



Supramolecular architectures of metal complexes containing 4-sulfobenzoate dianion and 1,2-bis(4-pyridyl)ethane

Humberto C. Garcia, Renata Diniz, Luiz Fernando C. de Oliveira *

Núcleo de Espectroscopia e Estrutura Molecular, Departamento de Química, Universidade Federal de Juiz de Fora, Campus Universitário s/n, Martelos, Juiz de Fora, MG 36036-900, Brazil

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ABSTRACT

In this work, synthesis, spectroscopic properties (infrared and Raman) and crystal structures of four new supramolecular arrangement named $[\text{Mn}(\text{Hbpa})_2(\text{H}_2\text{O})_2(4\text{-sb})_2]\cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Co}(\text{Hbpa})_2(\text{H}_2\text{O})_4](4\text{-sb})_2$ (**2**), $[\text{Ni}(\text{Hbpa})_2(\text{H}_2\text{O})_4](4\text{-sb})_2$ (**3**) and $[\text{Zn}(\text{Hbpa})_2(\text{H}_2\text{O})_4](4\text{-sb})_2$ (**4**) have been reported, where bpa is 1,2-bis(4-pyridyl)ethane, Hbpa is the protonated bpa species and 4-sb^{2-} is the sulfobenzoate dianion. All compounds crystallize in a triclinic system with space group $P\bar{1}$; however, only for the complex **1** it was observed the coordination between the metal site and the building block 4-sb^{2-} , being possible to assign the metal hardness. Despite this observed differentiation, the supramolecular arrangement exhibited a similar disposition of planes present in all structures (distinction of 4-sb^{2-} ligand), showing supramolecular interactions such as hydrogen bonding, π -stacking, $\text{C-H}\cdots\pi$ and electrostatics interactions, all of them responsible for the stability of the synthesized compounds. The vibrational spectra of all the compounds are very similar, in agreement with the crystal data. The Raman spectra have showed important bands to confirm the compound formation at 1637 and 1617 cm^{-1} , assigned $\nu(\text{O}=\text{C}=\text{O})$ and $\nu(\text{CC})/\nu(\text{CN})$ of the 4-sb^{2-} and Hbpa building blocks, respectively, in addition to the disappearance of a major band in the synthesized compounds at 801 cm^{-1} , related to the $\delta(\text{COOH})$ mode. Other very important vibrational markers for the bpa ligand can be seen at ca. 1020 cm^{-1} , all of them assigned to the $\nu(\text{ring})$ for compounds **1** to **4**, respectively. The lower value for the $\nu(\text{ring})$ was observed for compound **1**, then suggesting that the coordination by the 4-sb^{2-} building block is important for the weakness of this vibrational mode.

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1. Introduction

In the last years, the study of weak interactions known as beyond the molecule has become an very interesting focus of investigation by several research groups, especially in processes involving chemical solid-state [1,2]. The current interest observed in literature is due to not only by the great variety of observed structural arrangements but also to the much known processes of self-assembly and self-organization of higher complexity entities called building blocks [3–5]. 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 [6–10]. In many cases these weak interactions may be used as important tools in prevision of complicated array, in the crystal engineering field [11,12]. Under the focus of crystal engineering and solid-state architectures, the prior knowledge of these interactions are of great interest, due to their potential applications in materials with possible properties opto-

electronics, electrical conductivity, non-linear optical (NLO), magnetism gas storage, catalysis, host–guest complexes and drug delivery systems [13–18].

The use of different building blocks becomes interesting as an alternative to the formation of new supramolecular assemblies, where the presence of distinct coordination species, with different physical and chemical properties, can bring together the characteristics cited above [19,20]. Thereby the organic species 4-sulfobenzoic acid monopotassium salt (4-KHsb) appears as an interesting building block, containing variable coordination modes through the sulfonate and the carboxylate groups, acting as monodentate, chelating-bidentate, bridging-bidentate, bridging-multidentate as well as in the anionic form (as counter ion) [21,22]. The literature has also shown that 4-KHsb is a good ligand for the construction of coordination polymers with interesting structures, such as inorganic–organic hybrid, formed from systems heterometallic [23]; according to Zheng et al. [24] there can be found thirty different coordination modes for this building block, each one of them described by X-ray crystallography.

Another known ligand used in this study is 1,2-bis(4-pyridyl)ethane(bpa), which has been extensively employed as organic building block for the generation of supramolecular networks. It

* Corresponding author. Tel./fax: +55 (32) 3229 3310.

E-mail address: luiz.oliveira@ufjf.edu.br (L.F.C. de Olive).

can be used in coordination chemistry as a bidentate bridging ligand, but can also act as a terminal ligand or as a host molecule [25,26]. Furthermore, an important feature is related to the properties of new materials containing bpa, ranging from magnetism, catalysis, adsorption and NLO [27,28].

In the last years, our research group has been involved in the investigation of polycarbonylic compounds used as building blocks in crystal engineering, including oxocarbons and pseudo-oxocarbons [29,30] as well barbiturate ion and aromatic carboxylic acids [31,32]. The main purpose of this investigation is the understanding of the structural and spectroscopic properties of such compounds. In this sense, we report here the synthesis, spectroscopic properties and crystal structures of four new compounds of Mn^{2+} , Co^{2+} , Ni^{2+} e Zn^{2+} ions, all of them containing 4-sulfobenzoate dianion ($4-sb^{2-}$) and 1,2-bis(4-pyridyl)ethane (bpa).

2. Experimental

2.1. Materials and methods

All chemicals used in this study were used as purchased without further purification: 4-sulfobenzoic acidmonopotassium salt ($C_7H_5KO_5S$, 95.0%, Sigma Aldrich), 1,2-bis(4-pyridyl)ethane ($C_{12}H_{12}N_2$, 98.0%, Sigma Aldrich), $MnSO_4 \cdot H_2O$ (98.0%, Vetec), $CoCl_2 \cdot 6H_2O$ (99.5%, Sigma Aldrich), $NiCl_2 \cdot 6H_2O$ (97.0%, Vetec) and $ZnSO_4 \cdot 7H_2O$ (99.0%, Vetec). Elemental analyses of C, H and N were performed with a Perkin-Elmer 240 CHN analyser. Thermogravimetric analysis was obtained on a TG-60. All Samples (5–8 mg) was heated at 10 °C/min from room temperature to 900 °C in a dynamic nitrogen atmosphere (flow rate = 50 mL/min). Infrared spectra were obtained using a Bomem MB-102 spectrometer fitted with a CsI beam splitter, with the samples dispersed on KBr disks and the spectral resolution was acquired at 4 cm^{-1} . Good signal-to-noise ratios were obtained from the accumulation of 128 spectral scans. Fourier-transform Raman spectroscopy was performed using a Bruker RFS 100 instrument, Nd^{3+}/YAG laser operating at 1064 nm in the near-infrared region and a CCD detector cooled with liquid N_2 . Good signal-to-noise ratios were obtained from 2000 scans that were accumulated over a period of 30 min with a spectral resolution of 4 cm^{-1} . All spectra were obtained at least twice to show reproducibility, and there were no observed changes in band positions or intensities.

2.2. Synthesis

The synthetic procedure in general was similar for all complexes: 10 mL of an aqueous solution containing 65.0 mg (0.27 mmol) of 4-sulfobenzoic acid monopotassium salt (4-KHsb) was mixed with 10 mL of an ethanolic solution containing 50.0 mg (0.27 mmol) of 1,2-bis(4-pyridyl)ethane (bpa), resulting in a homogeneous colorless solution; to this solution was added by slow diffusion 5 mL of an aqueous solution containing 0.27 mmol of a metallic ion. After a few days suitable single crystals were obtained and separated by filtration, being colorless for Mn^{2+} [yield = 32%] and Zn^{2+} [yield = 42%] complexes, orange for Co^{2+} [yield = 35%] and green for Ni^{2+} [yield = 38%]. Elemental analysis: $[Mn(Hbpa)_2(H_2O)_2(4-sb)_2] \cdot 2H_2O$ (**1**): Calc.: for C, 50.83; H, 4.72; N, 6.24. Found: C, 51.03; H, 4.95; N, 6.02%; $[Co(Hbpa)_2(H_2O)_4(4-sb)_2]$ (**2**): Calc.: for C, 50.61; H, 4.69; N, 6.21. Found: C, 50.10; H, 4.84; N, 5.92%; $[Ni(Hbpa)_2(H_2O)_4(4-sb)_2]$ (**3**): Calc.: for C, 50.62; H, 4.70; N, 6.21. Found: C, 50.35; H, 4.91; N, 5.98%; $[Zn(Hbpa)_2(H_2O)_4(4-sb)_2]$ (**4**): Calc.: C, 50.25; H, 4.66; N, 6.17. Found: C, 51.15; H, 4.73; N, 6.04%.

2.3. X-ray crystallography

Single crystal X-ray data were collected using an Oxford GEMINI A Ultra diffractometer with $Mo\ K\alpha$ ($\lambda = 0.71073\text{ \AA}$) for every compound. Data collection, reduction and cell refinement were performed by CrysAlis RED, Oxford diffraction Ltda, Version 1.171.32.38 program [33]. The structures were solved and refined using SHELXL-97 [34]. The empirical isotropic extinction parameter x was refined according to the method previously described by Larson [35], and a Multiscan absorption correction was applied [36]. The structures were drawn by ORTEP-3 for windows [37] and Mercury [38] programs. Crystal and structural refinement data for both compounds are displayed in Table 1.

3. Results and discussions

The four transition metal complexes of general formula $[Mn(Hbpa)_2(H_2O)_2(4-sb)_2] \cdot 2H_2O$ (**1**) and $[M(Hbpa)_2(H_2O)_4(4-sb)_2]$, (where $M = Co^{2+}$, Ni^{2+} and Zn^{2+} , respectively complexes **2**, **3** and **4**) were obtained by slow diffusion of metal aqueous solutions into a solution containing the building blocks 4-sulfobenzoic acid monopotassium salt (4-KHsb) and 1,2-bis(4-pyridyl)ethane (bpa). In all synthesized compounds the analytical data (which can be seen in the Experimental section) suggest the proportion stoichiometry as 1: 2: 2 $[M^{2+}:Hbpa^+:4-sb^{2-}]$.

Thermogravimetric curves (TGA and DTA) of compounds **1**, **2**, **3** and **4** are deposited as Supplementary materials (Figs. S1–S4, respectively). For compound **1** the thermogravimetric analysis show the first weight loss around 108 °C, which can be associated to the exit of four water molecules mols (calcd./exp.: 8.0%/7.8%) by repeating unit. In this weight loss region it can be observed by DTA the presence of three endothermic events occurring consecutively at 89, 108 and 126 °C. In addition, the TG curve displays other weight loss steps above 200 °C, which can be attributed to the thermal decomposition of organic material, where as the residue can be related to the formation of the metallic species (calcd./exp.: 6.1/6.2%). For complexes **2**, **3** and **4** the thermogravimetric analyses showed a very similar profile, suggesting the same crystallization arrangement. It can be observed a first mass loss in the 66–83 °C range, which is associated to the exit of two water molecules (calcd./exp.: 4.0/4.1%, 4.0/4.2%) and 3.9/4.3% for complexes **2**, **3** and **4**, respectively). For the same compounds a second weight loss is observed at ca. 147–174 °C and attributed to the exit of another two water molecules mols by repeating unit (calcd./exp.: 4.0/4.0%, 4.0/4.1% and 3.9/4.6%, for compounds **2**, **3** and **4** respectively). All these events are also observed by DTA analysis, with the presence of two endothermic events in this region. Other important information obtained by DTA is observed through an exothermic event around 201, 197 and 206 °C for compounds **2**, **3** and **4**, respectively, suggesting a new structural rearrangement with energy liberation. Furthermore, all TG curves display other three weight loss steps which can be attributed to thermal decomposition. For the compound **2** the final residue can be identified as the metallic species (calcd./exp.: 6.5/6.6%); however, for compounds **3** and **4** the maximum temperature measurement at 900 °C was not enough for the complete decomposition of the entire sample, leaving a large amount of mass as the residue.

The structural arrangements for compounds **1**, **2**, **3** and **4** were revealed by X-ray single crystal analysis; all compounds crystallize in a triclinic crystal system with $P\bar{1}$ space group but only compounds **2**, **3** and **4** can be considered as isomorphous. The main geometrical parameters and hydrogen bond interactions observed in the compounds **1** to **4** are presented in Table 2, respectively.

Fig. 1 displays for compound **1** the repeating unit consisting of neutral blocks, formed by the metallic ion Mn^{2+} coordinated in a

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