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Structural characterization of a new dioxamic acid derivative by experimental (FT-IR, NMR, and X-ray) analyses and theoretical (HF and DFT) investigations

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ABSTRACT

Very few investigations concerning the crystal structure and chemical properties of dioxamic acids have been related in the literature. This work describes the chemical properties of *ortho*-phenylenebis(oxamic acid) (**2**) and its new derivative, hydrogeno *ortho*-phenylenebis(oxamato) benzimidazolium (**3**) using experimental (FT-IR, NMR, and X-ray single crystal diffraction) and theoretical (HF/3-21G* and B3LYP/6-31G* calculations) methodologies. Compound **2** displays intramolecular hydrogen bonding between the hydrogen of an amide group and the oxygen atom of another amide group present in the structure. Compound **3** was prepared by a newly developed synthetic route involving decomposition of the dioxamic acid in solution without the presence of metallic ions. Thermodynamic calculations indicate a process via two successive hydrolyzes of the amide groups of **2**, followed by condensation with formic acid and finally dehydration. The structure of **3** was solved by X-ray single-crystal diffraction and it consists of *meso*-helical chains stabilized by intra and intermolecular hydrogen bonds and π–π stacking interactions.

1. Introduction

Oxamic acids and their ester derivatives are biologically important, showing antiallergic, antirheumatic, and antiinflammatory activities [1,2]. For example, *meta*-phenylenebis(oxamic acid) exhibited significant anti-asthmatic properties, being up to 2500 times more active in rats than disodium cromoglycate, a known agent used in the treatment of bronchial asthma caused by allergy [3]. Bis-oxamato ligands have been used as structural components in molecule-based magnets assemblies, providing efficient coupling among magnetic moments of transition metal ions and lanthanides ions [4,5]. The strategy to prepare such molecule-based magnets with different dimensionalities and physical properties starts with the synthesis of a chelate-effect stabilized monometallic precursor [6–12]. This complex is then used as a building block for magnetic materials since it presents external carbonyl groups capable of bridging metal spin carriers.

Monometallic building blocks have been obtained from the basic hydrolysis of the *ortho*-phenylenebis(oxamic acid ethyl ester) (**1**, Fig. 1), followed by addition of transition metal ions [13,14]. The use of **1** as ligand was not successful in providing new precursors for molecule-based magnets containing Fe^{II}, Fe^{III}, Sn^{II}, or Sn^{IV}. In these cases, the high basicity of the reaction mixture either yields the corresponding metal hydroxide or promotes the formation of the *oxo*-bridged complexes, e.g., $(Et_4N)_4[Fe_2O(opba)_2]\cdot 3H_2O$, with opba standing for *ortho*-phenylenebis(oxamato) [15]. Our research group recently employed an efficient methodology to prepare a molecule-based magnet precursor, $[Fe(H_2opba)(dmso)_2]Cl$, using *ortho*-phenylenebis(oxamic acid) (**2**, Fig. 1) as pro-ligand. This precursor presents the ligand (**2**) in the iminoalcohol tautomeric form, which is not the tautomeric form observed in precursors containing other metallic ions (Cu^{II}, Mn^{II}, Ni^{II}, and Zn^{II}) [16].

The literature has described the synthesis of some dioxamic acids, but very few investigations about their crystal structures, chemical properties, and topological control of their dimensionality have been reported [17]. Recently, a successful example of the topological control of the hydrogen bond-directed self-assembly was reported. The aromatic dioxalamide series of *N*,*N*′-1,*n*-phenylenebis(oxamic acid ethyl ester) molecules with $n = 2$ (H_2Et_2opba), $n = 3$ (H_2Et_2mpba), and $n = 4$ (H_2Et_2ppba) present a supramolecular aggregation of molecules into a duplex (0D), a *meso*-helix (1D) and a brick-wall sheet (2D), respectively. These experimental and theoretical studies show the importance of the two oxalamide moieties as a hydrogen-bonded supramolecular synthons [17].

The application of the oxalamide derivatives as gelling systems has recently attracted considerable attention. The entanglement of

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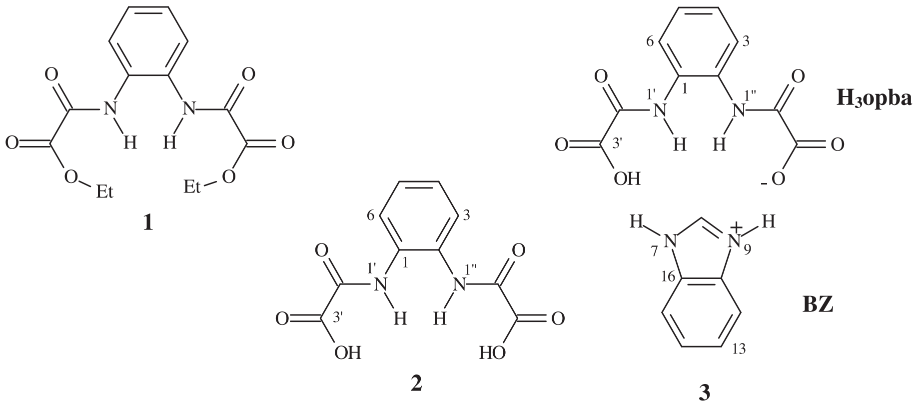

Fig. 1. Chemical structure of the diethyl *ortho*-phenylenebis(oxamato) (**1**), *ortho*-phenylenebis(oxamic) acid (**2**), and hydrogeno *ortho*-phenylene(oxamato) benzimidazolium (**3**; **H₃opba** = hydrogeno *ortho*-phenylenebis(oxamato) and **BZ** = benzimidazolium cation).

the gel fibers, formed by unidirectional self-assembly of these low-molecular organic compounds, can result into three-dimensional networks which traps the solvent. For example, chiral bis(amino acid)oxalamides are able to gel water, as well as a number of low-polarity organic solvents [18,19].

In the present work, the chemical properties of **2** and its new derivative, hydrogeno *ortho*-phenylenebis(oxamato) benzimidazolium (**3**, Fig. 1) were investigated using experimental and theoretical methodologies. Their chemical structures were analyzed from the 1D NMR (^{1}H and ^{13}C) and 2D NMR (^{1}H–^{13}C HMBC and ^{1}H–^{1}H NOESY) at different temperature and in different solvents, including solid-state MAS ^{13}C NMR data. Moreover, a new synthetic method is herein described for the preparation of **3**, whose crystals were suitable for X-ray structure determination. The theoretical studies were based on thermodynamic and carbon chemical shift calculations. Geometry optimizations were carried out using *ab initio* Hartree–Fock (HF) [20] and Density Functional Theory (DFT) [21] methods as recently reported for our studies of other compounds [22,23].

2. Experimental section

2.1. Materials and measurements

Melting points (m.p.) were measured using digital equipment MQAPF-302 Microquimica. Elemental analyses (C, H, N) were performed on a 2400 CHN-Perkin Elmer instrument. Infrared spectra were recorded on a Perkin–Elmer Spectrum GX FTIR spectrophotometer using KBr disks, in the 4000–400 cm^{-1} range. ^{1}H and ^{13}C NMR spectra in solution were recorded on a Bruker AVANCE DRX 400 spectrometer using tetramethylsilane (TMS) as internal standard. The samples (∼15 mg) were dissolved in DMSO-d_6 (∼0.5 mL). Chemical shifts are given in ppm (δ units). Solid-state NMR spectra were recorded on a Bruker AMX 400 wide-bore NMR spectrometer using a commercial triple resonance MAS 4 mm probe. Proton-decoupled ^{13}C MAS NMR spectra were acquired using cross polarization [24]. Typical acquisition parameters were the following: spin lock time 2.0 ms, recycle delay 3 s, ^{1}H B1 field 91 kHz, 3072 data points, 25,000 acquisitions, and spectral width of 50 kHz. The spectra were acquired at 298 K with a spinning speed of 10 kHz. Adamantane was used as reference (high field signal at 29.5 ppm).

One single crystal of **3** was chosen and mounted on an Enraf–Nonius Kappa-CCD diffractometer equipped with graphite monochromator. Mo Kα (λ = 0.71073 Å) radiation was used in the experiment. The final unit cell parameters were based on all reflections. Data collection used the COLLECT program [25]. Integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [26]. 3424 Independent reflections resulted from this integration. The absorption correction was tried, but did not improve the model: the crystal is small, as well as its absorption coefficient. 2911 Reflections with positive intensities were merged and used in the structure resolution and refinements. The structure was solved by direct methods with SHELXS-97 [27]. The model was refined by full-matrix least squares based on F^2, through SHELXL-97. All atoms were anisotropically refined. Hydrogen atoms bonded to carbon were stereochemically positioned and refined using the ridging model. Hydrogen atoms of the aromatic rings were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the atom in which each one is bonded. Hydrogen atoms H711 and H712, which are respectively bonded to N11 and N12, were found on the Fourier difference maps and fixed. Hydrogen atoms bonded to oxygen were also found in the Fourier difference synthesis. The hydrogen atoms HO1 and HO5 were located in special position (inversion center and two-fold axis, respectively), with occupancy factor fixed in 0.5. Their positions and isotropic displacement parameters were fixed. Experimental features are summarized in Table 1.

Table 1
Crystal data and refinement results for **3**.

$C_{11.33}H_{9.33}N_{2.67}O_4$	F_{000} = 1536
M_r = 246.88	D_x = 1.542 Mg m^{-3}
Hall symbol: -C 2yc	Mo Kα radiation, λ = 0.71073 Å
a = 31.299 (4) Å	α = 90°
b = 5.5320 (6) Å	β = 125.454 (6)°
c = 22.623 (4) Å	γ = 90°
V = 3190.8 (7) Å^3	0.068 × 0.213 × 0.048 mm
Z = 8	μ = 0.12 mm^{-1}
Kappa CCD diffractometer	R_{int} = 0.096
Radiation source: fine-focus sealed tube	θ_{max} = 24.7°
Monochromator: graphite	θ_{min} = 2.2°
T = 150 (2) K	h = −35 → 36
3624 Measured reflections	k = −5 → 6
2403 Independent reflections	l = −26 → 26
1056 Observed reflections ($I > 2\sigma(I)$)	
Refinement on F^2	Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.061	$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2]$
	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.127	$(\Delta/\sigma)_{max}$ < 0.001
S = 0.89	$\Delta\rho_{max}$ = 0.28 and Å^{-3}
2403 Reflections	$\Delta\rho_{min}$ = −0.30 and Å^{-3}
245 Parameters	Extinction correction: none