
Observed reflections [$F_o^2 > 2\sigma(F_o^2)$]	2576	4166	6794
No. of parameters refined	194	336	494
$R[F_o > 2\sigma(F_o)]$	0.0547	0.0778	0.0646
$wR[F_o^2>2\sigma(F_o)^2]$	0.1494	0.2178	0.1843
S	1.126	1.074	1.086
RMS peak (/)	0.193	0.178	0.147