



Vibrational and structural properties of barbiturate anions in supramolecular compounds



Humberto C. Garcia^a, Mariana T.C. Campos^a, Howell G.M. Edwards^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, Juiz de Fora, MG, 36036-900, Brazil

^b School of Life Sciences, University of Bradford, Bradford, BD7 1DP, West Yorkshire, UK

ARTICLE INFO

Article history:

Received 1 February 2016

Received in revised form 7 July 2016

Accepted 7 July 2016

Available online 9 July 2016

Keywords:

Supramolecular chemistry

Barbiturate anion

Raman analysis

Crystal structure

Metal complexes

Hydroxyhydrilate anion

ABSTRACT

In this work we have been successful in the synthesis, spectroscopic and structural characterization of five new supramolecular compounds of formulation $[\text{Ni}(\text{4dbpy}2)(\text{H}_2\text{O})_2]\text{Bb}_2 \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Mn}(\text{4dbpy}2)(\text{H}_2\text{O})_2]\text{Bb}_2 \cdot 4\text{H}_2\text{O}$ (**2**), $[\text{Mn}(\text{5dbpy}2)\text{Cl}(\text{H}_2\text{O})][(\text{C}_4\text{O}_3\text{N}_2\text{H}_2)_2\text{-OH}] \cdot \text{H}_2\text{O}$ (**3**), $[\text{Co}(\text{5dbpy}2)(\text{H}_2\text{O})_4]\text{Bb}_2 \cdot 2\text{H}_2\text{O}$ (**4**) and $[\text{6dbpy}2\text{H}][(\text{C}_4\text{O}_3\text{N}_2\text{H}_2)_2\text{-OH}] \cdot \text{H}_2\text{O}$ (**5**) which have been obtained from barbituric acid (HB) and 2,2'-bipyridine (4,4', 5,5' and 6,6'-dimethyl) building block ligands and transition metal ions, where Bb is the barbiturate monoanion and dbpy is the neutral substituted bipyridyl in the formulation. Compounds **1** and **2** are isomorphous, presenting the cationic block $[\text{M}(\text{4dbpy}2)(\text{H}_2\text{O})_2]^{2+}$ neutralized by two uncoordinated barbiturate anions, whilst for compound **4** the different cationic units $[\text{Co}(\text{5dbpy}2)(\text{H}_2\text{O})_4]^{2+}$ are neutralized by the same anion. For the compounds **3** and **5** the formation of a new building block is recognized and characterized as the hydroxyhydrilate anion which has been generated *in situ* from the oxidation reaction between alloxan and the barbiturate anion. The Raman spectral analysis clearly shows the similarity of compounds **1** and **2** through similar wavenumber positions of all the vibrational bands, especially the band at 679 cm^{-1} assigned to the ring breathing mode of the barbiturate anion which is present in compounds **1**, **2** and **4**. For compounds **3** and **5** the absence of this Raman band suggests that a noteworthy chemical modification has taken place in this building block and the appearance of a new band at 1745 cm^{-1} , assigned to the $\nu(\text{C}=\text{O})$ mode of the new hydroxyhydrilate anion generated *in situ*, supports this conclusion.

© 2016 Elsevier B.V. All rights reserved.

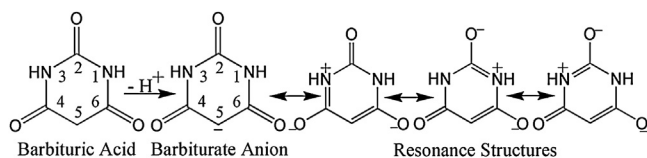
1. Introduction

The chemistry of barbituric acid derivatives (in this case *pyrimidine 2,4,6(1H,3H,5H)-trione*, or simply HBb) (Scheme 1) has been much studied due to their significance in biology and their medical usage as depressants for the central nervous system, anticonvulsants, hypnotic anesthetics, sedatives and also as azo dye pigments [1–3]. The presence of five atoms (three O and two N) with roles in coordination chemistry creates the possibility for the potential formation and stability of supramolecular arrangements through the donor-acceptor mechanism of protons in the building block arrangements [4,5]. In this way, barbituric acid can be classified as an organic building block which has the ability to act intra- and intermolecularly through the presence of these O and N

atoms. The loss of the hydrogen atom located on the CH_2 group (C5, representing the alpha carbon which is bonded to two other carbonyl groups so resulting in its acidity) promotes the formation of the barbiturate anion (Bb^-) which is stabilised as a planar carbanion through the formation of resonance structures (Scheme 1). The pyrimidine ring of HBb can hence be easily functionalized in this CH_2 position through different synthetic mechanisms [6,7] and an example of this is the work of Rajput et al. [8] who synthesised derivatives of arylidene barbituric acid through the condensation of aromatic aldehydes using CoFe_2O_4 nanoparticles as a catalyst. More recently, an intriguing study has been reported by Garcia et al. [9] using solvothermal synthesis to promote the opening of the barbituric acid ring; in this, the formation of a malonate anion which was coordinated to the cobalt ion and a 1,2-bis(4-pyridyl)-ethane (or bpa) ligand resulted in a complex of molecular formula $[\text{Co}_2(\text{mal})_2\text{bpa}(\text{H}_2\text{O})_2]$ which is noteworthy since malonic acid was the starting material with urea in Baeyer's [10] first synthesis of barbituric acid. These two

* Corresponding author.

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



Scheme 1. Molecular structure of barbituric acid, barbiturate anion and its resonance forms.

examples serve to show the potential versatility of barbiturate as a building block and its adoption for study here.

An interesting set of building blocks in supramolecular chemistry which will be used in this work are the three nitrogen monomeric chelating ligands based on dimethyldipyridine; 4,4'-dimethyl-2,2'-dipyridil (or 4dbpy2), 5,5'-dimethyl-2,2'-dipyridil (or 5dbpy2) and 6,6'-dimethyl-2,2'-dipyridil (or 6dbpy2) whose spectroscopic characteristics and magnetic, catalytic and optical properties combined with other molecules and metal ions [11–13] have been reported and for which the presence of two methyl groups in the ligands introduces a well-understood steric influence in their structural behavior.

In this work the synthesis, vibrational spectroscopic analysis (infrared and Raman) and crystal structures of five new supramolecular complexes that involve barbituric acid and 2,2'-dipyridil ligand analogues (4,4', 5,5' and 6,6'-dimethyl) and transition metal ions (Mn^{2+} , Co^{2+} and Ni^{2+}) are described. The central objective of this study was to understand the role of each building block in the formation of different crystallographic arrangements and the correlation with their vibrational spectra – from which the identification of a new building block generated *in situ* and incorporated into the supramolecular arrangement of some complexes resulted.

2. Experimental section

2.1. Chemical and reagents

All starting materials of this work were purchased and used without further purification: barbituric acid ($\text{C}_4\text{H}_4\text{N}_2\text{O}_3$, 99.0%, Merck), 4,4'-dimethyl-2,2'-dipyridil ($\text{C}_{12}\text{H}_{12}\text{N}_2$, 98.0%, Sigma Aldrich), 5,5'-dimethyl-2,2'-dipyridil ($\text{C}_{12}\text{H}_{12}\text{N}_2$, 98.0%, Sigma Aldrich), 6,6'-dimethyl-2,2'-dipyridil ($\text{C}_{12}\text{H}_{12}\text{N}_2$, 98.0%, Sigma Aldrich) and the metal salts $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99.5%, Sigma Aldrich), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (97.0%, Vetec), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (98.0%, Vetec), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (98.0%, Vetec). All solvents used were analytical grade.

2.2. Synthesis

A general synthetic method was adopted to obtain all the compounds described in this work. The compounds were prepared in two steps: initially 15 mL of an aqueous solution containing 100 mg (0.78 mmol) of barbituric acid (HBB) was mixed separately with 10 mL of an ethanolic solution containing 144 mg (0.78 mmol) of the nitrogen ligands 4dbpy2, 5dbpy2 and 6dbpy2. Then these individual solutions were added by the diffusion method to 0.78 mmol metal ions in aqueous solutions of NiCl_2 , MnSO_4 , MnCl_2 , CoCl_2 and MnCl_2 , to obtain the compounds **1** to **5**, respectively. After approximately two weeks, coloured crystallographic materials were obtained. Elemental analysis gave the following results: $[\text{Ni}(\text{4dbpy2})_2(\text{H}_2\text{O})_2]\text{Bb}_2 \cdot 4\text{H}_2\text{O}$ (**1**) (green crystals, yield = 38%): Calcd.: C, 48.69%; H, 5.36%; N, 14.19%; Observed: C, 48.38%; H, 5.21%; N, 14.05%. $[\text{Mn}(\text{4dbpy2})_2(\text{H}_2\text{O})_2]\text{Bb}_2 \cdot 4\text{H}_2\text{O}$ (**2**) (yellow crystals, yield = 43%): Calcd.: C, 48.92%; H, 5.39%; N, 14.26%; Observed: C, 48.20%; H, 5.31%; N, 14.25%. $[\text{Mn}(\text{5dbpy2})_2\text{ClH}_2\text{O}][(\text{C}_4\text{O}_3\text{N}_2\text{H}_2)_2\text{-OH}] \cdot \text{H}_2\text{O}$ (**3**) (yellow crystals, yield = 32%): Calcd.: C,

54.20%; H, 4.69%; N, 15.80%; Observed: C, 51.48%; H, 4.14%; N, 16.51%. $[\text{Co}(\text{5dbpy2})(\text{H}_2\text{O})_4]\text{Bb}_2 \cdot 2\text{H}_2\text{O}$ (**4**) (orange crystals, yield = 38%): Calcd.: C, 39.68%; H, 4.99%; N, 13.88%; Observed: C, 39.83%; H, 4.99%; N, 13.98%. $[\text{6dbpy2H}][(\text{C}_4\text{O}_3\text{N}_2\text{H}_2)_2\text{-OH}] \cdot \text{H}_2\text{O}$ (**5**) (yellow crystals, yield = 45%): Calcd.: C, 50.85%; H, 4.27%; N, 17.79%; Observed: C, 50.75%; H, 4.52%; N, 17.35%.

2.3. Physical measurements

Infrared spectra were obtained using an Alpha Bruker (FT-IR) spectrometer, with the sample supported as a KBr pellet, in the wavenumber region $4000\text{--}400\text{ cm}^{-1}$ with a 4 cm^{-1} spectral resolution. Good signal-to-noise ratios were obtained from an accumulation of 128 spectral scans. Fourier-transform Raman spectroscopy was performed using a Bruker RFS 100 instrument equipped with a Nd^{3+} /YAG laser operating at 1064 nm in the near-infrared region and a Ge detector cooled with liquid N_2 ; good signal-to-noise ratios were obtained from 2000 scans that were accumulated over a period of 30 min with a spectral resolution of 4 cm^{-1} , in the range $4000\text{--}50\text{ cm}^{-1}$ and an average of 50 mW of laser power at the sample; no further mathematical treatments were used to process any of the obtained spectra. 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 $\text{MoK}\alpha$ ($\lambda = 0.71073\text{ \AA}$) for each 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.

3. Results and discussions

The crystal structures of supramolecular compounds **1–5** obtained from reactions involving barbituric acid, nitrogen bipyridine (4,4', 5,5' and 6,6'-dimethyl) ligands and different metal transition ions has been revealed by X-ray single crystal analysis. The crystallographic data for all compounds are listed in Table 1. Other crystallographic information as bond distances, angles and supramolecular interaction hydrogen bonding are displayed in Table S2. Almost all compounds exhibit the same monoclinic crystal system; the only exception was compound **3**, which exhibited a triclinic crystallographic arrangement.

Complexes **1** and **2** are isomorphous, presenting a $C2/c$ space group and general formula $[\text{M}(\text{4dbpy2})_2(\text{H}_2\text{O})_2]\text{Bb}_2 \cdot 4\text{H}_2\text{O}$ (where M is Ni^{2+} or Mn^{2+}). Fig. 1 shows the unit cell for these compounds; the metal center occupies a distorted octahedral coordination geometry comprising two aqua ligands and two bipyridine ligands coordinated as a chelate, giving rise to a cationic block of charge 2+. The average M–N and M–O bond distances are, respectively, 2.074 (2) and 2.078(2) Å for compound **1**, 2.147(4) and 2.116(3) Å for compound **2**. In the manganese ion compound (**2**) the longest bond distances are observed; similar results have been reported for the crystal structure of Mn^{2+} and Ni^{2+} with the 4-sulfobenzoate dianion and 1,2-bis(4-pyridyl)ethane [20]. This observation could be explained by the bigger covalent radius of Mn^{2+} ion, providing a lower attraction to the coordinated ligand which then resulted in larger bond distances. Completing the charge neutrality of the system, two uncoordinated barbiturate ions (Bb^-) act as anions neutralizing the cationic block and generating supramolecular interactions via hydrogen bonds with water molecules of coordination $\text{O1-H1B} \cdots \text{O8}$ equal to 2.722(3) Å and 2.726(4) Å

Download English Version:

<https://daneshyari.com/en/article/1249513>

Download Persian Version:

<https://daneshyari.com/article/1249513>

[Daneshyari.com](https://daneshyari.com)