

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/229223770>

Synthesis, structural studies and vibrational spectroscopy of Fe²⁺ and Zn²⁺ complexes containing 4,4'-bipyridine and barbiturate anion

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · AUGUST 2010

Impact Factor: 1.6 · DOI: 10.1016/j.molstruc.2010.01.035

CITATIONS

9

READS

16

4 AUTHORS, INCLUDING:



Renata Diniz

Federal University of Juiz de Fora

84 PUBLICATIONS 491 CITATIONS

SEE PROFILE



Luiz Fernando Cappa De Oliveira

Federal University of Juiz de Fora

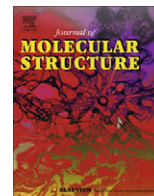
175 PUBLICATIONS 1,758 CITATIONS

SEE PROFILE



Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis, structural studies and vibrational spectroscopy of Fe^{2+} and Zn^{2+} complexes containing 4,4'-bipyridine and barbiturate anion[☆]

Humberto C. Garcia^a, Renata Diniz^a, Maria I. Yoshida^b, Luiz Fernando C. de Oliveira^{a,*}

^a 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

^b Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil

ARTICLE INFO

Article history:

Received 10 November 2009

Received in revised form 8 January 2010

Accepted 19 January 2010

Available online xxxx

Keywords:

Coordination polymers

Crystal structure

Supramolecular chemistry

Vibrational spectroscopy

ABSTRACT

Two new coordination polymers of general formula $\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**1**) and $\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**2**) (where B = barbiturate anion; bpy = 4,4'-bipyridine) were synthesized and characterized by X-ray diffraction, vibrational spectroscopy (Raman and infrared) and thermal analysis. The two complexes are isostructural and crystallize in a hexagonal crystal system with space group $P6_422$. The compound contains the 4,4'-bipyridine ligand coordinated to the metal sites in a bis-monodentate mode, and also four water molecules, in a slightly distorted octahedral geometry, giving rise to the cationic unit with two barbiturate anions. Each structure shows one covalent linear $[\text{M}(\text{bpy})(\text{H}_2\text{O})_4]^{2+}$ one-dimensional chain, which interacts via hydrogen bond with barbiturate anions and crystallization water molecules, resulting in a three-dimensional arrangement. The vibrational spectra of both compounds are very similar; in all infrared spectra is observed an intense band at 1686 cm^{-1} assigned to the νCO stretching mode of the barbiturate anion, as well as a medium band around 1610 cm^{-1} , attributed to the $\nu\text{CC}/\nu\text{CN}$ stretching modes of the 4,4'-bipyridine ligand. The Raman spectra show intense and conclusive bands for the nitrogen ligand at 1615 , 1295 and 1020 cm^{-1} , assigned to the $\nu\text{CC}/\nu\text{CN}$, $\nu_{\text{ring}} + \delta\text{CH}$ and ν_{ring} modes, respectively. The barbiturate anion is observed through the presence of a marker band at 680 cm^{-1} , assigned to the ring breathing mode.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The synthesis of supramolecular architectures is currently subject of considerable interest, mainly as an approach to materials with novel physicochemical properties [1,2]. One aspect of this field is the self-assembly of coordination complexes from suitable ligands and metal ions [3]. To this end, a variety of compounds are formed showing properties as non-linear optical (NLO) [4], catalytic [5], molecular recognition, magnetism and electrical conductivity [6].

Several supramolecular architectures are formed by non-covalent forces such as hydrogen bonds, hydrophobic interactions, π - π stacking and/or electrostatic interaction [7,8]. These weaker non-covalent interactions, especially hydrogen bonds, play a crucial role in fundamental biological processes, such as the expression and transfer of genetic information, and are essential for molecular recognition between receptors and substrates as well as construction of complicated arrays through self-organization of molecules in the field of supramolecular chemistry [9].

The supramolecular chemistry has been a topic for extensive investigation since the advent of the “chemistry beyond the molecule” [10]. The motivation lies not only in the fundamental understanding of self-assembly and molecular recognition processes pertinent to the origin of life and evolution but also toward the designing of a new class of materials and devices for future technologies. The use of building blocks, molecules with ability of coordinating to other molecules or metallic ions, is elemental for the construction of crystalline supermolecular systems.

One building block recently employed in the synthesis of these supermolecular systems is the barbituric acid [11,12] (Fig. 1), due to its ability to associate with complementary molecules via hydrogen bonding interactions, through its three carbonyl oxygen atoms acting as hydrogen bond acceptors and also the two imino groups acting as hydrogen bond donors [13]. Barbituric acid and their derivatives are compounds containing pyrimidine ring which play an important role in many biological systems, being widely pharmacologically used as sedative hypnotic [14–16]. They have also been used as non-linear optical materials (NLO), disperse dyes with strong fluorescent properties, as well as charge generation agents for electrophotography and photoreception [9]. However, investigation focused mainly on crystalline structures of barbiturates with transition metal ions has been incipient [11,17].

[☆] In honor to Prof. Heinz Oberhammer.

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

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

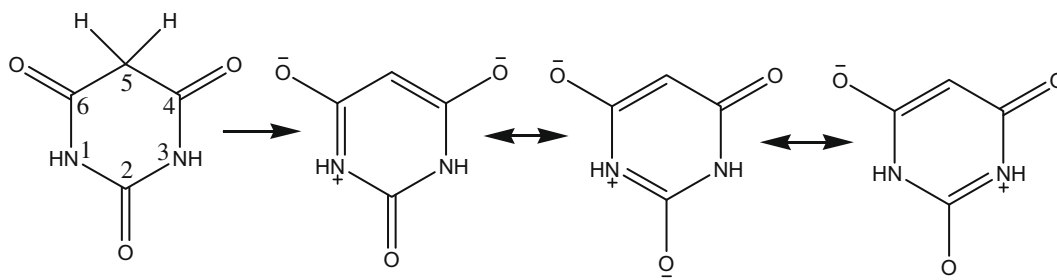


Fig. 1. Molecular structure of barbituric acid and its resonance forms.

It is very known the use of nitrogen ligands as building blocks in supramolecular chemistry, mainly due to their capability to give rise to bi or three-dimensional structures. In this work, we have used 4,4'-bipyridine (bpy), an excellent rigid, rodlike organic building block, which has been extensively employed for the construction of infinite one-dimension, two-dimension and three-dimension, presenting properties of non-linear optical (NLO), heterogeneous catalysis and host–guest chemistry [18–20].

In the present work are reported the synthesis and the structural and spectroscopic characterization of two new coordination polymers involving the transition metal ions Fe^{2+} and Zn^{2+} bonded to 4,4'-bipyridine and barbiturate anion.

2. Experimental

2.1. Synthesis

To a solution of barbituric acid (HB) (41.0 mg, 0.32 mmol) in water (10 mL) was added an aqueous solution (10 mL) of 4,4'-bipyridine (bpy). The final solution was heated to 50 °C and stirred for 20 min, generating a homogeneous mixture yellow. After the mixture reached room temperature, an aqueous solution of the appropriate hydrate metal sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (0.32 mmol in 5.0 mL of water) was added by slow diffusion. After a few days suitable single crystals were obtained, which were separated by filtration and dried in vacuum; such crystals were analyzed by vibrational spectroscopy, thermogravimetric analysis and X-ray diffraction techniques. Elemental analysis gave the following results: $\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**1**) (red crystals, yield = 10%): calcd.: C, 33.45%; H, 5.30%; N, 13.0%; Found: C, 33.20%; H, 5.10%; N, 12.20%. $\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**2**) (yellow crystals, yield = 30%): calcd.: C, 32.96%; H, 5.23%; N, 12.81%; Found: C, 32.79%; H, 4.92%; N, 12.33%.

2.2. Materials and physical measurements

All solvents and chemicals were reagent grade and used as received without further purification. The elemental analyses for C, H and N were carried out on a Perkin-Elmer 2400 analyzer. Thermogravimetric measurements (TG/DTA) were done using a Shimadzu TG-60 with thermo balance; the samples were heated at 10 °C min^{-1} from room temperature to 750 °C in dynamic nitrogen atmosphere, with a flow rate equal to 100 mL min^{-1} . Infrared spectra were obtained using a Bomem Michelson MB-102 spectrometer fitted with a CsI beam splitter, with the samples dispersed in KBr disks and a spectral resolution of 4 cm^{-1} . Good signal-to-noise ratios were obtained from accumulation of 128 spectral scans. Fourier-transform Raman spectroscopy was carried out using a Bruker RFS 100 instrument, $\text{Nd}^{3+}/\text{YAG}$ laser operating at 1064 nm in the near-infrared and CCD detector cooled with liquid nitrogen. Good signal-to-noise ratios were obtained from 2000 scans accumulated over a period of about 30 min, using 4 cm^{-1} as spectral

resolution and 50 mW of laser power. All spectra were obtained at least twice to show the reproducibility, and no changes in band positions and intensities were observed. Single crystal X-ray data were collected using a Bruker Kappa CCD diffractometer with $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) at room temperature (298 K). Data collection, reduction and cell refinement were performed by COLLECT, EVAL-CDD and DIRAX programs [21]. The structures were solved and refined using SHELXL-97 [22]. An empirical isotropic extinction parameter x was refined, according to the method described by Larson [23]. A multiscan absorption correction was applied [24]. The structures were drawn by ORTEP-3 for windows [25] and Mercury [26] programs. CCDC 748240 and 748241 contain the supplementary crystallographic data for both compounds. These data can be obtained free of charge at www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussions

Transition metal complexes of general formulae $\text{MB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$, where $\text{M} = \text{Fe}^{2+}$ and Zn^{2+} , were obtained by slow diffusion of metal sulfate aqueous solution into an aqueous solution containing barbituric acid (HB) and 4,4'-bipyridine (bpy). For each compound, the analytical data suggest the formation of compounds with stoichiometry proportion of 1:2:1 (referring $\text{M}^{2+}:\text{B}^-:\text{bpy}$). The thermogravimetric data (TGA/DTA), which are deposited as [Supplementary material \(Figs. S1 and S2\)](#), reveal that both curves show mass losses below 100 °C which can be attributed to the loss of eight (calcd./exp.: 22.27%/21.87%) and seven (calcd./exp.: 19.21%/19.11%) water molecules for compounds **1** and **2**, respectively. A second weight loss is observed above 100 °C which referring the loss of half 4,4'-bipyridine molecule and other two water molecules (calcd./exp.: 17.64%/17.43%) for compound **1**, and one 4,4'-bipyridine molecule with three water molecules (calcd./exp.: 32.01%/33.28%) for compound **2**. However, all curves display other weight loss steps which can be attributed to thermal decomposition. The final residue can be identified as 1 mol of the metal oxide, associated with the presence of carbonized organic residues. For compound **1** the metal oxide calculated was 11.13% while the total observed residue was 19.63%, which makes a difference of 8.5% in mass corresponding to the amorphous residue. For compound **2** the metal oxide calculated is 12.40%, the total observed residue is 18.66% and the amorphous residue is 6.26%.

The polymeric structures of the $\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**1**) and $\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**2**) complexes were revealed by X-ray single crystal analysis. [Tables 1 and 2](#) display the crystal data and main geometrical parameters of the complexes; comparing the listed crystallographic parameters it can be noticed that both compounds are isostructural, crystallizing in a hexagonal crystal system with space group P6_422 . For both complexes one extended one-dimensional chain is observed ([Fig. 2](#)) which is formed between the

Table 1Crystal data of FeB₂bpy·10H₂O (**1**) and ZnB₂bpy·10H₂O (**2**) complexes.

Compound	FeB ₂ bpy·10H ₂ O (1)	ZnB ₂ bpy·10H ₂ O (2)
Formula	C ₁₈ H ₃₄ FeN ₆ O ₁₆	C ₁₈ H ₃₄ ZnN ₆ O ₁₆
Formula weight/g mol ^{−1}	646.35	655.88
Crystal system	Hexagonal	Hexagonal
Space group	P6 ₄ 22	P6 ₄ 22
<i>a</i> /Å	11.702 (4)	11.669 (5)
<i>b</i> /Å	11.702 (4)	11.669 (5)
<i>c</i> /Å	18.720 (1)	18.765 (1)
<i>V</i> /Å ³	2220.6 (2)	2212.6 (2)
<i>Z</i>	3	3
Crystal size/mm	0.25 × 0.29 × 0.36	0.06 × 0.12 × 0.08
<i>D</i> _{calcd} /g cm ^{−3}	1.450	1.477
μ (Mo K α)/cm ^{−1}	0.588	0.912
Transmission factors (min/max)	0.736/0.831	0.850/0.900
Reflections measured/unique	3496/1142	19,908/1695
Observed reflections [<i>F</i> _o ² > 2 σ (<i>F</i> _o ²)]	885	1455
No. of parameters refined	102	102
<i>R</i> [<i>F</i> _o > 2 σ (<i>F</i> _o)]	0.0325	0.0418
<i>wR</i> [<i>F</i> _o ² > 2 σ (<i>F</i> _o ²)]	0.0846	0.0932
<i>S</i>	1.126	1.161
RMS peak/	0.041	0.046

Table 2Selected geometrical parameters and hydrogen interactions for the FeB₂bpy·10H₂O (**1**) and ZnB₂bpy·10H₂O (**2**) complexes.

	FeB ₂ bpy·10H ₂ O (1)	ZnB ₂ bpy·10H ₂ O (2)
<i>Bond distance/Å</i>		
M—O1	2.090 (2)	2.060 (2)
M—N1	2.268 (3)	2.249 (3)
N1—C1	1.338 (4)	1.335 (3)
N2—C4	1.360 (4)	1.358 (3)
N2—C5	1.392 (4)	1.396 (4)
O2—C4	1.239 (5)	1.247 (4)
O3—C5	1.269 (4)	1.264 (3)
C5—C6	1.390 (4)	1.392 (3)
<i>Average of bond angles/°</i>		
O—M—O	89.99 (15)	89.53 (16)
O—M—O	172.52 (14)	172.82 (14)
N—M—O	93.74 (7)	93.59 (7)
N—M—O	86.26 (7)	86.41 (7)
<i>Hydrogen bond</i>		
<i>D...A/Å</i>		
N2...O3 ^{vii}	2.828 (4)	2.817 (4)
O1...O4	2.668 (6)	2.671 (6)
O1...O2	2.767 (4)	2.770 (4)
O4...O3 ^{vii}	2.740 (5)	2.728 (3)
O4...O5 ^x	2.743 (6)	2.718 (7)
O5...O4	2.743 (6)	2.718 (7)
<i>D—H...A/°</i>		
N2—H2...O3 ^{vii}	171	167
O1—H1A...O4	176	175
O1—H1B...O2	174	174
O4—H4A...O3 ^{vii}	165	163
O4—H4B...O5 ^x	162	165

Symmetry code: (vii) 1 − *x*, 1 − *y*, *z*; (vi) *y* − *x*, *y*, −*z*; (x) *x* − 1, *y*, *z*.

4,4'-bipyridine ligands and the metal ions Fe²⁺ and Zn²⁺ coordinated to four water molecules. Two uncoordinated barbiturate anions can also be seen in the structure, neutralizing each monomeric fragment, besides six crystallization water molecules, which are not represented in the figure for a better visualization. The coordination sphere of Fe²⁺ and Zn²⁺ metallic ions shows one slightly distorted octahedral geometry, where each pyridyl ring of the 4,4'-bipyridine adopt an axial position, whereas four aqua ligands are in the equatorial position. The average of M—O and M—N bond distances is 2.090(2) and 2.268(3) Å for compound **1** and 2.060(2) and 2.249(3) for compound **2**. The 4,4'-bipyridine ligand present a

bis-monodentate coordination mode (or in bridge) between two adjacent metallic centers (Fe...Fe = 11.705(2) Å, Zn...Zn = 11.669(2) Å) in one-dimensional infinite chains. The two pyridyl rings in the 4,4'-bipyridine group are not coplanar, and the torsion angle is 26.11° for **1** and 26.17° for **2**.

In both compounds the barbiturate anions generate a one-dimensional zigzag chain via hydrogen bonds (Fig. 3), which can be classified as moderate to weak due to the interaction distance [9]. These moderate to weak hydrogen bonds have O...N distances of 2.828(4) Å (N2...O3) for compound **1** and 2.817(4) Å (N2...O3) for compound **2**, occurred through of two NH group of one barbiturate ion serves as an hydrogen donor and interact with three carbonyl group hydrogen acceptor of other barbiturate anion of classified mode head-to-tail, these supramolecular interaction occurs with every barbiturates anion in the structure, contributed with stability crystalline arrangement.

The crystallization and coordination water molecules, together with barbiturate anion, are connected by hydrogen bonds to each other. This interaction generates a two-dimensional supramolecular arrangement parallel to the *c*-axis, as can be seen in Fig. 4. The average O...O bond distance is 2.743(3) Å in compound **1** and 2.730(3) Å in compound **2**. In both complexes the barbiturate layers are connected by hydrogen bonds with water molecules, the hydrated and coordinated ones. This pattern can be described as graph set networks N₁ = C(5)R₂²(8) and N₂ = 2R₅³(12)4R₃³(9)2R₆⁶(18). These graph sets representation [27,28] describes the hydrogen interaction design, where the symbols C and R are determinate to an infinite chain and ring set, respectively, whereas the numbers in subscript indicate the quantities of donor atoms and the numbers in superscript indicate the acceptor atoms in each set. The barbiturates anions are interacting with both coordination and crystallization water molecules and the geometrical descriptions of these interactions are listed in Table 2.

The three-dimensional arrangement via hydrogen interaction for the complexes are presented in Fig. 5; observation along the *a*-crystallographic axis reveals the presence of layers, formed by the covalent one-dimensional [M(bpy)(H₂O)₄]²⁺ parallel linear chains, giving three different spatial orientations which are almost parallel to the *b*-crystallographic axis and crusade with layers also parallels of the barbiturate anions in one-dimension. This crystalline arrangement is stabilized by hydrogen bonds which are formed by interaction between barbiturate anions and each crystallization or coordination water molecules present in the structure.

In both complexes the centroid-centroid distance between adjacent rings of barbiturate anion and pyridyl is larger than 4 Å, indicating that in these compounds π -stacking interactions between rings is not observed [29]. Garcia et al. [9] synthesized the same complexes with Cu²⁺ and Ni²⁺ metallic ion, and observed the formation of the cavities via hydrogen interaction formed by the two barbiturates anions and four water molecules crystallization encapsulated the covalent [M(bpy)(H₂O)₄]²⁺ linear chains. However these cavities were not observed for the FeB₂bpy·10H₂O (**1**) and ZnB₂bpy·10H₂O (**2**) complexes investigated here, due to the different localization of the crystallization water molecules responsible by the change of the space group in relation to the Cu²⁺ and Ni²⁺ complexes (P6₅22).

The vibrational spectra of the both complexes are very similar and are in agreement with the crystal data. The main vibrational modes for the complexes, barbiturate anion and 4,4'-bipyridine are listed in Table 3 along with the Figs. 6 and 7 shows the infrared and Raman of all compounds, respectively.

Previous literature has shown that the analysis of the vibrational spectra of compounds of this type can be very useful in understanding the structural data [9,30–32]. The barbiturate salt which was used in the vibrational measurements was synthesized

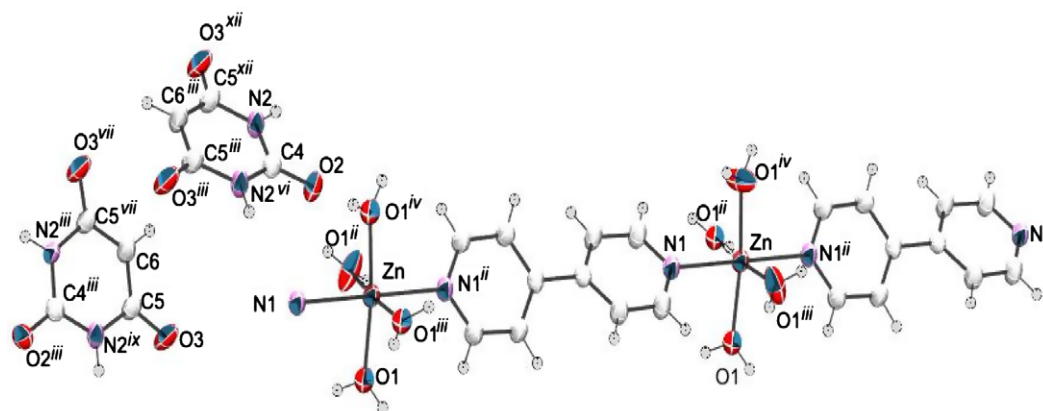


Fig. 2. ORTEP representation of the one-dimensional covalently bonded chain and barbiturate anion. Thermal ellipsoids are drawn at the 50% probability level for compounds (1) and (2). The crystallization water molecules are omitted for clarity. Symmetry code: (i) x, y, z ; (ii) $-x, -y, z$; (iii) $-y, -x, -z + 1/3$; (iv) $y, x, -z + 1/3$; (v) $x - y, -y, -z$; (vi) $-x + y, y, -z$; (vii) $x, x - y, -z + 2/3$; (viii) $-x, -x + y, -z + 2/3$; (ix) $-y, x - y, z + 1/3$; (x) $y, -x + y, z + 1/3$; (xi) $x - y, x, z + 2/3$; (xii) $-x + y, -x, z + 2/3$.

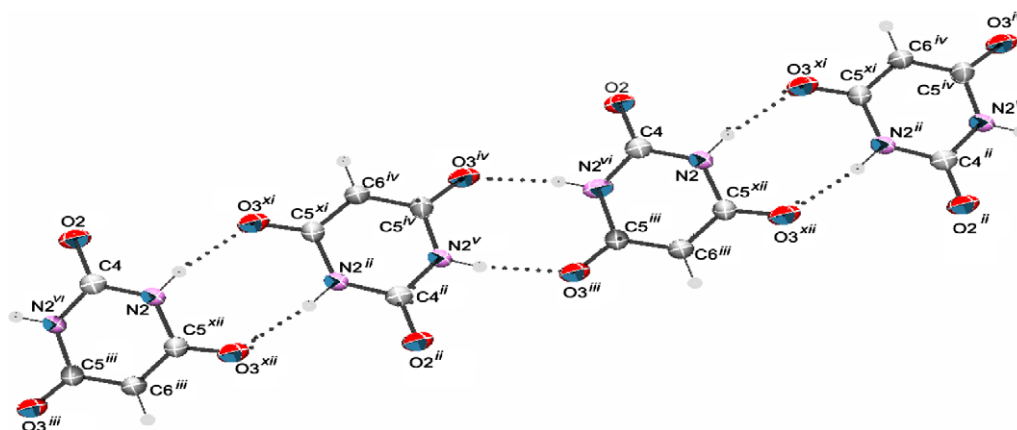


Fig. 3. ORTEP representation of the one-dimensional interaction hydrogen in the barbiturates anions. Symmetry code: (i) x, y, z ; (ii) $-x, -y, z$; (iii) $-y, -x, -z + 1/3$; (iv) $y, x, -z + 1/3$; (v) $x - y, -y, -z$; (vi) $-x + y, y, -z$; (vii) $x, x - y, -z + 2/3$; (viii) $-x, -x + y, -z + 2/3$; (ix) $-y, x - y, z + 1/3$; (x) $y, -x + y, z + 1/3$; (xi) $x - y, x, z + 2/3$; (xii) $-x + y, -x, z + 2/3$.

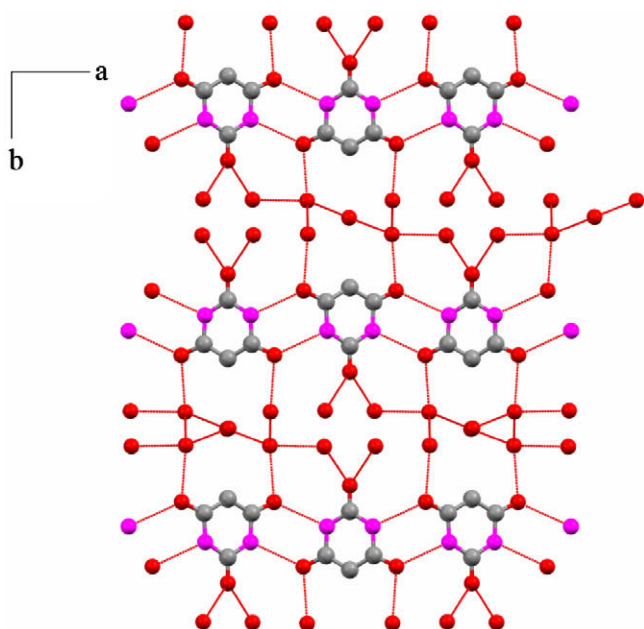


Fig. 4. Diagram showing the hydrogen bond two-dimensional network view along the c -axis for compounds 1 and 2.

from a reaction between barbituric acid and sodium hydroxide. In the infrared spectrum of the barbiturate anion, two bands at 1695 and 1636 cm^{-1} can be observed, assigned to νCO the carbonyl groups ($\text{C}_4=\text{O}$ and $\text{C}_2=\text{O}$, respectively, following the numbering of Fig. 1); other effective band appears at 1369 cm^{-1} , assigned to the δNH in-plane bending, according to Barnes and coworkers [33]. In the Raman spectrum of the barbiturate anion can be observed a high intensity band at 684 cm^{-1} which is assigned to the ring breathing mode. This same vibrational mode appears originally in the barbituric acid as a band at 665 cm^{-1} , and the observed shift to higher wavenumbers is due to the electronic delocalization through the ring due to the formation of the barbiturate anion (Fig. 1). Therefore this mode is very important for the confirmation of the barbiturate anion presence in the complexes. Other bands of less intensity also appear at 1627 and 1702 cm^{-1} , which can be assigned to νCO modes. Previous studies carried out on barbiturate salts [30] have observed that the carbonyl stretching modes were shifted by *ca.* 30 cm^{-1} to lower wavenumbers in relation to barbituric acid, where this band can be seen at 1735 cm^{-1} .

In the infrared spectrum of the free 4,4'-bipyridine ligand, it can be observed a band at 1591 cm^{-1} , assigned to $\nu\text{CC}/\nu\text{CN}$ stretching modes of the pyridyl ring, whereas the bands at 1408 and 808 cm^{-1} are attributed to the ν_{ring} and δCH , respectively. In the bpy Raman spectrum, these bands are also present showing an

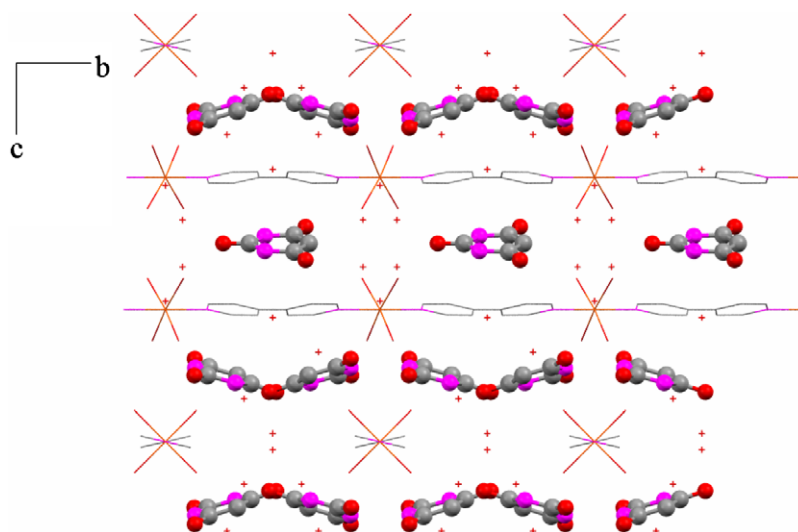


Fig. 5. Three-dimensional array via hydrogen interaction for $\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**1**) and $\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**2**) complexes.

Table 3

Raman (R) and infrared (IR) wavenumbers (in cm^{-1}) and tentative assignment of the most important bands observed for the $\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**1**) and $\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (**2**) complexes.

Barbiturate anion		bpy	$\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (1)		$\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (2)		Tentative assignment	
IR	R	IR	R	IR	R	IR	R	
498 m	406 m		315 m		294 w		306 w	δ_{ring}
	508 m							$\delta\text{CO}_{\text{i.p.}}$ bending
								$\delta\text{ring}_{\text{i.p.}}$ bending
								$\delta\text{ring}_{\text{i.p.}}$ bending
			609 s	542 m	543 m	542 m	543 m	ν_{MN}
	620 w			623 w		640 m		$\delta_{\text{o.p.}}$ CO
	684 vs				680 m		680 s	Ring breathing
			757 m		770 w		777 m	$\delta_{\text{ring}} + \nu_{\text{ring}}$
	969 m	808 vs		806 m		808 m		δ_{CH}
		990 m	1000 vs		1019 s		1020 s	ν_{ring}
		1078 w		1067 w	1073 m	1072 m	1075 m	$\nu_{\text{ring}} + \delta_{\text{CH}}$
		1221 m		1217 w		1215 m	1220 m	δ_{CH}
1234 m			1297 vs	1298 m	1297 s	1304 s	1290 vs	ν_{CN}
1369 w	1367 w			1365 m		1371 s		$\nu_{\text{ring}} + \delta_{\text{CH}}$
1412 s		1408 s		1410 m		1418 s		$\delta_{\text{i.p.}}$ NH
		1489 w				1491 w		ν_{ring}
		1533 m	1513 w		1517 w		1519	ν_{CN}
		1591 vs	1606 s	1607 vs	1615 vs	1612 vs	1614	$\nu_{\text{ring}} + \delta_{\text{CH}}$
1636 s	1627 w							$\nu_{\text{C=O}}$
1695 vs	1702 w			1686 vs		1686 vs		$\nu_{\text{C4,6=O}}$
		3028 m	3052 m					ν_{CH}
	3114 m							ν_{NH}

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; B, barbiturate anion.

intensity enhancement when compared with the infrared spectrum; other bands, such as the ones at 1606 and 1297 cm^{-1} , attributed to $\nu_{\text{CC}}/\nu_{\text{CN}}$ stretching and $\nu_{\text{ring}} + \delta_{\text{CH}}$ combination modes, respectively, and the band at 1000 cm^{-1} , assigned to ν_{ring} , are also observed [32]. For the ligand 4,4'-bipyridine the region spectral (infrared and Raman) between 1590 and 1650 cm^{-1} , where CC and CN stretching modes are expected, is very important in the coordination analysis ligand. The bands at 1591 and 1606 cm^{-1} for the free ligand are shifted for higher wavenumbers when bpy is coordinated to the metal ion, whereas the infrared spectra of the synthesized complexes present one band at 1610 cm^{-1} which can be assigned to the $\nu_{\text{CC}}/\nu_{\text{CN}}$ stretching mode, suggesting the coordination of the ligand by the nitrogen atom, and confirmed by the appearance of one medium intensity band in the Raman

and infrared spectra at 543 cm^{-1} , assigned to $\nu(\text{M}-\text{N})$ stretching. The presence of characteristic bands of the barbiturate anion in the infrared spectrum of the complexes is confirmed by the intense band at 1686 cm^{-1} , assigned to the ν_{CO} stretching mode, which is shifted for low wavenumber when compared to the free barbituric acid (occurring at 1728 cm^{-1}). Another band at 1367 cm^{-1} has also been observed and attributed to the δ_{NH} in-plane bend mode (Table 3). The broad band around 3300 cm^{-1} can be associated to the ν_{OH} stretching mode of the crystallization and coordination water molecules present in the structure, which are involved in hydrogen interactions responsible for the stability of the crystal-line network.

Raman spectra (Fig. 7) of the compounds obtained with 1064 nm excitation are also very supportive of the observations

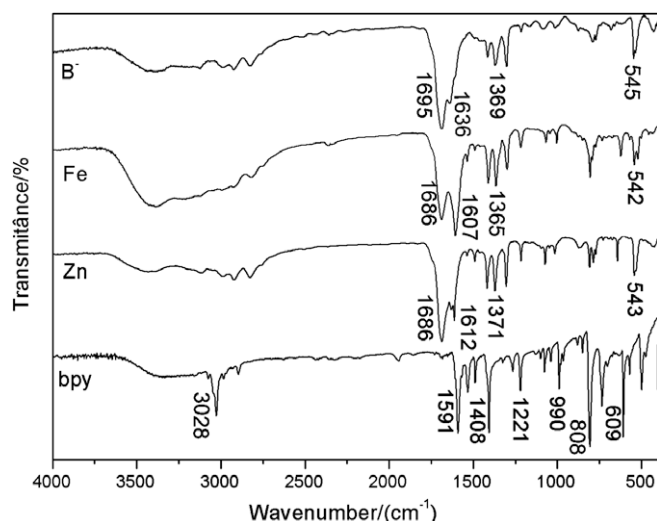


Fig. 6. Infrared spectra of $\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (1), $\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (2), barbiturate anion (B^-) and 4,4'-bipyridine (bpy); for comparison purposes the spectra of the ligands (bpy and B^-) are also displayed.

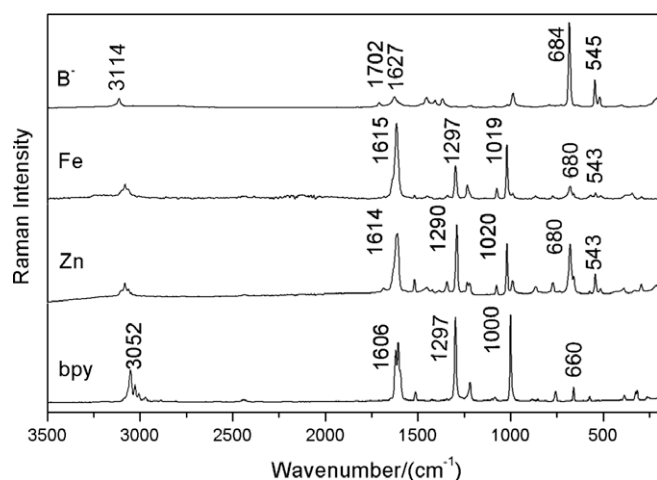


Fig. 7. Raman spectra (excited at 1064 nm) of $\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (1), $\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (2) complexes, barbiturate anion (B^-) and 4,4'-bipyridine (bpy); for comparison purpose the spectra of the ligands (bpy and B^-) are also displayed.

made based on the infrared spectra. The presence of the 4,4'-bipyridine ligand in the structure is confirmed through the observation of the bands at 1020 and 1615 cm^{-1} , assigned to the ν_{ring} and $\nu_{\text{CC}}/\nu_{\text{CN}}$ stretching modes, respectively. These bands are shifted to a high wavenumber region when compared to the free ligand (where they occur at 1000 and 1606 cm^{-1} , respectively) due to the perturbation caused by its coordination to the metal sites. This observation can be explained based on the type of bonding involved in the interaction between the metal and the ligand. The ligand π -electrons involved in the bond imply in a strengthening of the CN bond, and consequently in an increase in the bond order, and with a decrease in the bond length. This result is in a good agreement with the coordination of the pyridine nitrogen atoms of 4,4'-bipyridine to the metal ion, and is also supported by the comparison with other analogous compounds reported in the literature [9,34]. Other band which can be observed in the spectra is the one at 1295 cm^{-1} , assigned to the $\nu_{\text{ring}} + \delta\text{CH}$ combination mode of the bpy ligand. Regarding the barbiturate anion, it was not possible to observe

the presence of any trace of the ν_{CO} mode in the Raman spectrum in the region around 1700 cm^{-1} , probably due to a change in the symmetry which turns this mode inactive or with a very low intensity. However, one very important and unique band is observed for the barbiturate anion characterization in both complexes, around 680 cm^{-1} , assigned to the ring breathing mode, appearing shifted in relation to barbituric acid (665 cm^{-1}). Another interesting observation is the shifting of ca. 15 cm^{-1} occurring for the ring breathing mode, due to the delocalization of the electronic charge over the barbiturate anion, and explained by the resonance structures depicted in Fig. 1; this electronic delocalization can lead to a strengthening of the CN and CC bonds of the barbiturate ring and, consequently, to the observed shift of to higher wavenumber values, as observed in the Raman spectra (Fig. 7).

4. Conclusions

In summary, this paper describes the synthesis and structural characterization of two supramolecular complexes namely $\text{FeB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (1) and $\text{ZnB}_2\text{bpy} \cdot 10\text{H}_2\text{O}$ (2), where bpy is the nitrogen ligand 4,4'-bipyridine and B the barbiturate anion. Both synthesized compounds are isostructural, crystallizing in a hexagonal crystal system with space group $P6_322$, just being different in the location of the crystallization water molecules, responsible for the change of the space group in relation to the Cu^{2+} and Ni^{2+} complexes ($P6_522$) [9]. The metallic sites present a slightly distorted octahedral geometry, coordinated to 4,4'-bipyridine in a bis-monodentate mode; the metal ions are also coordinated to four water molecules, giving rise to a cationic one-dimensional chain linear $[\text{M}(4,4'\text{-bpy})(\text{H}_2\text{O})_4]^{2+}$. The polymeric unit is neutralized by two barbiturate anions, leading to a zigzag chain via hydrogen interaction within the presence of the six crystallization water molecules per repetition unit. It has also been observed that the one-dimensional polymeric chain interacts by hydrogen bond with barbiturate anion and the crystallization waters, resulting in a three-dimensional arrangement which is responsible for the stability of the whole network crystal. Vibrational spectra of these compounds are very similar, and in a good agreement with the crystal data. In the infrared spectra for both compounds can be observed the bands at 1686 and 1609 cm^{-1} , assigned to the ν_{CO} stretching mode of the barbiturate anion and to the $\nu_{\text{CC}}/\nu_{\text{CN}}$ stretching modes of 4,4'-bipyridine, respectively. The Raman spectra show intense and conclusive bands at 1615, 1295 and 1020 cm^{-1} , assigned to $\nu_{\text{CC}}/\nu_{\text{CN}}$, $\nu_{\text{ring}} + \delta\text{CH}$ and ν_{ring} modes, respectively. The barbiturate anion is observed through the presence of a unique marker band at 680 cm^{-1} , assigned to the ring breathing mode.

Finally this work shows that the use of multiple ligands with supramolecular characteristics act as H-donor and H-acceptor, such as barbiturate anion, coupled with the use of non-flexible ligands acting as build blocks, such as 4,4'-bipyridine, can contribute significantly for the construction of different crystalline n -dimensional and well-defined arrangements, very important for supramolecular chemistry.

Acknowledgements

The authors thank CNPq, CAPES, FAPEMIG (PRONEX 526/07, 390/07) and FINEP (PROINFRA 1124/06) for financial support and also LDRX (Instituto de Física–Universidade Federal Fluminense) for X-ray facilities.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.01.035.

References

- [1] S. Thakurta, J. Chakraborty, G. Rosair, R.J. Butcher, S. Mitra, *Inorg. Chim. Acta* 362 (2009) 2828.
- [2] D. Braga, F. Grepioni, G.R. Desiraju, *Chem. Rev.* 98 (1998) 1375.
- [3] S.E.H. Etaiw, D.M.A. El-Aziz, A.S.B. El-din, *Polyhedron* 28 (2009) 873.
- [4] Z.-X. Zhang, Y. Li, K.-C. Li, W.-D. Song, Q.-S. Li, *Inorg. Chem. Commun.* 10 (2007) 1276.
- [5] S.-N. Li, Q.-G. Zhai, M.-C. Hu, Y.-C. Jiang, *Inorg. Chim. Acta* 362 (2009) 2217.
- [6] (a) M. Du, Z.-H. Zhang, W. Guo, X.-J. Fu, *Cryst. Growth Des.* 9 (2009) 1655;
(b) H.E. Toma, *An. Acad. Bras. Cienc.* 72 (2000) 5.
- [7] P.V. Bernhardt, *Inorg. Chem.* 28 (1999) 3481.
- [8] J.D. Badjic, A. Nelson, S.J. Cantrill, W.B. Turnbull, J.F. Stoddart, *Acc. Chem. Res.* 38 (2005) 723.
- [9] H.C. Garcia, R. Diniz, M.I. Yoshida, L.F.C. de Oliveira, *CrystEngComm* 11 (2009) 881.
- [10] M. Ruben, J.-M. Lehn, P. Müller, *Chem. Soc. Rev.* 35 (2006) 1056.
- [11] Y. Xiong, C. He, T.-C. An, C.-H. Cha, X.-H. Zhu, *Trans. Met. Chem.* 28 (2003) 69.
- [12] E. Peppas, J. Anastassopoulou, T. Theophanides, *J. Mol. Struct.* 55 (2001) 219.
- [13] P.T. Muthiah, M. Hemamalini, G. Bocelli, *Struct. Chem.* 18 (2007) 171.
- [14] T. Kolev, R. Bakalska, R.W. Seidel, H. Mayer-Figge, I.M. Opper, M. Spittler, W.S. Sheldrick, B.B. Koleva, *Tetrahedron* 20 (2009) 327.
- [15] N. Romain, C. Giroud, K. Michaud, P. Mangin, *Forensic Sci. Int.* 131 (2003) 103.
- [16] R.N. Westhorpe, C. Ball, *Int. Congr. Ser.* 1242 (2002) 57.
- [17] E. Peppas, J. Anastassopoulou, T. Theophanides, *J. Mol. Struct.* 559 (2001) 219.
- [18] Y. Wang, L. Feng, Y. Li, C. Hu, E. Wang, N. Hu, H. Jia, *Inorg. Chem.* 41 (2002) 6351.
- [19] L. Li, B. Chen, Y. Song, G. Li, H. Hou, Y. Fan, L. Mi, *Inorg. Chim. Acta* 344 (2003) 95.
- [20] L.-N. Zhu, Q.-L. Wang, W.-Z. Wang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, *J. Mol. Struct.* 649 (2003) 111.
- [21] (a) COLLECT, Enraf-Nonius, Nonius BV, Delft, The Netherlands, 1997–2000;
(b) A.J.M. Duisenberg, *J. Appl. Crystallogr.* 25 (1992) 92;
(c) A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs, *J. Appl. Crystallogr.* 36 (2003) 220.
- [22] G.M. Sheldrick, *SHELXL-97 – A Program for Crystal Structure Refinement*, University of Goettingen, Germany, 1997.
- [23] A.C. Larson, *Crystallogr. Compd.* (1970) 291.
- [24] R.H. Blessing, *Acta Crystallogr. A* 51 (1995) 33.
- [25] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.
- [26] C.F. Macrae, P.R. Edgington, P.Mc. Cabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* 39 (2006) 453.
- [27] J. Bernstein, R.E. Davis, L. Shimon, N.-L. Chang, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1555.
- [28] M.C. Etter, J.C. MacDonald, J. Bernstein, *Acta Crystallogr. B* 46 (1990) 256.
- [29] A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schröder, *Coord. Chem. Rev.* 222 (2001) 155.
- [30] J.N. Willis, R.B. Cook, R. Jankow, *Anal. Chem.* 44 (1972) 1228.
- [31] L.F.C. de Oliveira, P.S. Santos, J.C. Rubim, *J. Raman Spectrosc.* 22 (1991) 485.
- [32] A. Topaçlı, S. Akyüz, *Spectrochim. Acta A* 51 (1995) 633.
- [33] A.J. Barnes, L. Le Gall, J. Lauransan, *J. Mol. Struct.* 56 (1979) 15.
- [34] W.M. Teles, N.G. Fernandes, A. Abras, C.A.L. Filgueiras, *Trans. Met. Chem.* 24 (1999) 321.