
Multi-Metal Citrate Complex

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Abstract: Hydrothermal synthesis of multi-metal citrate metal-organic framework complexes was carried out using different route of synthesis and characterized by different techniques of spectroscopy.

Keywords: Citric acid; metal-organic framework; powder X- ray diffraction; luminescence; stability.

INTRODUCTION

Metal-organic frameworks comes under the category of coordination polymers with porous crystalline nature. These framework can be easily upgraded by several metals having different properties. These complexes shows properties like exceptionally large surface area, tunable structure, high porosity, variable pore dimensions .¹⁻⁵ The mixed metal oxides such as hollow ZnO-NiO hybrid microspheres fabricated by the annealing of Zinc-Nickel-Citrate in air constitute the most promising candidates as anode material due to their excellent electrochemical properties, replacing the traditional graphite anodes in lithium ion batteries used in devices such as electric vehicles.

EXPERIMENTAL

Materials and Physical measurements

All the chemicals used were commercially available analytical grade and used as obtained without further purification.

Synthesis of complex 1: Complex 1 was synthesized by dissolving 10mmol each of NiSO₄.6H₂O and ZnSO₄.7H₂O in 20 mL of double distilled water. Lime juice was squeezed from fresh fruit and strained. 20 mL of fresh lime juice was added to the solution of NiSO₄.6H₂O and ZnSO₄.7H₂O. The resultant mixture was heated to 30-40 °C under stirring for 30 minutes and stirring continued for another four hours. The pH of the reaction mixture was between 3 and 4. The mixture was left undisturbed at room temperature. The bluish green crystals of the complex 1 separated out in 58% yield after 48 hours and subsequently re-crystallized from distilled water.

Synthesis of complex 2: Complex 2 was synthesized by dissolving 10mmol each of CuSO₄.5H₂O and FeSO₄.7H₂O in 20 mL of double distilled water. The same procedure was followed as reported for complex 1. Yellow green crystals in 42% yield were obtained after the solution being kept undisturbed for ten days.

Synthesis of complex 3: Complex 3 was synthesized by dissolving 10mmol each of CuSO₄.5H₂O, FeSO₄.7H₂O and NiSO₄.6H₂O in 20 mL of double distilled water. The same procedure was followed as reported for complex 1. Dark green crystals in 60% yield were obtained after the solution being kept undisturbed for four days.

Synthesis of complex 4: Complex 4 was synthesized by the same procedure as adopted for complexes 1, 2 and 3 by mixing a solution of 10mmol each of CuSO₄.5H₂O, FeSO₄.7H₂O, NiSO₄.6H₂O and ZnSO₄.7H₂O in 20 mL of double distilled water with 20 mL of fresh squeezed and strained lime juice. Bluish green crystals were obtained in 54% yield after four days.

RESULTS AND DISCUSSION

All four complexes have been characterized by Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, Energy Dispersive Spectroscopy, Fluorescence spectroscopy and Powder X - ray diffraction techniques. The crystal structure of these complexes could not be established by single crystal X-ray diffraction technique probably due to overlapping of reflections caused by their large unit cells.⁶The stability of these complexes has been established by their Thermogravimetric analysis.

Fourier Transform Infrared spectroscopy of the multi-metal citrate complexes

The Fourier Transform Infrared spectroscopy of the multi-metal citrate complexes synthesized by hydrothermal technique, in KBr indicates the presence of vibrationally active carboxylate group. The FTIR spectra of the complexes exhibit both symmetric and anti-symmetric stretching vibrations of the carboxylate groups present in the coordinated citrate ligand. A strong band between 1630 cm^{-1} and 1620.5 cm^{-1} is assigned to anti-symmetric stretching vibrations while the one between 1401.2 cm^{-1} and 1384.0 cm^{-1} is due to symmetric stretching vibrations of the carboxylate groups of citrate ligand in the complexes.⁷ The difference between the anti-symmetric and symmetric stretching vibrations being greater than 200 cm^{-1} suggests that the carboxylate groups of citrate ligand in these complexes are coordinated to metal ions in a mono dentate fashion.⁸ A peak at 1726.5 cm^{-1} in complex **1** reveals that a fraction of the hydrogen atoms of carboxylate groups of citric acid remain bound while others are replaced by metal atoms forming multi-metal citrate complexes.⁹ A similar peak at 1726.7 cm^{-1} and 1724.2 cm^{-1} was also observed in complexes when synthesized using commercially available citric acid.³⁰ A peak around 1100 cm^{-1} in all complexes can be assigned to C-O being coordinated to metal cations.³¹ A weak band between 575.5 cm^{-1} and 573.0 cm^{-1} in these complexes can be attributed to the in plane vibration of O-C-O group. A vibrational band around 980 cm^{-1} appears due to C-C skeletal bond of citric acid moiety. The characteristic vibrational bands of alcoholic hydroxyl group of citric acid at 3450 , 1290 , 1265 , 1165 , 1125 , 1060 , 925 , 890 and 820 cm^{-1} are absent in the FTIR spectra of the prepared complexes. In-plane and out-of-plane O-H bending vibrational bands of carboxylic acid at 1430 cm^{-1} and 930 cm^{-1} also disappear in these complexes. The hydroxyl group of citrate ligand is thus coordinated as shown by Hedwig *et al.* through potentiometric and spectroscopic study for the synthesis of Ni^{2+} complex with citric acid in aqueous solution in the pH range of 3-6. The removal of proton from the hydroxyl group of citric acid depends upon the nature of metal ion bound to citric acid, with Cu bound to citric acid tetraionised Cit^{4-} is formed at pH 4. A broad band between 3732.2 cm^{-1} and 3200 cm^{-1} in these complexes is assigned to hydrogen bonded hydroxyl group of coordinated water, lying between the tetrahedral and octahedral sheets in the complexes. Further two vibrational bands between 765.2 cm^{-1} - 750.7 cm^{-1} and 635.9 cm^{-1} - 615.0 cm^{-1} due to rocking $\nu(\text{H}_2\text{O})$ and wagging $\nu(\text{H}_2\text{O})$ vibrations of water confirm the presence of coordinated water molecules in these complexes. Absorption band at 3154.8 cm^{-1} in complex **1** is assigned to symmetric -OH stretching mode associated to tetrahedral coordinated water molecules. Based on their Fourier transform infrared spectroscopy, a layered structure similar to the one reported in the literature for metal carboxylates is thus proposed for the multi-metal citrate complexes synthesized from lime juice in the present research. The infra-red spectra of complexes **1-4**.

Absorption and fluorescence spectroscopy

The electronic spectra and fluorescence spectra of the multi-metal citrate complexes **1-4** were recorded in water at room temperature. The excitation spectra were recorded from 350 to 600 nm to monitor the transition between the metal 3d orbitals. Each complex shows one absorption line at 392 nm. The crystal-field splitting of the 3d orbital was not observed in the complexes because of the large coordination number. Emission spectra were recorded for **1-4** upon excitation at 310 nm and emission was observed in between 400-422 nm, which corresponds to excitation into the lowest energy d-level of metal.

CONCLUSIONS

The multi-metal citrate complexes synthesized through green synthetic pathways using lime juice squeezed from a fresh fruit as the source of citric acid, are well defined crystalline solids with cubic geometry. These complexes exhibit an extraordinary high thermal stability and possess a highly stable rigid supramolecular structure due to extensive hydrogen bonding between the layers. The devised method has the merits of being a simple one pot synthesis and being environmentally benign as the use of harmful organic solvent such as DEF and DMF has completely been avoided. The extraction of citric acid from citrus fruit or its artificial synthesis, which itself is a time consuming process has been eliminated in the present synthesis. The adopted method is thus appreciably economical in terms of time and energy. The complexes thus prepared may reveal the potential applications in hydrogen storage for mobile applications as a green automobile fuel due to vacant metal sites associated with a combination of metal ions in their structure, as an optical material and in bio-medical field due to their photo luminescent properties.

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