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Supramolecular complexes obtained from the interaction of violuric acid with manganese ion and nitrogenous ligands

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Three new complexes obtained from violuric acid, manganese ion and nitrogenous ligands.
- X-ray diffraction and vibrational data to understand the crystal structure.
- [Mn(H₂Vi)₂(H₂O)₄)](bpy)₂ (1) presents violuric acid in a monodentate coordination.
- [Mn(bpa)₂(H₂O)₄](H₂Vi)₂ (2) presents violuric acid as counter ion.
- [Mn(bpp)₂(H₂Vi)₂]·(bpp)₂(H₂O)₂ (**3**) presents violuric acid in a chelate form.

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ABSTRACT

This work describes the synthesis, spectroscopic characterization (Raman and infrared) and structural arrangement of three new supramolecular complexes named $[Mn(H_2Vi)_2(H_2O)_4)](bpy)_2$ (1), $[Mn(bpa)_2$ $(H_2O)_4](H_2Vi)_2$ (2) and $[Mn(bpp)_2(H_2Vi)_2] \cdot (bpp)_2(H_2O)_2$ (3); these compounds have been obtained making use of different building blocks such as 4,4'-bipyridyne (bpy), 1,2-bis(4-pyridyl)ethane (bpa) and 4,4'-trimethylene-dipyridine (bpp) acting as spacers with violuric acid and manganese ion, presenting behavior related to processes of molecular self-assembling and self-organization, very common in studies of supramolecular systems. In all these compounds the violurate anion appears in the crystalline arrangement as monodentate, anionic and chelate forms for 1, 2 and 3, respectively. The important to note is that monodentate coordination in **1** and chelate in **3** through O2 and O3 oxygen atoms from the oxime group can be considered the first example in literature involving violuric acid, both in coordination or interaction with manganese ion. Moreover, it can be seen a good agreement between the structural results and the spectroscopic data; for instance the presence of an intense band in the Raman spectrum around 1603 and 1012 cm⁻¹ in all obtained compounds, assigned to the v(CC)/v(CN) and v(ring) modes of the pyridyl ligand, respectively. Other important band can be observed in 1031 cm⁻¹ only for compound **3**, assigned to the v(N–O) mode of the violurate ligand; the band at 1284 cm⁻¹ referring to the v(N=O) mode, very characteristic of violurate species is not seen in the spectrum, thus confirming the coordination of this building block by the oxime moiety.

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Introduction

During the past 60 years the assembly and study of new crystalline systems, based on molecules called building blocks have attracted attention of several research groups, receiving the suggestive name of crystal engineering; firstly introduced by Pepinsky [1]. A better understanding of this type of study and the growing number of works in this area are closely related to the chemistry and crystallography of small molecules [2]. The main advantage of the synthesis of such systems is the obtaining of new structural arrangements, which have a composition and spatial ordering previously defined by each one of the used building blocks as well as the metal ions. These new materials may be presenting different functionalities such as optical, electronic, magnetic and catalytic processes [3,4].

In all the studies involving crystalline engineering the weak non-covalent interactions such as hydrogen bonding, electrostatic interaction, C—H \cdots , π -stacking and hydrophobic interactions are the main responsible for the solid assembling, being defined by Lehn as "the chemistry beyond the molecule" [5,6]. Such interactions are also responsible for the stability of many physical and biological systems, especially in solid small molecular arrangements, acting in the construction of complicated extended arrays of molecular self-organization [7], as will be addressed and discussed for different systems synthesized in this investigation.

Among the building blocks used in this work it can be mentioned as [2,4,6(1H,3H)-pyrimidinetrione-5-oxime, H₃Vi] or violuric acid (Scheme 1). H₃Vi and its derivatives have been used in the spectrophotometric determination of transition metal ions, due their strong complexing character; as an example it can mentioned the work of Awadallah and coworkers [8], who synthesized different salts of violurate with alkaline and transition metals, including manganese ion which is rarely mentioned in this building block literature. Another well-known property of this building block is its acid-base equilibrium; the first ionization of H₃Vi occurs in a pK_1 = 4.35 although the oxime group deprotonates easily, generating the violurate anion H₂Vi⁻, the second and third ionization occurs in a $pK_2 = 9.64$ and $pK_3 = 14.2$, respectively, since the NH groups are much weaker acid species, giving rise to HVi^{2-} and Vi^{3–}, respectively [9]. It is straightforward to note that when this chemical species loses its protons, its solution presents a very intense purple coloration, caused by the electronic transitions $\pi - \pi^*$ and $n - \pi$ in the visible region of the electromagnetic spectrum, and also by the different resonance canonic structures [10]. Furthermore, from the supramolecular chemistry point of view it can be seen through Scheme 1 that H₃Vi provides multiple sites of coordination and interactions, such as the -C=O, =N-OH and -N-H groups, thus resulting in a greater stability in the formed structural arrangement.

Another class of well-known building blocks is the nitrogenous ligands; in this work it has been used 4,4'-bipyridyl (bpy), 1,2-bis(4-pyridyl)ethane (bpa) and 4,4'-trimethylene-dipyridine (bpp) [11–13]. This is a class of compounds widely used in crystal

engineering for presenting aliphatic chains different sizes separating two pyridyl rings, thus acting as a spacer ligand in the production of new arrangements that can provide cavities of different sizes.

This work aims the synthesis, structural and spectroscopic characterization of three new compounds obtained from the interaction between violuric acid and nitrogenous ligands (bpy, bpa and bpp) with manganese ion, trying to understand the influence of the spacers in the obtained structures, as well as to develop an understanding about the characteristics of possible different forces involved in the supramolecular interactions in each one of the obtained compounds. In this sense, X-ray diffraction together with infrared and Raman vibrational techniques were used to determine the solid state assembly for each one of the synthesized compounds.

Experimental section

Chemicals and reagents

All chemicals were used as purchased without further purification: violuric acid monohydrate ($C_4H_3N_3O_4$ · H_2O , 97.0%, Sigma Aldrich), 4,4'-bipyridyl ($C_{10}H_8N_2$, 98.0%, Sigma Aldrich), 1,2-bis(4pyridyl)ethane ($C_{12}H_{12}N_2$, 99.0%, Sigma Aldrich), 4,4'-trimethylene-dipyridine ($C_{13}H_{14}N_2$, 98.0%, Sigma Aldrich), MnSO₄· H_2O (98.0%, Vetec), MnCl₂·4H₂O (98.0%, Vetec), Na₂CO₃ (99.0%, Sigma Aldrich) and AgNO₃ (99.0%, Sigma Aldrich).

Synthesis

For compounds **1** and **2** the synthesis procedure was similar: 10.0 mL of an aqueous colorless solution containing 96 mg (0.55 mmol) of violuric acid (H₃Vi) was neutralised with 29 mg (0.27 mmol) of sodium carbonate, resulting in a purple solution. To this purple solution was added under stirring 10.0 mL of an ethanolic solution containing 85 mg (0.55 mmol) of bpy (for compound 1) and 100 mg (0.55 mmol) of bpa (for compound 2). To this solution it was slowly added 5.0 mL of an aqueous solution containing 92 mg (0.55 mmol) of manganese sulfate; the resulting solution was kept for few days to crystallize. To obtain compound 3 the synthesis procedure was divided into three steps: First step – A 20 mL of a colorless aqueous solution containing 288 mg (1.65 mmol) of H₃Vi was added to 10 mL of a solution containing 280 mg (1.65 mmol) of AgNO₃, resulting in a reddish precipitate (AgH₂Vi), partially insoluble, and a solution of the same color; it is noteworthy that the synthesis involving silver salt must be conducted in an darkness environment, in order to prevent reduction of the silver. Second step – The AgH₂Vi precipitate was filtered and used to react with 20 mL of an aqueous solution containing 170 mg (0.86 mmol) of MnCl₂·4H₂O; the white AgCl precipitate was discarded and a resulting reddish solution of $Mn(H_2Vi)_2$ was obtained. **Third step** –10 mL of an ethanolic solution containing 171 mg (0.86 mmol) of bpp was slowly added to the previous reddish



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solution to allow diffusion between them. After three days the formation of a reddish crystalline material was obtained, which was filtered, washed and dried. Elemental analysis: $[Mn(H_2Vi)_2 (H_2O)_4)](bpy)_2$ (1): Calcd.: C, 44.75%; H, 3.76%; N, 18.64%; Found: C, 44.85%; H, 3.89%; N, 18.24% [yield = 42%]; $[Mn(bpa)_2(H_2O)_4]$ ($H_2Vi)_2$ (2): Calcd.: C, 47.59%; H, 4.49%; N, 17.34%; Found: C, 47.63%; H, 4.81%; N, 17.13% [yield = 63%]; $[Mn(bpp)_2(H_2Vi)_2]$ -(bpp)₂(H₂O)₂ (3): Calcd.: C, 60.14%; H, 5.55%; N, 16.37%; Found: C, 60.60%; H, 5.00%; N, 15.70% [yield = 33%].

Physical measurements

Infrared spectra were obtained using a Bomem MB-102 spectrometer fitted with a CsI beam splitter, with the samples prepared as KBr pellets 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, equipped with a Nd³⁺/YAG laser operating at 1064 nm in the near-infrared region and a InGaAs 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 changes in the band positions or intensities observed. Single crystal X-ray diffraction data were collected using an Oxford GEMINI A Ultra diffractometer with Mo K α (λ = 0.71073 Å) for every compound. Data collection, reduction and cell refinement were performed by CrysAlis RED, Oxford diffraction Ltda, Version 1.171.32.38 program [14]. The structures were solved and refined using SHELXL-97 [15]. The empirical isotropic extinction parameter x was refined according to the method previously described by Larson [16], and a Multiscan absorption correction was applied [17]. The structures were drawn by ORTEP-3 for windows [18] and Mercury [19] programs. CCDC 958393, 958394 and 971466 contained the supplementary crystallographic data for compounds 1, 2 and 3 respectively. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk> or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 IEZ, UK [Fax: (internat.) 1 44 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Results and discussion

The crystalline nature of supramolecular compounds 1, 2 and 3 obtained from reactions involving H₃Vi, the pyridyl nitrogenous ligands (bpy, bpa and bpp) and manganese ion have been revealed by X-ray single crystal analysis; the crystal data and some bond distances, bond angles and hydrogen interactions are displayed in Tables 1 and 2, respectively. Compound 1 crystallizes in a triclinic system presenting P-1 space group; Fig. 1 represents the repetition unit of the structure, formed by three neutral blocks. One of blocks is constituted by the metal ion exhibiting slightly distorted octahedral coordination geometry, defined by four aqua ligands (two O5 and two O6) in the equatorial positions and two anionic H₂Vi⁻ which are bonded in monodentate geometry through the oxygen atoms in an axial position, neutralizing the charge in the block. It is interesting to notice that this coordination mode appears to be the first reported in literature, since previous works have shown that the chelate coordination mode through the N5 and O6 atoms (see Scheme 1) are the common geometry [20-22]. The other two building blocks are formed by the uncoordinated bpy in its neutral form. A hydrogen bond of 2.842(3) Å, which can be classified as weak [23], is observed between the nitrogen atoms (N1–HN1 \cdots N4) of H₂Vi⁻ and bpy blocks. Due to the presence of several groups considered proton acceptors and donors, many other hydrogen bonds are observed for this structure, all of them are displayed in Table 2. The supramolecular structural arrangement of this compound can be seen in more details in Fig. 2, where it can be seen that at each vertex of the unitary cell is a bpy moiety. This same ligand appears involved in a supramolecular interaction of the type C–H··· π (C··· π distance = 3.659(3) Å) with other bpy block (which is crystallographically different from the previous bpy), located inside the unitary cell. A set of hydrogen bonds of medium intensity can be observed through the coordination of the water molecules and the bpy located at the vertex of the unitary cell, specifically $O5-H5B\cdots N5 = 2.766(3)$ Å. Another non-covalent interaction occurs through the aromatic ring of the bpy building block and the H_2Vi^- moiety, being classified as π -stacking and presenting centroid-centroid distance of 3.670(2) Å [24]. It can said that the

Table 1

 $Crystal \ data \ of \ [Mn(bpy)_2(H_2O)_4] \cdot (H_2Vi)_2 \ \textbf{(1)}, \ [Mn(bpa)_2(H_2O)_4] \cdot (H_2Vi)_2 \ \textbf{(2)} \ and \ [Mn(bpp)_2(H_2Vi)_2] \cdot (bpp)_2(H_2O)_2 \ \textbf{(3)} \ compounds.$

Compound	$[Mn(bpy)_2(H_2O)_4] \cdot (H_2Vi)_2$ (1)	$[Mn(bpa)_2(H_2O)_4] \cdot (H_2Vi)_2$ (2)	$[Mn(bpp)_2(H_2Vi)_2] \cdot (bpp)_2(H_2O)_2$ (3)
Compound Formula Formula weight/g mol ⁻¹ Crystal system Space group a/Å b/Å c/Å α β γ V/Å ³ Z Crystal size/mm $D_{calc}/g cm^{-3}$ μ (Mo K α)/cm ⁻¹ Transmission factors (min/max)	$[Mn(bpy)_{2}(H_{2}O)_{4}] \cdot (H_{2}Vi)_{2} (1)$ $C_{28}H_{28}MnN_{10}O_{12}$ 751.54 Triclinic P-1 8.6117(5) 9.5665(5) 11.3309(7) 85.769(5) 67.885(5) 69.349(5) 807.36(9) 1 0.55 × 0.25 × 0.18 1.546 0.489 0.864/0.917	$[Mn(bpa)_2(H_2O)_4] \cdot (H_2Vi)_2 (2)$ $C_{32}H_{35}MnN_{10}O_{12}$ 806.64 Triclinic P1 9.4388(3) 9.9758(2) 10.3210(3) 76.536(2) 83.520(3) 63.365(3) 844.78(5) 1 0.44 × 0.20 × 0.13 1.586 0.473 0.892/0.943	$[Mn(bpp)_{2}(H_{2}Vi)_{2}] \cdot (bpp)_{2}(H_{2}O)_{2} (3)$ $C_{60}H_{56}MnN_{14}O_{10}$ 1188.13 Triclinic $P-1$ 9.1274(6) 9.8119(5) 17.4463(11) 101.742(5) 104.758(5) 92.248(5) 1472.42(16) 1 0.39 × 0.12 × 0.08 1.340 0.295 0.957/0.978
Transmission factors (min/max) Reflections measured/unique Observed reflections $[F_0^2 > 2\sigma(F_0^2)]$ N°. of parameters refined $R[F_0 > 2\sigma(F_0)]$ $wR[F_0^2 > 2\sigma(F_0)^2]$ S RMS peak/	0.489 0.864/0.917 13183/3300 2754 257 0.0399 0.0961 1.050 0.065	0.473 0.892/0.943 43028/6904 5052 504 0.0672 0.1748 1.041 0.128	0.957/0.978 10921/6024 3584 476 0.0802 0.1876 1.034 0.078

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Table 2

Select bond distances (in Å) and hydrogen interactions of [Mn(bpy)₂(H₂O)₄]-(H₂Vi)₂ (1), [Mn(bpa)₂(H₂O)₄]-(H₂Vi)₂ (2) and [Mn(bpp)₂(H₂Vi)₂]-(bpp)₂(H₂O)₂ (3).

Bond distance/Å	$[Mn(bpy)_2(H_2O)_4] \cdot (H_2Vi)_2$ (1)	Bond distance/Å	[Mn(bpa) ₂ (H ₂ O) ₄]∙ (H ₂ Vi) ₂ (2)	Bond distance/Å	$[Mn(bpp)_2(H_2Vi)_2] \cdot (bpp)_2(H_2O)_2$ (3)
Mn1-01 Mn1-05 Mn1-06 N2-62	2.273(1) 2.146(2) 2.121(2) 1.222(2)	Mn105 Mn106 Mn107 Mn108	2.170(5) 2.168(6) 2.134(6) 2.190(6)	Mn1-02 Mn1-03	2.113(2) 2.184(3)
N2-C2	1.380(3)	Mn1-08 Mn1-N4 Mn1-N5	2.269(6) 2.263(7)	Mn1–N4	2.259(3)
01–C1 02–C2 03–N3 04–C4	1.229(2) 1.229(2) 1.271(2) 1.218(2)	01–C1 02–C2 03–N3 04–C4	1.188(9) 1.268(9) 1.289(6) 1.232(10)	01–C1 02–C2 03–N3 04–C4	1.215(5) 1.236(4) 1.229(4) 1.230(6)
Hydrogen bond (D···A/Å) N1—HN1···N4 N2—HN2···O2 O5—H5A···N3 O5—H5B···N5 O6—H6A···O2 O6—H6A···O3 06—H6B···O3	2.842(3) 2.857(3) 2.852(3) 2.766(3) 2.806(2) 2.913(3) 2.640(3)	$\begin{array}{l} Hydrogen \ bond \ (D^{A}/\text{Å}) \\ N10-HN10\cdots N6 \\ N2-HN2\cdots N7 \\ N1-HN1\cdots 011 \\ N8-HN8\cdots 03 \\ 05-H5A\cdots 03 \\ 05-H5A\cdots 04 \\ 05-H5B\cdots 09 \\ 06-H6A\cdots 01 \\ 06-H6B\cdots 010 \\ 06-H6B\cdots 011 \\ 07-H7A\cdots 02 \\ 07-H7B\cdots 010 \\ 08-H8A\cdots 04 \end{array}$	2.829(10) 2.780(10) 2.748(8) 2.770(9) 2.721(7) 2.825(9) 2.765(9) 2.724(7) 2.798(8) 2.806(8) 2.768(9) 2.784(9) 2.773(8)	Hydrogen bond (D […] A/Å) N2—HN2…N6 N1—HN1…N5	2.803(5) 2.796(5)



Fig. 1. ORTEP view of $[Mn(bpy)_2(H_2O)_4] \cdot (H_2Vi)_2$ (**1**) crystal structure. Ellipsoids are drawn at the 50% probability level, except for hydrogen atoms which are represented by circles of arbitrary radius. The water molecules of crystallization are omitted for clarity. Symmetry code: (i) -x, 1 - y, 1 - z; (ii) -1 + x, y, -1 + z; (iii) 1 - x, 1 - y, 2 - z.



Fig. 2. Supramolecular interactions: hydrogen bonds, π -stacking and C—H··· π for [Mn(bpy)₂(H₂O)₄]·(H₂Vi)₂ (1) compound.

stability of this supramolecular arrangement becomes more effective and evident due to the large variety and the high number of different interactions present in the system, such as hydrogen bonds, π -stacking and C—H $\cdots \pi$.



Fig. 3. ORTEP view of $[Mn(bpa)_2(H_2O)_4] \cdot (H_2Vi)_2$ (**2**) crystal structure. Ellipsoids are drawn at the 50% probability level, except for hydrogen atoms which are represented by circles of arbitrary radius. The water molecules of crystallization are omitted for clarity. Symmetry code: (i) *x*, -1 + y, 1 + z.

Fig. 3 exhibits the asymmetric units of complex 2, being constituted by a cationic block formed by the metal ion covalently bonded to four aqua ligands in equatorial positions, and two bpa species in axial and terminal positions, giving rise to a slightly distorted octahedral geometry. Neutralizing each cationic bock it can be observed the presence of two uncoordinated violurate anions. The presence of different donor and acceptor protons blocks favors the appearance of hydrogen bonds; due to these interactions, it can be observed the presence of a supramolecular cavity formed through hydrogen bonds and classified as $N_1 = R_2^3(12)$, where the symbol R is related to a ring, whereas the numbers indicate the number of donor (subscript) and acceptor (superscript) moieties and the number in parentheses indicates the number of atoms involved in the arrangement in each set [25]. Fig. 4 shows the supramolecular arrangement involved in the plane perpendicular to the *bc* diagonal, with the formation of weak and medium hydrogen bonds between $[Mn(H_2O)_4(bpa)_2]^{2+}$ and H_2Vi^- building blocks, thus generating a two-dimensional network described as $N_2 = C(19)2R_2^2(10)R_4^4(38)$. Another π -stacking supramolecular



Fig. 4. Supramolecular interactions: hydrogen bonds and π -stacking for [Mn(bpa)₂(H₂O)₄]-(H₂Vi)₂ (**2**) compound.



Fig. 5. ORTEP view of $[Mn(bpp)_2(H_2Vi)_2]\cdot(bpp)_2(H_2O)_2$ (**3**) crystal structure. Ellipsoids are drawn at the 50% probability level, except for hydrogen atoms which are represented by circles of arbitrary radius. The water molecules of crystallization are omitted for clarity. Symmetry code: (i) 1 - x, -y, 1 - z.

interaction can be observed across the two pyridyl rings of the bpa ligand, presenting centroid–centroid distance of 3.786(2) Å. Although it is possible to note the presence of several rings in the macro structure, only the effective approximation of two bpa ligands are responsible for observing the π -stacking interaction. This fact can be explained by the presence of the aliphatic chain (–CH₂–CH₂–) in the molecular structure of the nitrogenous ligand, showing a steric effect that disfavors the approach of the pyridyl rings. This same aliphatic chain only allows the formation of C–H··· π interaction of 3.586(3) Å (C··· π distance) for the ring from the H₂Vi⁻ building block. The interaction between two different planes in Fig. 4 occurs via hydrogen bonds between the carbonyl group with the coordinated water molecule, O5–H5B···O9 = 2.765(9) Å, and through the NH and the oximato groups, N1–HN1···O11 = 2.748(8) Å.

Fig. 5 displays the repeating unit of compound 3; it comprises a neutral block formed by manganese ion in a slightly distorted octahedral geometry coordinated to two nitrogen atoms from bpp in the axial position, adopting a conformation Trans-Trans (or TT) with N-to-N separation distances of 9.632(2) Å, or by the Trans arrangement between the $-CH_2$ groups of the aliphatic chain [26]. Completing the coordination sphere, it can be observed the presence of two H₂Vi⁻, violurate anions, originating a chelate through the O2 and O3 oxygen atoms from the carbonyl and oxime groups, respectively; such structure forms two five-member rings, which contributes to increase the thermodynamical stability of the structure. Due to the chelate formation, it can be observed a lower O3–N3 = 1.229(4) Å bond distance for compound 3 when compared to 1.271(2) Å and 1.289(6) Å for the compounds 1 and 2, respectively; this fact can be attributed to a decrease in this bond order between these two atoms, via a new bond which is responsible for the appearance of such ring. Completing the compound **3** repeating unit it can be mentioned the presence of two neutral bpp and two water molecules of crystallization, which due to the complexity of arrangement they are not shown in Fig. 5. Moreover, the two uncoordinated bpp species present the nitrogen and carbon atoms (N7A, C24A, C25A, C26A, C27A, C28A C29A and C30A) from one of its pyridyl rings in a disordered position; despite this disorder, the main features of the solid state structure and the



Fig. 6. Supramolecular interactions: hydrogen bonds and $C-H\cdots\pi$ of compound $[Mn(bpp)_2(H_2Vi)_2]\cdot(bpp)_2(H_2O)_2$ (3).

main driving forces responsible for the arrangement could be accessed and solved.

The bi-dimensional array of compound **3** can be seen across Fig. 6, formed by [Mn(bpp)₂(H₂Vi)₂] building blocks interacting via N1–HN1 \cdots N5 = 2.796(5) Å hydrogen bonds, between the H₂Vi⁻ and bpp ligands, respectively, and classified as of medium intensity [23]. This type of supramolecular interaction in the zigzag form observed in these structures for bpp and H₂Vi⁻ ligands, giving rise to geometrical figures such as a rectangle, is common in the literature involving only the coordination of bpp ligand [27]. As an example it can mentioned the work of Garcia et al. [28] describing a bis-monodentate bpp coordination which occurs through the two nitrogen atoms of the ligand; in that structure the counter ion aminosalicylate is not influencing the bpp coordination mode. In this investigation, since the H₂Vi⁻ coordination occurs as a chelate to the metal site, it happens an hindering of the bis-monodentate coordination in the zigzag form, being only observed the monodentate coordination of bpp, leaving the (N5) nitrogen atom uncoordinated to perform a hydrogen interaction with the other (N1) nitrogen atom of the violurate moiety. Another important supramolecular interaction called C–H··· π = 3.752(2)Å can be noted between the hydrogen atom of an aliphatic chain and the pyridyl ring, from distinct bpp ligands. To connect the layers observed in Fig. 6, it can be seen the presence of π -stacking interactions between the rings of the coordinated and uncoordinated pyridyl ligands presenting centroid-centroid distance of 3.531(3) Å. Other hydrogen bonding interaction between the layers occurs involving the nitrogen atom (N6) of the uncoordinated bpp and the nitrogen atom (N2) atom of the violurate anion, N2–HN2 \cdots N6 = 2.803(5) Å.

The vibrational spectra of the building blocks and complexes **1**, **2** and **3** are shown in Figs. 7 and 8, related to infrared and Raman



Fig. 7. Infrared spectra of $[Mn(bpy)_2(H_2O)_4] \cdot (H_2Vi)_2$ (1), $[Mn(bpa)_2(H_2O)_4] \cdot (H_2Vi)_2$ (2) and $[Mn(bpp)_2(H_2Vi)_2] \cdot (bpp)_2(H_2O)_2$ (3) compounds; for comparison purposes, the spectra of the ligands (bpy and NaH₂Vi) are also displayed.



Fig. 8. Raman spectra (excited at 1064 nm) of $[Mn(bpy)_2(H_2O)_4] \cdot (H_2Vi)_2$ (1), $[Mn(bpa)_2(H_2O)_4] \cdot (H_2Vi)_2$ (2) and $[Mn(bpp)_2(H_2Vi)_2] \cdot (bpp)_2(H_2O)_2$ (3) compounds; for comparison purposes, the spectra of the ligands (bpy and NaH₂Vi) are also displayed.

techniques, respectively. The main vibrational modes and the respective assignments have been based on similar chemical systems [29–31], and are listed in Table 3. Each vibrational spectrum presents some characteristic bands which are related to different coordination modes of H_2Vi^- as well the nitrogen ligands, and will be discussed below.

In the infrared spectrum of hydrated NaH₂Vi violurate salt can be observed the presence of a set of three bands at 1732, 1701 and 1676 cm⁻¹, all of them assigned to the v(C=0) mode of different carbonyl groups present in this building block. In an earlier work by de Oliveira et al. [29], analyzing the Raman spectra of different violurate species, no significant changes in wavenumbers were observed, suggesting the proton loss by O5 atom has no influence on the bond order of these chemical bonds. An important band, that can be attributed as a characteristic marker of this structure, occurs at 1277 cm⁻¹, and can be assigned to the $v(ring) + \delta(NH_{i.p.})$ coupled mode, after the proton loss. The assignment of this band is important in this work in order to observe the type of coordination and/or interaction of this building block in the supramolecular unit: as a counter ion, monodentate or chelate species, since the degree of electronic delocalization over the structure is responsible for changes in position and wavenumber for such vibrational mode. On the other hand, for the three nitrogen spacers bpy, bpa and bpp, although the difference in their structures occurs due to the insertion of the aliphatic chain, it can be observed the presence of some bands in their spectra that occur in similar positions, and related to the pyridyl group which is the common chemical group in all these building blocks. As an example it can be cited the bpy ligand which presents an intense band occurring at 1591 cm⁻¹ assigned to the v(CC)/v(CN) mode of the pyridyl ring; for bpa and bpp this same band appears at 1597 and 1605 cm⁻¹, respectively. Thus this band can be considered as very important in the vibrational spectroscopy analysis of these species, acting as marker; it is also clear that shifts to a different wavenumber by the coordination process with the metal site, caused by an increasing of the bond order due to the use the electrons pair non-bonding in the formation bond metal ligand, can be expected. Other important band occurs at 1408, 1414 and 1416 cm⁻¹, assigned to v(ring) mode of the bpy, bpa and bpp species respectively; however, for this band there are no observed shifts caused by any coordination processes.

For the compounds **1**, **2** and **3** the infrared spectrum presents one broad band in the $3600-3400 \text{ cm}^{-1}$ region, assigned to the v(NH) and v(OH) modes of the H_2Vi^- and H_2O building blocks, respectively. Other strong band, observed at 1670, 1688 and 1726 cm⁻¹, can be assigned to the stretching of the carboxyl group v(CO) of the violurate ion building block. It can be said that the high wavenumber shift observed for this band occurs for compound **1**; this fact can be explained by the coordination of this building block via the oxygen atom of the carboxyl group (–C=O), thus weakening the bond and consequently shifting the band to lower wavenumber. Furthermore in this region the spectrum of compound **1** is more defined with a smaller number of bands, which can be related to the CO stretching mode overlap after coordination of one of the carbonyl groups. For compound **2** the shift of

Table 3

Raman (R) and infrared (IR) wavenumbers (in cm⁻¹) and tentative assignment of the most important bands observed for $[Mn(bpy)_2(H_2O)_4] \cdot (H_2Vi)_2$ (1), $[Mn(bpa)_2(H_2O)_4] \cdot (H_2Vi)_2$ (2) and $[Mn(bpp)_2(H_2Vi)_2] \cdot (bpp)_2(H_2O)_2$ (3) compounds.

NaH ₂ Vi bpy/bpa/bpp		/bpp	$[Mn(bpy)_2(H_2O)_4] \cdot (H_2Vi)_2$ (1)		$[Mn(bpa)_2(H_2O)_4] \cdot (H_2Vi)_2$ (2)		$[Mn(bpp)_2(H_2Vi)_2 \cdot (bpp)_2(H_2O)_2$ (3)		Tentative assignment	
IR	R	IR	R	IR	R	IR	R	IR	R	
518 m	516 m			513 m	512 w	515 m	512 w	517 m	518 m	$\delta(ring) + \delta(C=0)_{i.p.}$
571 m	570 m			571 m	564 w	567 m	565 w	561 m	562 w	δ ring)
	655 vs				657 s		655 s		653 s	Ring Breathing
729 w	728 w			723 w		731 w				$\delta(N=0)_{o,p}$ + $\delta(C=0)_{o,p}$
785 w				785 w		788 w	800 w	793 w	792 w	δ (NH) _{0,p}
826 w	825 m			806 w		829 w		816 w		$v(ring) + \delta(ring)$
		989 m	1000 s		1012 vs		1016 vs		1011 vs	v(ring)
									1031s	v(N-O)
1142 m	1144 w			1130 w		1141 w		1130 w		v(ring)(vC-N)
		1219 m	1218 m	1221 m	1224 sh		1216 s		1218 vs	$v(ring) + \delta(CH)$
1227 s	1228 vs				1233 s	1227 s	1234 s	1230 s	1241 m	v(ring)(vC-C)
1277 s				1279 s		1271 s				$v(ring) + \delta(NH)_{i.p.}$
	1287 s			1296 sh	1285 vs	1296 vs	1284 m			v(N=O)
			1406 s		1414 vs		1410 vs			
1438 s	1436 sh			1433 w		1437 sh		1436 sh		$v(ring)(vC-N) + \delta(NH)_{i.p.}$
		1591 s	1606 s	1595	1603 vs	1609 m	1615 s	1609 vs	1608 s	v(CC)/v(CN)
1676 vs	1646 sh			1649 s	1650 s	1655 s	1652 m	1636 s	1637 m	v(C=0)
1701 vs	1681 s			1670 vs	1695 s	1688 s	1698 s	1693 s	1695 s	v(C=0)
1732 vs	1726 sh							1726 s	1722 s	v(C=0)
							2926 m		2928 m	v(CH) _{aliphatic}
					3073 m		3064 s		3058 vs	v(CH) _{aromatic}

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; i.p., in plane; o.p., out of plane.

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this same vibrational mode is due to appearance of different resonance canonic structures originated from the H₂Vi⁻ building block as a counter ion, and the broadening band in this region can be attributed to the CO groups of the building block under different chemical environments. For compound 3 the carboxyl bond appears stronger when compared to the other compounds; this fact could be explained by the chelate coordination appearing in the structure, thus preventing the formation of a resonance structure in the ring, which is responsible for wakening this band. Furthermore the similarity in this region between compound 3 and NaH₂Vi suggests that coordination of such compound and its precursor may be the almost the same. Another important band can be observed at 1433, 1437 (shoulder) and 1436 (shoulder) cm⁻¹ for compounds 1, 2 and 3 respectively, and attributed to a set of coupled modes [$vring + v(C-N) + \delta(NH)_{i.p.}$]. Bands at 1279 and 1271 cm⁻¹ for compounds **1** and **2** respectively, which are assigned to the $[v(ring) + \delta(NH)_{i.p.}]$ coupled mode, are also important to characterize such compounds, since are related to the electronic delocalization over the ring. This same vibration does not appear in compound **3** spectrum, strongly suggesting the inexistence of electronic delocalization, as seen for compounds 1 and 2, due to coordination in chelate form. To confirm the presence of bpy, bpa and bpp nitrogenous ligands in the synthesized structures, only two bands can be analyzed: the one at 1595, 1609 and 1609 cm⁻¹, assigned to the v(CC)/v(CN) mode and presenting a small wavenumber shift when compared to the free ligand for compounds 1 and 3, suggesting the presence of uncoordinated species in their neutral form in these structures, which is confirmed by structural analysis. Another important set of bands that can be observed to confirm the nitrogen ligands bpy, bpa and bpp in the formation of compounds occur around 1408 cm⁻¹, assigned to the coupled modes $v(ring)/\delta(CH)$; however, this region is not used for assignments, due to the presence of bands relative to the other building block (NaH₂Vi) used in this study.

In the NaH₂Vi Raman spectrum (Fig. 8) some characteristic bands can also be observed, as for instance a broad band featuring shoulders at 1726, 1681 and 1646 cm⁻¹, assigned to different v(CO)modes of the violurate species. Such bands appear shifted to lower wavenumbers when compared to violuric acid, which can be explained by the proton exit producing a bond weakening due to the formation of different resonance canonic structures. Another fact which contributes to this discussion is the appearance of an intense band at 1287 cm⁻¹, assigned to the v(N=O) mode, that is not present in its precursor spectrum, just showing up an intense band at 1577 cm⁻¹ concerning v(C=N). In the same way, the presence of an intense band at 655 cm⁻¹ shifted to higher wavenumber when compared to the free violuric acid (645 cm⁻¹), assigned to the ring breathing mode, v(ring) [29].

In general, the Raman spectra of bpy, bpa and bpp exhibit characteristic bands which can be discussed together the obtained complexes. Among the main vibrational bands it can be mentioned the ones at ca. 1600 and 1000 cm⁻¹, assigned to the v(CC)/v(CN)and v(ring) modes, respectively. These two modes are important band markers for these compounds, since their coordination to the metal ion can be observed through their shift to higher wavenumber values, thus being related to an increase in the bond order by means of ligand coordination. Other important band appears at 1297, 1216 and 1218 cm⁻¹ for bpy, bpa and bpp, respectively, being assigned to $[\delta(ring) + \delta(CH)]$ coupled modes. It is important to note that this vibrational mode in particular does not present a pronounced shift in the process of ligand coordination.

Compounds **1**, **2** and **3** exhibit one set of intense bands in the region of $1720-1650 \text{ cm}^{-1}$, assigned to the v(C=0) mode of different carbonyl groups. Due to the different coordination and interaction of these compounds it can be observed the shift of such different bands. As an example, it can be mentioned the band at

 1722 cm^{-1} for compound **3**, which shows a wavenumber shift less pronounced when compared to the violuric acid (1737 cm^{-1}), since the chelate coordination of the structure makes difficult the formation of resonance structures when compared to the other compounds. Another important band can be observed at 1285 and 1284 cm⁻¹ for compounds **1** and **2**, respectively, assigned to the v(N=0) mode. It can be seen that the presence of this band corroborates with the presence of this building block in a monodentate geometry and also as a counter ion for these compounds. The important to be noted in this mode is the absence of this band for compound **3**, which strengthens its coordination by the (O5) oxygen atom, which can be verified by the appearance of a new band at 1031 cm⁻¹ and attributed to the v(N-O) mode. Another band that can be used as a marker for these building blocks appears at 655 cm^{-1} for each compound, referring to the ring breathing mode: such band appears shifted to a higher wavenumber values when compared to the precursor (645 cm^{-1}), due to the bond strengthening caused by the proton loss. The presence of a pyridyl ligand in the formation of supramolecular complexes can be confirmed through two important marker bands at 1603 and 1012 cm⁻¹, assigned to the v(CC)/v(CN) and v(ring) modes, respectively. The band at 1600 cm⁻¹ is very important because its huge shift to higher wavenumber values strongly suggest the coordination of the nitrogen ligand to the metal site in the same geometry as compound 2; a small wavenumber shift can suggest the existence of intermolecular forces or even the uncoordination of this building block.

As a final remark it can be said that these results demonstrate the importance in choosing the appropriate ligands in crystal engineering, related to the formation of different supramolecular arrangements. For compound 3 it can be said that the adopted synthesis procedure favored the formation of the chelate complex, followed by bpp coordination in replacing the water molecules as well as the presence of other bpp in the neutral form for completing the crystal lattice. The synthesis procedures for compounds 1 and 2 were similar, and this reflects the existence of weak intermolecular forces for both compounds: for compound **1** the hydrogen bond formed between the N4 atom of bpv and N1 atom of H₂Vi⁻ favors the violurate anion coordination through the carboxyl group, whereas for compound 2 the bpa coordination is the responsible for the stabilization of the complex formed, preventing the coordination water molecules exit which plays an important role in the formation of hydrogen bond with other violurate anions.

Conclusions

It has been described the synthesis, spectroscopic (Raman and infrared) and structural characterization of three novel supramolecular arrangements: $[Mn(H_2Vi)_2(H_2O)_4)](bpy)_2$ (1), $[Mn(bpa)_2$ $(H_2O)_4$ $(H_2Vi)_2$ (2) and $[Mn(bpp)_2(H_2Vi)_2] \cdot (bpp)_2(H_2O)_2$ (3), obtained through diffusion or precipitation techniques. The formation of these new compounds can be considered the first investigation involving the interaction and coordination between manganese ion and violurate ligand in three different forms: monodentate, chelate and counter ion. Compound 3 presents the chelate coordination form through O2 and O3 oxygen atoms, a type of coordination which has not been described in literature for this building block: compound **2** presents the bpa ligand coordinated to the manganese ion, whereas for compound 1 the inverse can be seen, i.e., the coordination from violurate ion, both presenting a monodentate form of coordination. Additionally the use of crystal engineering in the formation of these new compounds is only possible due to the presence of manganese central ion, which shows the importance and especially the great affinity of this metal ion with the building blocks used in synthesis of the different

supramolecular assemblies. All the vibrational data (Raman and infrared) are in good agreement with the crystal data, reinforcing the idea of how important is to understand the weak intermolecular forces which are responsible for the generation of different crystal lattices.

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