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Characterization of mechanochemically synthesized imidazolates of Ag^{+1}, Zn^{+2}, Cd^{+2}, and Hg^{+2}: Solid state reactivity of nd^{10} cations

J.F. Fernández-Bertrán[a], M.P. Hernández[b,*], E. Reguera[b,c], H. Yee-Madeira[d], J. Rodriguez[b], A. Paneque[a], J.C. Llopiz[b]

[a]Center of Pharmaceutical Chemistry, 21 Avenue and 200 Street, Playa, P.O. Box 16042, Havana, Cuba
[b]Instituto de Ciencia y Tecnologia de Materiales, Zapata y G, P. O. Box 10400, Universidad de La Habana, Cuba
[c]Center of Applied Science and Advanced Technologies of IPN. Mexico, D.F., Mexico
[d]Escuela Superior de Física y Matemáticas-IPN, UP "ALM", Colonia Lindavista 07738, México

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Abstract

Silver, zinc, cadmium, and mercury imidazolates have been synthesized mechanochemically by milling imidazole and the metal oxides in an agate mortar. The reaction products were characterized by FTIR and XRPD techniques. The results obtained for the mechanochemical imidazolates have been compared with those obtained by precipitation reported in the literature. The mechanochemical Ag imidazolate has the same orthorhombic crystal structure as the precipitated one. The mechanochemical Zn imidazolate has a tetragonal structure with similar crystal parameters to those of $Zn(Imz)_2H_2O$, but no water molecules are present in the structure. This new anhydrous form is a polymorph of the one obtained by precipitation. The mechanochemical Cd imidazolate has a monoclinic structure which is the polymorph of the precipited orthorombic form. The mechanochemical Hg imidazolate presents a hexagonal structure which is a polymorph of the orthorombic structure obtained by precipitation. The influence of the nd^{10} electronic configuration of the cations on the mechanochemical reaction is discussed.

Keywords: A. Polymer; B. Chemical synthesis; C. Infrared spectroscopy; C. X-ray diffraction; D. Crystal structure

1. Introduction

Imidazole is a small nitrogen heterocycle molecule of paramount biological importance. Its five membered ring includes an acidic pyrrolic NH group and a basic pyridinic N [1] (see Fig. 1). As a part of hystidine, imidazole is the binding site for cations in metalloproteins. In neutral solutions, imidazole forms complexes with transition metal salts retaining the anion in the structure while in basic solutions it forms imidazolates with the loss of the pyrrolic proton and the incorporation of the cation with formation of polymeric species [1].

Imidazolates do not only have importance as model compounds for metalloproteins but as metal–organic nanometric materials with interesting physico-chemical properties and promising applications in the fields of mechanical and thermal stability, absorptive and catalytical properties, electronic, magnetic, optical, anticorrosive and biocidal activity, protein staining, etc. [2–4 and references therein] The imidazolate anion (see Fig. 1) acts as a rigid angular exobidentate ligand forming open zeolitic-type structures [4].

Imidazolates are normally obtained by mixing a water-soluble salt of the metal with a basic imidazole solution. The product precipitates in microcrystalline form and is easily filtered, washed and dried. The imidazolate polymers are prone to appear in different polymorphic forms [1,4–7]. The synthetic procedure, nature of the solvent and of the metal salt used can have an effect on the crystalline structure of the products. For example, Co(II) imidazolates crystallize in seven different polymorphic forms [4,5], while Cu(II) imidazolates have five

*Corresponding author. Fax: +53 7 2736471.
E-mail addresses: fernandezbertran@yahoo.com (J.F. Fernández-Bertrán), mayrap@fisica.uh.cu (M.P. Hernández).

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