

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



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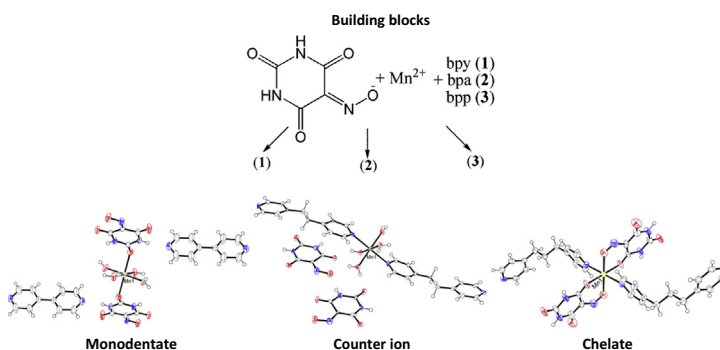
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HIGHLIGHTS

- Three new complexes obtained from violuric acid, manganese ion and nitrogenous ligands.
- X-ray diffraction and vibrational data to understand the crystal structure.
- $[\text{Mn}(\text{H}_2\text{Vi})_2(\text{H}_2\text{O})_4](\text{bpy})_2$ (**1**) presents violuric acid in a monodentate coordination.
- $[\text{Mn}(\text{bpa})_2(\text{H}_2\text{O})_4](\text{H}_2\text{Vi})_2$ (**2**) presents violuric acid as counter ion.
- $[\text{Mn}(\text{bpp})_2(\text{H}_2\text{Vi})_2] \cdot (\text{bpp})_2(\text{H}_2\text{O})_2$ (**3**) presents violuric acid in a chelate form.

GRAPHICAL ABSTRACT



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ABSTRACT

This work describes the synthesis, spectroscopic characterization (Raman and infrared) and structural arrangement of three new supramolecular complexes named $[\text{Mn}(\text{H}_2\text{Vi})_2(\text{H}_2\text{O})_4](\text{bpy})_2$ (**1**), $[\text{Mn}(\text{bpa})_2(\text{H}_2\text{O})_4](\text{H}_2\text{Vi})_2$ (**2**) and $[\text{Mn}(\text{bpp})_2(\text{H}_2\text{Vi})_2] \cdot (\text{bpp})_2(\text{H}_2\text{O})_2$ (**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 $\nu(\text{CC})/\nu(\text{CN})$ and $\nu(\text{ring})$ modes of the pyridyl ligand, respectively. Other important band can be observed in 1031 cm^{-1} only for compound **3**, assigned to the $\nu(\text{N}=\text{O})$ mode of the violurate ligand; the band at 1284 cm^{-1} referring to the $\nu(\text{N}=\text{O})$ 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... π , 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 pK₁ = 4.35 although the oxime group deprotonates easily, generating the violurate anion H₂Vi[−], the second and third ionization occurs in a pK₂ = 9.64 and pK₃ = 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 π – π^* and n – π 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.

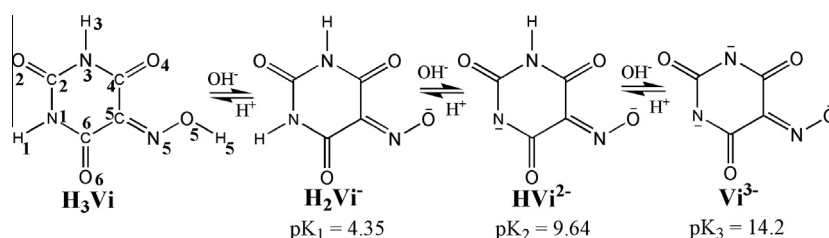
Experimental section

Chemicals and reagents

All chemicals were used as purchased without further purification: violuric acid monohydrate (C₄H₃N₃O₄·H₂O, 97.0%, Sigma Aldrich), 4,4'-bipyridyl (C₁₀H₈N₂, 98.0%, Sigma Aldrich), 1,2-bis(4-pyridyl)ethane (C₁₂H₁₂N₂, 99.0%, Sigma Aldrich), 4,4'-trimethylene-dipyridine (C₁₃H₁₄N₂, 98.0%, Sigma Aldrich), MnSO₄·H₂O (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(H₂Vi)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



Scheme 1.

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