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Characterization of compounds derived from copper-oxamate and imidazolium by X-ray absorption and vibrational spectroscopies

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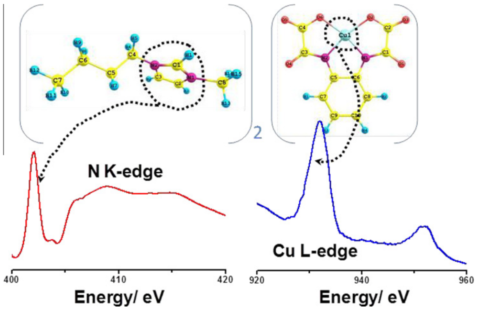
HIGHLIGHTS

- Salts of copper-oxamate anions and imidazolium cations were studied.
- Raman and IR band assignments were supported by DFT calculations.
- Electronic distribution around —Cu—N— sites is changed by anion–cation interaction.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, compounds derived from copper-oxamate anions (*ortho*, *meta*, and *para*)-phenylenebis(oxamate) and imidazolium cations (1-butyl-3-methylimidazolium) were synthesized. The compounds were characterized by Raman and FTIR spectroscopies and the band assignments were supported by DFT calculations. Strong IR bands from 1610 to 1700 cm^{-1} dominated the spectra of the complex and can be assigned to $\nu C{=}O$ vibrations of the $[Cu(opba)]^{2-}$ anions by the comparison with the DFT data. In opposition to the FTIR spectra, the main vibrational bands in the Raman spectra are observed in the 1350–1600 cm^{-1} range. All bands in this region are associated to the modified benzene vibrations of the copper-phenylenebis(oxamate) anions. X-ray absorption near edge (XANES) at different energies (NK and Cu $L_{2,3}$ edges) was also used to probe the interionic interactions. XANES data show that anion–cation interaction in the Cu-oxamate–imidazolium changes the electronic structure around the —Cu—N— sites in the oxamate anion.

Introduction

The emerging field of molecular magnetism has the potential to design unparallel new magnetic materials which can exhibit bulk physical properties, such as long-range magnetic ordering. Our group has been developed a series of copper complexes with phenylenebis(oxamate) derivates as ligands [1–8]. In addition, the combination of different cations to these anionic copper-complexes can change the crystal packing and also the magnetic behavior. Nowadays the family of salts derived from imidazolium cations (known as ionic liquids, ILs) open up the possibility to modulate the

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structural characteristics of the cations bonded to the copper-phenylene-bis(oxamate) anions in order to obtain molecule-based magnets with new behavior and in a liquid state.

Ionic liquids (ILs) are a broad family of salts that are liquid at temperatures lower than 100 °C. Commonly the ionic liquids are composed by a large cation and a weakly coordinating anion [9]. There are a very large range of combinations between cations and anions those can form ionic liquids, about 10^{18} different combinations [9]. The ionic liquids derived from imidazolic ring are the most studied ones [10,11]. Parameters like the carbonic chain length bonded to the cation or the anion type can drastically change the properties of the ILs, thus being possible to achieve a desired function by designing the structure of a specific IL [12]. In most cases, ILs have high thermal stability, a broad electrochemical window, an organized structure at medium distances (in opposition to molecular liquids, that are organized at small distances) and very low vapor pressure, properties that make them important in many areas like green chemistry, organic and inorganic synthesis and many others [13]. The ILs are salts with low melting points and the most unusual characteristic of these systems is that, although they are liquids, they present features similar to solids, such as structural organization at intermediate distances and negligible vapor pressure [9].

Our group start the preparation of compounds derived from Cu-(*ortho*, *meta*, and *para*)-phenylenebis (oxamate) anions combined with different imidazolium cations. The main objective is to prepare compounds derived from ionic liquids with different magnetic behavior. In addition, the presence of a carbonic chain opens the possibility to enhance the interactions between the metal-complex and carbon nanotubes [14,15]. The electronic interactions between the $[Cu(opba)]^{2-}$ anions (where opba = *ortho*phenylenebis(oxamate)) and single wall carbon nanotubes (SWCNTs) were recently investigated by our group [14–16]. It is observed that the electronic interactions show a dependence on the SWCNT diameter, being the interaction stronger for metallic tubes. This interaction is also influenced by the amount of complex that is probably adsorbed on the carbon surface of the SWCNTs. Some charge transfer can be also occurring between the metallic complex and the SWCNTs. Hence, the characterization of the vibrational and electronic signatures of these new ionic liquids is crucial for their future use with single or double walled carbon tubes [17,18].

The Raman and FTIR are commonly used as fundamental techniques in the study of vibrational behavior of these kinds of compounds. The X-ray absorption spectroscopy near edge spectroscopy (XANES) involves the excitation of "core" electrons of the atoms [19]. Each absorption energy edge is related to a specific atom present in the material and, more specifically, to a quantum-mechanical transition that excites an electron in a particular atomic core-orbital to the free or unoccupied continuum levels (ionization of the core orbital above the Fermi energy). In addition, the wavelength associated to the photoelectron formed by the absorption process is higher than the atomic distances. Thus, the mean free path of the photoelectron is sufficient to cause multiple scatterings; this is the main characteristic of the XANES regime [20]. This phenomenon turns the XANES spectra sensible to the electronic density around the absorbing atom, implying that it can be used to monitor the oxidation state and also the density of unoccupied electronic states [21]. In fact, the XANES spectra, particularly for molecules with high electronic delocalization, are very complicated, because many pre-edge peaks can appear due to the resonance and/or conjugation effects [22–27].

XANES spectroscopy was used for investigation of the electronic structure around the Cu atoms in the copper-oxamate anions ((*ortho*, *meta*, and *para*)-phenylenebis(oxamate)) bonded to the imidazolium cations (1-butyl-3-methylimidazolium). For this trend, XANES spectra at Cu L-edge and N K-edge were used for investigation the changes in the electronic densities around Cu and N atoms in these new copper complexes. Hence, in the present work, a vibrational (Raman and FTIR) and electronic (UV–Vis, XANES and XPS) spectroscopies were used for investigation of the ionic liquids derived from copper-oxamate anions ((*ortho*, *meta*, and *para*)-phenylenebis(oxamate)) and imidazolium cations (1-butyl-3-methylimidazolium). The experimental findings are supported by DFT calculations.

Experimental methods

Reagents

The water used in the experiments was deionized from a MilliQ (Millipore System) system. The dichloromethane (Synth), acetonitrile (Synth) and $CuCl_2{\cdot}2H_2O$ (Sigma–Aldrich) were analytical grade and they were used as received without any further purification. Tetrahydrofuran (THF, Synth) was treated with $CaCl_2$ and metallic sodium for removing the water, as described by Morita [28]. The $[Bu_4N]_2Cu(opba)$ (where Bu_4N = tetra-*n*-butyl-ammonium and opba = *ortho*-phenylenebis(oxamate)) material was prepared according to the Ref. [2]. The Et_2H_2mpba (where mpba = *meta*-phenylenebis(oxamate)) material was prepared according to the Ref. [29], the Et_2H_2ppba (where ppba = *para*-phenylenebis (oxamate)) material was prepared according to the Ref. [30], and the $[C_4MIm]ClO_4$ was prepared according to the Ref. [31]. In this work, imidazolic ILs will be abbreviated as $[C_nMIm]^+$ for 1-*alkyl*-3-methylimidazolium, where *n* is the number of carbons in the alkyl chain. The description of the synthetic routes used to acquire the $[C_4MIm]_2Cu(opba){\cdot}3H_2O$, $[C_4MIm]_4[Cu_2(mpba)_2]$, and $[C_4MIm]_4[Cu_2(ppba)_2]$ compounds were described in the Appendix A.

Instrumentation

Raman spectra for the ILs samples at 647.1 nm (1.92 eV, Kr^+ laser) were taken with a triple monochromator, XY Dilor Micro-Raman System, equipped with a CCD detector. For Raman spectra at 785.0 nm (1.58 eV, solid state laser) were taken with a Senterra Bruker Raman spectrometer, equipped with a CCD detector, and finally for Raman spectra at 632.8 nm (1.96 eV, He–Ne laser) were taken with a Renishaw in via Raman spectrometer, equipped with a CCD detector. All Raman spectra were collected at room temperature and using a backscattering geometry and the laser line was focused on the sample using a 50× objective and the power incident on the sample was kept lower than 2 mW to avoid heating effects. Different acquisition times between 5 and 30 s were used for each sample in an attempt to optimize the signal-to-noise ratio of the Raman spectra. Different laser lines were used in order to avoid some fluorescence and/or to maximize the signal-to-noise relation for each IL sample.

The equilibrium geometry of the $[Cu(opba)]^{2-}$, $[Cu_2(mpba)_2]^{4-}$, $[Cu_2(ppba)_2]^{4-}$, and $[C_4MIm]^+$ as well its respective vibrational frequencies (Raman and IR bands) were obtained with the Gaussian 03 software [32] using B3LYP density functional theory. This method uses Becker's three-parameter exchange functional (B3) [33,34], in combination with the (LYP) correlation functional [35]. The calculations were done using the 6-31+G(d) or 6-311++G(d,p) basis set [36,37]. The scale factor values of 0.96 [38,39] or 0.9679 [40] were used in the correction of vibrational frequencies calculated by 6-31+G(d) or 6-311++G(d,p) basis set, respectively. The geometry of $[Cu(opba)]^{2-}$ was constrained to the C_{2v} point group. The cutoffs on forces and step size that are used to determine optimization convergence were tightened, and the ultrafine grid option was also used to ensure the calculated values for the low frequency vibrational modes.