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An interesting pseudo-honeycomb supramolecular arrangement obtained from the interaction between 4-aminosalicylic acid, *trans*-1,2-bis(4-pyridyl)ethylene and transition metal ions[†]

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In this work, three new compounds containing coordination polymers named $[Co(bpe)(H_2O)_4]$ AS₂·4H₂O (1), $[Ni(bpe)(H_2O)_4]$ AS₂·4H₂O (2) and $[Zn(bpe)(H_2O)_4]$ AS₂·4H₂O (3) (where AS is aminosalicylate anion and bpe is *trans*-1,2-bis(4-pyridyl)ethylene) were synthesized and characterized by X-ray diffraction and vibrational spectroscopy (infrared and Raman). All complexes are isomorphous, crystallizing in a monoclinic system with space group P_{21}/c . The crystalline arrangement shows the presence of a cavity called pseudo-honeycomb imperfect, parallel to the *bc*-plane formed through hydrogen bonding between aminosalicylate anions and water molecules of crystallization. The vibrational spectra of the compounds are very similar, in agreement with the crystal data. The Raman spectra show bands for bpe at 1642 and 1614 cm⁻¹, assigned to $\nu(C=C)$ and $\nu(CC)/\nu(CN)$, respectively. This study can be considered as the first work in the literature where the aminosalicylate anion is associated with coordination polymers just filling the cavities of pseudo-honeycomb structures.

Introduction

The synthesis and characterization of novel supramolecular arrangements have become a focus of study of a large number of scientific groups in the last few years. Work involving the understanding of chemical bonds (such as covalent bonds) is increasingly losing pace to that of weak intermolecular interactions, such as the already known hydrogen bonding, electrostatic, C–H… π and π -stacking interactions.¹⁻⁴ The search for a more accurate understanding of these interactions, so important as they extend beyond the individual molecules, has developed a new branch of science which has received the suggestive name of supramolecular chemistry.^{5,6}

The study of these weak non-covalent interactions, especially the hydrogen bonds, plays a crucial role in fundamental biological processes, as for instance, the transfer of genetic information and molecular recognition between receptors and substrates. These weak interactions can be major contributors to the binding of drugs to proteins and DNA targets and can form the basis for developing sensors to monitor the concentration of specific ions or molecules. In terms of coordination chemistry, the weak supramolecular interactions are responsible for the construction of complicated extended arrays of molecular selforganization and self-assemblies. This arrangement is the result of the association of several chemical entities organized in higher complexity and known as building blocks, giving rise to compounds with a wide range of applications in biological, optic, electronic and microporous materials.⁷⁻⁹

In this context, the organic ligand 4-aminosalicylic acid (HAS) has appeared as a hopeful building block, due to the possibility of different coordination sites, as well as its pharmacological properties.¹⁰ HAS is an antibiotic used since the 1940's in the treatment of tuberculosis;¹¹ on the other hand, there are only a few studies in the literature involving this type of structure associated with transition metal ions, nitrogen ligands, or generating anionic building blocks,^{12,13} mainly due to the instability of the aminosalicylate salt, evidenced by the darkening of the solution.

Another organic ligand used in this study is the nitrogenous compound named *trans*-1,2-bis(4-pyridyl)ethylene (bpe), which is an excellent building block in the design and construction of molecular complexes.^{14,15} It can not only act as a chelating ligand, but can also serve as a terminal ligand or an uncoordinated guest molecule, which may be further involved in hydrogen bonding, C–H··· π and π -stacking interactions, due to the presence of the pyridyl ring. Furthermore, magnetic properties, host–guest and non-linear optical (NLO) materials are also observed for this ligand, mainly when associated with transition metal ions.^{16,17}

In the present work the synthesis, crystal structures and vibrational spectroscopic analysis (infrared and Raman) of three

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new supramolecular complexes containing aminosalicylate anion (AS⁻) and nitrogen ligand *trans*-1,2-bis(4-pyridyl)ethylene (bpe) as building blocks and transition metal ions (Co²⁺, Ni²⁺ and Zn²⁺) are described, together with thermal analysis. The correlation between crystal data and vibrational spectra is also investigated, aiming to understand the possible type of interactions which are present in the solid state of these compounds, as well as the influence of such interactions in the crystal packing.

Experimental section

Chemicals and reagents

All chemicals used in this study were used as purchased without further purification: 4-aminosalicylic acid ($C_7H_7NO_3$, 99.0%, Sigma Aldrich), *trans*-1,2-bis(4-pyridyl)ethylene (bpe) (98.0%, Sigma Aldrich), $CoCl_2 \cdot 6H_2O$ (98.0%, Vetec), $NiCl_2 \cdot 6H_2O$ (99.9%, Sigma Aldrich) and $ZnSO_4 \cdot 7H_2O$ (99.0%, Vetec).

Synthesis

The aminosalicylate salt (AS⁻) used for vibrational measurements (infrared and Raman) was prepared by the direct reaction between 4-aminosalicylic acid and sodium carbonate solution, in a 2 : 1 stoichiometry ratio. The resulting solution was evaporated (by reduced pressure), with the formation of a white solid. Elemental analysis for $C_7H_{10}NO_5Na$ (or NaAS·2H₂O): calc.: C, 38.82%; H, 4.77%; N, 6.63%; found: C, 39.03%; H, 4.95%; N, 6.78%.

The compounds named [Co(bpe)(H₂O)₄]AS₂·4H₂O (1), [Ni $(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (2) and $[Zn(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (3) were prepared by mixing 10 mL of an alcoholic solution containing approximately 50 mg (0.27 mmol) of bpe and 5 mL of an aqueous solution containing 0.27 mmol of the metal salts: CoCl₂·6H₂O (65 mg), NiCl₂·6H₂O (65 mg) and ZnSO₄·7H₂O (79 mg); after the addition, there was the immediate formation of a precipitate of orange, green and white colors, for the respective salts used for synthesis. Then to this solution was added 10 mL of a solution (water and ethanol 1/1 ratio) containing 42.0 mg (0.27 mmol) of 4-aminosalycilic acid, followed by stirring and heating (50 °C) until complete dissolution of the precipitate, providing orange, green and yellow homogeneous solutions for the Co(II), Ni(II) and Zn(II) ions. After approximately seven days suitable single crystals were obtained, being orange for Co(II) [52% yield], green for Ni(II) [63% yield] and yellow for Zn(II) [68% yield]. Elemental analysis: [Co(bpe)(H₂O)₄]AS₂·4H₂O (1): calc.: C, 45.29%; H, 5.55%; N, 8.13%; found: C, 45.40%; H, 5.37%; N, 8.16%; $[Ni(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (2): calc.: C, 45.30%; H, 5.56%; N, 8.13%; found: C, 45.73%; H, 5.50%; N, 8.20%; [Zn $(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (3): calc.: C, 44.87%; H, 5.50%; N, 8.05%; found: C, 44.83%; H, 5.39%; N, 8.09%.

Physical measurements

Thermogravimetric measurements (TG/DTA) were performed using a Shimadzu TG-60 with a thermo balance; samples were heated at a rate of 10 °C min⁻¹ from room temperature to 1000 °C in a dynamic nitrogen atmosphere, at a flow rate of 100 mL min⁻¹. 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, an Nd³⁺/YAG laser operating at 1064 nm in the near-infrared region and a CCD detector cooled with liquid N₂. 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. Single crystal X-ray data were collected using an Oxford GEMINI A Ultra diffractometer with MoKa $(\lambda = 0.71073 \text{ Å})$ at room temperature (298 K) for compounds 1, 2 and 3. Data collection, reduction and cell refinement were performed by the CrysAlis RED, Oxford diffraction Ltd, Version 1.171.32.38 program.¹⁸ The structures were solved and refined using SHELXL-97.19 The empirical isotropic extinction parameter x was refined according to the method previously described by Larson,²⁰ and a multiscan absorption correction was applied.²¹ The structures were drawn by ORTEP-3 for windows²² and Mercury²³ programs.

Results and discussions

Transition metal complexes of general formula $[M(bpe)(H_2O)_4]$ AS₂·4H₂O (where M = Co²⁺, Ni²⁺ and Zn²⁺) were obtained as single crystals after a slow crystallization of a mixture containing all the building blocks used in this study. In all cases, analytical data suggest the formation of compounds with a stoichiometric proportion of 1 : 2 : 1 (referring to M²⁺ : AS⁻ : bpe), which is slightly different from the synthesis stoichiometry (1 : 1 : 1).

The thermogravimetric analyses of all compounds reinforce that the metallic complexes are hydrated. Thermogravimetric curves of the investigated compounds are shown in ESI⁺ (Fig. S1–S3). All curves show a similar weight loss around 100 °C which can be attributed to the loss of eight water molecules for compounds 1, 2, and 3, at the calculated/experimental ratios of 20.88%/20.83%, 20.89%/20.66% and 20.68%/19.82%, respectively. This fact suggests a weak chemical interaction between crystallization and coordination water molecules within the chemical environment of the obtained supramolecular structures. A second weight loss similar to all compounds can be observed near 200 °C, being attributed to the thermodecomposition of one bpe molecule for compounds 1 (calcd/exp.: 26.42%/ 26.77%), 2 (calcd/exp.: 26.43%/26.46%) and 3 (calcd/exp.: 26.18%/25.35%). The final residue starts to be formed above 700 °C for all compounds, and can be identified as one mol of metal (calcd/exp.: 8.55%/8.86%, calcd/exp.: 8.51%/8.36% and calcd/exp.: 9.48%/9.11% for compounds 1, 2 and 3, respectively).

The structural design of the supramolecular compounds was revealed by X-ray single crystal analysis. Tables 1–3 display the crystallographic data, the main geometrical parameters and the hydrogen interactions of the three new compounds containing coordination polymers. Comparing the listed crystallographic parameters it can be noticed that the compounds are isomorphous, crystallizing in a monoclinic crystal system with space group $P2_1/c$. Fig. 1 presents the crystal structure of the complexes, where it can be seen as an extended one-dimensional chain, formed by the bpe ligand covalently bonded to the metal

Table 1	Crystal data for	[M(bpe)(H ₂ O) ₄]AS ₂	·4H ₂ O compounds	containing coordination	polymers
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Compound	$[Co(bpe)(H_2O)_4]AS_2 \cdot 4H_2O(1)$	$[Ni(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (2)	$[Zn(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (3)		
Formula	C ₂₆ H ₃₈ CoN ₄ O ₁₄	C ₂₆ H ₃₈ NiN ₄ O ₁₄	C ₂₆ H ₃₈ ZnN ₄ O ₁₄		
Formula weight/g mol ⁻¹	689.53	689.29	695.99		
Temperature/K	298(2)	298(2)	298(2)		
Crystal system	Monoclinic	Monoclinic	Monoclinic		
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$		
a/Å	13.7314(2)	13.6410(3)	13.7232(3)		
b/Å	7.6426(2)	7.6543(2)	7.6423(2)		
c/Å	14.8068(3)	14.7589(4)	14.8063(4)		
β	96.755(2)	96.689(2)	96.804(2)		
V/Å ³	1543.09(6)	1530.51(6)	1541.90(7)		
Ζ	2	2	2		
Crystal size/mm	0.24 imes 0.32 imes 0.87	0.16 imes 0.28 imes 0.38	0.29 imes 0.36 imes 0.93		
θ Range/°	2.76-32.84	2.65-32.78	2.76-32.83		
$d_{\rm calc}/{\rm g~cm^{-1}}$	1.484	1.496	1.499		
μ (Mo K α)/mm ⁻¹	0.631	0.709	0.871		
Transmission factors (min/max)	0.785/0.859	0.788/0.893	0.693/0.777		
Reflections measured/unique	7772/3166	7406/3143	8212/3165		
R _{int}	0.0321	0.0313	0.0313		
Observed reflections $[F_0^2 > 2\sigma(F_0^2)]$	2615	2550	2640		
No. of parameters refined	242	249	250		
$R[F_{0} > 2\sigma(F_{0})]$	0.0396	0.0429	0.0328		
$wR[F_0^2 > 2\sigma(F_0)^2]$	0.1336	0.1446	0.1005		
S	1.182	1.130	1.158		
RMS peak	0.074	0.108	0.154		

	$[Co(bpe)(H_2O)_4]AS_2 \cdot 4H_2O(1)$	$[Ni(bpe)(H_2O)_4]AS_2 \cdot 4H_2O~(\textbf{2})$	$[Zn(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (3)
Bond distance/Å			
M-O4	2.077(2)	2.046(2)	2.079(2)
M-O5	2.125(2)	2.079(2)	2.133(2)
M-N2	2.165(2)	2.119(2)	2.161(2)
O3–C5	1.354(3)	1.362(3)	1.355(2)
O1–C7	1.250(3)	1.242(4)	1.240(3)
N2-C8	1.337(3)	1.332(3)	1.336(3)
N2-C12	1.347(3)	1.337(3)	1.334(3)
O2–C7	1.278(3)	1.286(3)	1.297(3)
C3-N1	1.365(3)	1.369(4)	1.364(3)
C13-C13	1.313(6)	1.340(6)	1.327(5)
Average of bond an	igles/°		
O4–M–O4	180.0	180.0	180.0
O4-M-O5	89.08(7)	89.81(8)	89.47(7)
O4-M-O5	90.92(7)	90.19(8)	90.53(7)
O5–M–O5	180.00(10)	180.0	180.00(10)
O4-M-N2	90.25(7)	90.06(8)	90.40(6)
O5–M–N2	91.24(8)	91.27(9)	91.49(7)



Fig. 1 ORTEP representation of the 1D covalently bonded chain and aminosalicylate anion. Thermal ellipsoids are drawn at the 50% probability level for the compounds $[M(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$. The water molecules are omitted for clarity. Symmetry code (iii): -x, -y, -z.

site, which is also coordinated to four water molecules, thus giving rise to a polymeric repeating unit with general formula $[M(bpe)(H_2O)_4]_n^{2+}$. Two uncoordinated aminosalicylate ions act as anions, balancing the charge of the cationic blocks. Besides the electrostatic supramolecular interaction, the aminosalicylate anion also interacts with the polymeric unit via hydrogen bonding through its carboxylate group with the water molecules involved in the coordination; completing the repeating unit are four crystallization water molecules, which are omitted from Fig. 1 for better visualization. The coordination sphere of metallic ions shows a slightly distorted octahedral geometry, where each pyridyl ring of bpe adopts an axial position, whereas four aqua ligands are in the equatorial positions. The averages of M-O and M-N bond distances are 2.101(2) and 2.165(2) Å for compound 1, 2.063(2) and 2.119(2) Å for compound 2 and 2.106(2) and 2.161(2) Å for compound 3, respectively. The bpe ligand presents a bis-monodentate coordination mode between two adjacent metallic centers (Co…Co = 13.731(2) Å, Ni…Ni = 13.641(2) Å, Zn…Zn = 13.723(2) Å) in a one-dimensional infinite chain. It can also be observed that the two pyridyl rings of the bpe ligand are coplanar, since both carbon atoms of the aliphatic chain present π bonds.

Fig. 2(a) shows an interesting supramolecular arrangement parallel to the *a*-crystallographic axis involving one-dimensional polymer chain $[M(bpe)(H_2O)_4]_n^{2+}$ common to the three synthesized complexes. Another interaction occurs only through hydrogen bonding between aminosalicylate anions and water molecules of crystallization with the formation of a 2D cavity which encapsulates the one-dimensional polymer chain throughout the full length. The one-dimensional polymer chain interacts with the supramolecular cavity through hydrogen interactions between the coordination water molecules and the crystallization water molecules, as well as the carboxylic and hydroxyl groups from the aminosalicylic anion.

Fig. 2(b) shows that the cavity parallel to the *bc*-plane consists of three aminosalicylate anions and five water molecules, which interact *via* hydrogen bonds through the carboxyl and hydroxyl groups. These interactions are classified as moderate and weak because the interaction distances 2.797(3) Å (O1…O7), 2.830 (3) Å (O6…O7), 2.835(3) Å (O2…O6) and 2.934(3) Å (O7…O3) for complexes **1**, **2** and **3** (see Table 3) between donor and receptor atoms present in the structure are 2.5 Å < x < 2.8 Å or x > 2.8 Å.²⁴ The geometrical parameters of these hydrogen bonds are listed in Table 3. Another classification for this



Fig. 2 Two different views of the 1D covalent linear chain [M(bpe) $(H_2O)_4]_n^{2+}$: (a) along the *a*-crystallographic axis and (b) in the *bc*-plane involved in the cavity.

supramolecular cavity formed by the hydrogen interaction can be represented as a net graph: $N_1 = C_4^4(16)R_8^8(26)S(6)$, where the symbols *C*, *R* and *S* describe an infinite chain, ring set and intramolecular interaction respectively, whereas the subscript numbers indicate the quantities of donor atoms and the superscript numbers indicate the acceptor atoms in each set.^{25,26} Another two types of supramolecular hydrogen bonding interactions can be observed: one between two parallel polymer chains and two crystallization water molecules, and other between the aminosalicylate anion, the polymeric chains and the crystallization water molecules, generating net graphs classified as $N_2 = R_4^2(34)$ and $N_3 = C_4^3(16)R_4^3(27)$, respectively. These supramolecular interactions can be seen in Fig. S4 and S5, ESI†.

Fig. 3 displays the two-dimensional supramolecular arrangement formed parallel to the bc-plane through holes which are connected to each other by hydrogen bonds between aminosalicylate anions and crystallization water molecules. Each one of these connectors gives rise to three independent cavities in the structure, resembling imperfect hexagons; the interaction between them creates a new macrostructure that resembles a honeycomb. However, such supramolecular structure only exists through intermolecular forces, more precisely by hydrogen interactions; due to this fact, the system can be classified as an



Fig. 3 Supramolecular interactions of the cavities, with formation of the pseudo-honeycomb structure.

Table 3 Selected geometrical parameters of $[M(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$, taking into account the hydrogen interactions

	$[Co(bpe)(H_2O)_4]AS_2 \cdot 4H_2O(1)$	$[Ni(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (2)	$[Zn(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (3)
D····A/Å			
N1…07	3.021(3)	3.024(4)	3.017(3)
03…02	2.534(3)	2.523(3)	2.522(2)
04…01	2.732(3)	2.731(3)	2.726(2)
04…02	2.726(3)	2.747(3)	2.738(2)
05…06	2.792(3)	2.776(3)	2.780(3)
O6…O7	2.830(3)	2.844(4)	2.839(3)
O6…O2	2.835(3)	2.836(3)	2.822(3)
O7…O3	2.934(3)	2.925(3)	2.945(3)
O7…O1	2.797(3)	2.790(3)	2.792(3)
$D - H \cdots A / \circ$			
N1-HN1A…07	173(3)	162(5)	159(3)
O3–H3…O2	147.00	147.00	147.00
O4–H4A…O1	158.00	175(3)	172(2)
O4−H4B…O2	164(3)	177(3)	172(3)
O5–H5A…O6	158.00	172(3)	168(2)

imperfect pseudo-honeycomb. Inside each cavity, which comprises the observed pseudo-honeycomb parallel to the crystallographic a axis, the presence of the one-dimensional polymer chain generated by its monomeric fragment $[M(bpe)(H_2O)_4]_n^{2+}$ can be seen, covalently expanded in only one dimension. The presence of hydrogen bonds in the pseudo-honeycomb structure generates a 2D system parallel to the bc-plane; this arrangement interacts with other arrangements (or neighbors) via hydrogen bonding parallel to the a-axis, thus causing the structure to present a 3D supramolecular arrangement. Besides the hydrogen bonds, which contribute significantly to the stability of the crystal lattice, other supramolecular interactions can also be observed between the rings of the pyridyl moiety and the aminosalicylate anion, as for instance the π -stacking interactions, showing centroid-centroid distances of 3.699(2) A, 3.701(2) A and 3.701(2) Å and horizontal offsets of 1.435(3), 1.429(2), and 1.434(3) for compounds 1, 2 and 3, respectively. The N-H $\cdots\pi$ interactions (similar to C-H··· π) can also be seen between the hydrogen of the amino group of one aminosalicylate and the ring of another aminosalicylate anion, with $N \cdots \pi$ distances of 3.516(2) Å, 3.497(2) Å and 3.512(2) Å for compounds 1, 2 and 3, respectively.27,28 It is important to mention that the literature has shown only a few examples of pseudo-honeycombs; for instance, Kulynych and Shimizu²⁹ have applied the term "pseudo" for the formation of irregular hexagons, with formation of covalently linked cavities originated from the interaction between 5-sulfoisophthalic acid and copper ion, whereas Perruchas et al.³⁰ have used the same term for the description of the intermolecular forces through cationic blocks responsible for the creation of the arrangements which resemble a honeycomb. In our study, the interesting feature is the cavity formed by the mixture between anionic and neutral molecular blocks. However, the major difference rests on the guest moiety, which in our case is the polymeric chain formed by metal ions and bpe ligand; from our knowledge, this can be considered as the first work in the literature reporting this type of structure for aminosalicylate anions.

The vibrational spectra of all ligands and complexes investigated in this work are displayed in Fig. 4 and 5 (infrared and Raman spectra, respectively). All spectra are very similar and in agreement with the crystal data, which indicates the same crystalline arrangement for all compounds obtained. The main vibrational modes are summarized in Table 4, as well as the tentative assignment based on similar chemical systems.^{31–34}

In the infrared spectrum of the aminosalicylate anion can be observed a broad band around 3200-3500 cm⁻¹ region, assigned to the stretching modes of H₂O and NH₂ groups. These same bands are also observed for the three complexes, suggesting the hydration of all synthesized compounds, previously confirmed by the data from elemental analysis and X-ray diffraction. The strong band observed at 1637 cm⁻¹ can be assigned to the ν (C= O) of the carboxyl group; this mode appears to be shifted by *ca*. 15 cm⁻¹ to lower wavenumbers when compared to the acidic species, due to the loss of the acidic hydrogen atom and a consequent increase of the electronic delocalization over the carboxyl group in the anionic species formed. In a vibrational study involving infrared, Raman and SERS, Panicker and coworkers³² have assigned the main modes of aminosalicylic acid and its corresponding salt, especially in the spectral region between 1400 and 1600 cm⁻¹, which presents some intense bands



Fig. 4 Infrared spectra of $[M(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (where M = Co, Ni and Zn, AS^- is aminosalicylic anion and bpe is 1,2-bis(4-pyridyl)-ethylene); for comparison purposes the spectra of the ligands (AS^- and bpe) are also displayed.

assigned to the CC stretching modes of the phenyl ring. Another very characteristic band can be observed at 1188 cm⁻¹, referring to the ν (C–O) of the hydroxyl group. The Raman spectrum of the aminosalicylate anion shows a strong band at 1625 cm⁻¹, also tentatively assigned to the ν (C=O) of the carboxyl group, and in the region 1400–1600 cm⁻¹ some intense bands can be seen which are related to the (CC) stretching modes of the phenyl ring, in the same way as observed in the infrared spectrum.

In the infrared spectrum for the free bpe ligand, a very intense band at 1597 cm⁻¹ can be assigned to the coupled $\nu(CC)/\nu(CN)$ stretching modes of the pyridyl rings, whereas two other important and intense bands appear at around 1416 and 989 cm⁻¹ are



Fig. 5 Raman spectra of $[M(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (where M = Co, Ni and Zn, AS^- is aminosalicylic anion and bpe is 1,2-bis(4-pyridyl) ethylene); for comparison purposes the spectra of the ligands (AS⁻ and bpe) are also displayed.

NaAs		bpe		$\frac{[Co(bpe)(H_2O)_4]}{AS_2 \cdot 4H_2O(1)}$		$[Ni(bpe)(H_2O)_4]$ AS ₂ ·4H ₂ O (2)		$[Zn(bpe)(H_2O)_4] \\ AS_2 \cdot 4H_2O (3)$			
IR	R	IR	R	IR	R	IR	R	IR	R	Tentative assignment	
459 w	440 w 532 m			465 w		464 w		465 w		$\delta(CC)$ $\delta(C-O) + \delta(C=O)$	
		556 vs		557 m		559 m		557 m		$\delta(CH) + \delta(C-C)$	
629 m			670 w	623 m		625 m		623 m		$\delta(CC)$ Ring breathing	
706 m	777 m			701 w	750 w	704 w	751 w	702 w	751 w	$\delta(CC) \\ \delta(NH)_2$	
810 m		829 vs		797 m		795 m		795 m		$\delta(CC)$ $\delta(C-N) + \nu(C-C)$	
831 m	834 m			829 m		829 m		829 m		δ(CH)	
862 m	858 m		879 w		880 w		879 w		881 w	$\delta(CH)$ $\delta(C=C)$	
973 m	973 m			968 m		968 m		968 m		$\delta(NH)_2$	
		997 vs	996 m	1018 m	1020 m	1022 m	1023 w	1020 m	1021 m	Ring breathing	
1168 w				1151 m		1151 m		1151 m		$\delta(CH) + \delta(C-C)$	
1188 m				1194 w		1194 w		1194 w		ν (C–O) _h	
			1197 s		1201 m		1201 s		1201 s	$\nu(C-C)$	
1228 m	1232 s			1221 w		1221 w		1223 w		ν (C–O) _h	
			1237 m		1243 w		1243 w		1245 w	$\delta(CH)$	
1304 s	1318 s			1315 s		1315 s		1313 s		$\nu(CC)$	
			1342 w	1352 m	1339 w	1352 m	1339 w	1352 m	1340 w	$\delta(CH) + \nu(CC)$	
1388 s	1392 s			1390 s		1391 s		1391 vs		ν (C–O) _c	
		1418 vs								$\nu(CC)$	
1448 s	1450 m			1458 vs		1458 vs		1458 s		$\nu(CC)$	
			1492 w							$\nu(CN) + \nu(CC)$	
1508 m				1518 m		1514 m		1514 m		$\nu(CC)$	
		1556 s	1548 w	1578 vs	1555 w	1578 vs	1554 w	1580 vs	1556	$\nu(CN) + \nu(CC)$	
1 () 7	1.625	1597 vs	1596 vs	1612 s	1614 vs	1612 s	1614 vs	1612 vs	1614 vs	$\nu(CC)/\nu(CN)$	
1637 s	1625 m		1.641	1.640	1.640	1.640	1.641	1.642	1.642	$\nu(C=O)$	
		2026	1641 vs	1643 s	1642 vs	1643 s	1641 vs	1643 s	1643 vs	$\nu(C=C)_{\nu}$	
	20(2	3036 w	3054 w	20(0.1	2000	2074 1	2075	2072 1	2064	$\nu(CH)$	
2224	3062 m			3068 sh	3066 W	30/4 sh	3065 W	30/2 sh	3064 W	$\nu(CH)$	
2402 m				3340 Dr		3335 Dr 2456 m		3350 Dr		$\nu(OH)$	
5402 III				5450 m		5450 m		3430 m		$\nu(1 n_2)$	

Table 4 Raman (R) and infrared (IR) wavenumbers (in cm⁻¹) and tentative assignment of the most important bands observed in the $[M(bpe)(H_2O)_4]$ AS₂·4H₂O spectra^{*a*}

^{*a*} Abbreviations: vs, very strong; s, strong; m, medium; w, weak; v, vinyl; sh, shoulder; br, broad. The subscript c designates a motion of the carboxyl group, the subscript h a motion of a hydroxyl group.

attributed to the $\nu(CC)$ and ν ring respectively. The Raman spectrum displays two intense bands at 1641 and 1596 cm⁻¹, which can be assigned to the $\nu(C=C)$ stretching referring to the carbon atoms of the aliphatic chain between the pyridyl rings and $\nu(CC)/\nu(CN)$ of the same ring respectively. Another less intense band which shows the same characteristic as before is located at 996 cm⁻¹ and attributed to ring breathing. For the bpe ligand the spectral regions (in both infrared and Raman) around 1590 and 1650 cm⁻¹, where CC and CN stretching modes are expected, are very important in the confirmation of coordination or any other disturbance caused to the structure, found through the simple displacement of the vibrational modes.

For the compounds 1, 2 and 3 the infrared spectrum exhibits an intense band around 1643 cm^{-1} that can be attributed to the carbon–carbon stretching mode in the aliphatic chain present between the two pyridyl rings of the bpe ligand. The interesting feature in the appearance of this band is the ratification of the bpe ligand coordination, since this mode has no activity through the infrared technique when the ligand is in the free form. Another vibrational mode which confirms the presence of this ligand in the formation of the supramolecular complex is the

band at 1612 cm⁻¹, assigned to the $\nu(CC)/\nu(CN)$ stretching of the pyridyl ring; this same band appears to be shifted by ca. 15 cm⁻¹ compared to the free ligand which occurs at 1597 cm⁻¹, as previously assigned as a mode involving pyridine ligands in the coordination environment.35 The presence of the aminosalicylate anion in the formation of the supramolecular structure is observed through a band of medium intensity at 1194 cm⁻¹, referring to the ν (C–O) of the hydroxyl group. Other vibrational modes characteristic of this structure are seen in the 1350-1550 cm⁻¹ region, and assigned to the stretching of the CC modes of the phenyl ring. The spectroscopic analysis indicates the disappearance of the vibrational mode referring to the carbonyl stretch at 1637 cm⁻¹, which may be understood by a symmetry change in the structure, thus favoring the intensity decrease of the CO stretching in the infrared technique. The Raman spectra of complexes 1, 2, and 3 showed a very similar profile, with the high intensity bands related to the bpe ligand. For instance, two vibrational modes can be mentioned occurring at 1614 and 1021 cm⁻¹, assigned to the $\nu(CC)/\nu(CN)$ and ring breathing modes, respectively. As discussed before, both vibrational modes appear to be shifted to high wavenumber, thus suggesting the coordination of the nitrogen atom of bpe to the metal site. Another two modes of high intensity, but which present a small wavenumber shift after coordination to the metal site, appear at 1642 and 1201 cm⁻¹, assigned to the ν (C=C) and ν (C-C) modes, present in the aliphatic chain between the pyridyl rings. Another intriguing fact about the Raman spectra is the decrease or absence of the main vibrational modes concerning the characterization and/or confirmation of the aminosalicylate anion in the supramolecular structure. Vibrations such as the aromatic ring modes, between 1400 and 1600 cm⁻¹, or related to the carbonyl stretching mode at 1637 cm⁻¹, show a decrease or even a disappearance, which can be explained by the formation of the [M(bpe)(H₂O)4]_n²⁺ polymeric complex exhibiting better scattering than the aminosalicylate anion, thus providing a better Raman spectrum.

As a final remark it can be said that supramolecular chemistry pursues the understanding of the role in which building blocks are involved in the macrostructures, being responsible for creating new assemblies related to drugs, electronic and magnetic devices, among others. Thus it is essential to comprehend the basic properties, such as the main forces driving the solid state structures, as a starting point in the formation of more complex systems.

Conclusions

In this paper three new supramolecular complexes have been reported named $[Co(bpe)(H_2O)_4]AS_2 \cdot 4H_2O(1), [Ni(bpe)(H_2O)_4]$ $AS_2 \cdot 4H_2O$ (2) and $[Zn(bpe)(H_2O)_4]AS_2 \cdot 4H_2O$ (3). All compounds were characterized by X-ray diffraction, elemental and thermogravimetric analysis as well as vibrational techniques. For all structures the same crystalline system (monoclinic) and space group $(P2_1/c)$ were observed. All structures show one polymeric $[M(bpe)(H_2O)_4]_n^{2+}$ chain covalently linked parallel to the a-crystallographic axis. Each one of the polymer chains appears to be involved in a two-dimensional supramolecular structure formed by hydrogen bonds between aminosalicylate anions and crystallization water molecules, with formation of cavities defining a pseudo-honeycomb imperfect interaction, a new structure in the literature of the aminosalicylate anion. The vibrational spectra of the compounds are very similar, in agreement with the crystal data. In the Raman spectra the most important bands can be assigned to the bpe ligand, showing up at 1642, 1614 and 1021 cm⁻¹ and assigned to ν (C=C), ν (CC)/ ν (CN) and ring breathing stretching, respectively. The intriguing feature in the Raman spectra of the synthesized compounds is the disappearance of all vibrational modes for the AS⁻, which can be explained by the fact that the polymer chain appears as a better scatterer than the aminosalicylate anion. This study demonstrates that the mixture of different building blocks with supramolecular characteristics can provide the formation of new bonds and interactions not yet described.

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