HYDROTHERMAL SYNTHESIS AND CHARACTERISATION OF AMINE-TEMPLATED METAL PHOSPHATE FRAMEWORK

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ABSTRACT

Two coordination polymers \( [\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{M}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2 \) (\( \text{M} = \text{Ni} \) for compound I and \( \text{M} = \text{Zn} \) for compound II) incorporating ethylammonium-4-aminobenzoate, were hydrothermally synthesized (autogenous pressure for 5 days) at 105°C. The Scanning Electron Micrographs revealed a greenish rectangular block for the Ni(II) complex and a colourless square plate for the Zn(II) complex. The complexes were characterised by IR-spectroscopy and the Infrared spectra of the two compounds exhibited similar essential features. The Spectra clearly showed the presence of co-ordinated water and terminal –NH\(_2\). The broad band at 3914 cm\(^{-1}\) (I) and 3926 – 3760 cm\(^{-1}\) (II) is due to the presence of water molecule in the structure. The bands at 3542 - 3401 cm\(^{-1}\) (I) and 3434 cm\(^{-1}\) are associated with stretching vibration of ν(N-H\(_2\)). The strong absorption bands at 1108 - 1014 cm\(^{-1}\) (I) and 1108 – 1018 cm\(^{-1}\) (II) are associated with the asymmetric stretching vibration of ν(P=O) groups, whereas those at 936 - 629 cm\(^{-1}\) (I) and 934 – 718 cm\(^{-1}\) (II) correspond to its bending mode. The complexes were thermally stable up to 300°C, after which the organic components starts decomposing. The solubility test in a wide spectrum of solvents (at room temperature) showed that the complexes were insoluble in water, ethanol, DMF and DMSO.

KEYWORDS: Hydrothermal synthesis, metal phosphates, p-aminobenzoic acid, ethylacetoacetate, ethylammonium-4-aminobenzoate.

INTRODUCTION

One of the major areas of materials science is the development of solid state materials with extended structures that have empty spaces between their components, such as porous (Rowell and Yaghi, 2004), layered (Logar et al., 2005), or one-, two-, or three-dimensional compounds (Chen et al., 2008). The presence of pores, inter-layer or inter-chain spaces allows for many applications of these materials. A metal-organic framework (MOF) is composed of two major components: a metal ion or cluster of metal ions and an organic molecule called a linker. The organic units are typically mono-, di-, tri-, or tetravalent ligands (Czaja, Trukhan and Muller, 2009). Transition metal ions are often used as versatile connectors in the construction of MOFs. The first row transition metal ions such as Zn\(^{2+}\), Co\(^{2+}\), Cd\(^{2+}\), Fe\(^{2+}\) are especially commonly used (Ayi, Choudhury and Rao, 2005; Natarajan et al., 2006). Some alkaline metal ions (Ayi et al., 2011), alkaline earth metal ions (Murugavel et al., 2000) and rare earth metal ions (Clearfield and Demadis, 2012) have also been employed as metal nodes for constructing MOF structures.

The important characteristics of metal connectors are the number and orientation of their building sites (coordination numbers and coordination geometries). Depending on the metal and its oxidation state, coordination numbers can range from 2 to 7, giving rise to various geometries such as linear, T- or Y-shaped, square-planar, tetrahedral, square pyramidal, octahedral etc, which play an important role in directing the MOF structures (Kitagawa, Kitaura and Noro, 2004). The ligands used in the construction of coordination polymers have to bridge between metal ions. This requires usually multidentate ligands with two or more donor atoms. Such bridging ligands are called di-, tri-, tetratopic depending on the number of donor atoms. Of special importance are rigid bridging ligands since they allow for a certain control of the steric consequences in the assembly process (Halper et al., 2006).

Hydrothermal synthesis is currently one of the principal methods of synthesis for the preparation of new inorganic materials. It involves the heating of solid and liquid reagents with a suitable solvent (usually water) in a sealed vessel called autoclave at temperature above the boiling point of the liquid and up to 250°C and requires a long reaction time (days to weeks).

This paper reports hydrothermal synthesis and spectral characterisation of two metal phosphates incorporating ethylammonium ion.

EXPERIMENTAL

Synthesis of Ethyl ammonium bis(4-carboxyphenyl) amino Ni(II) dihydrogen phosphate

\[ [\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2 \] – I

The resultant mixture with molar composition 3C\(_2\)H\(_3\)NH\(_2\) + 2NH\(_2\)C\(_6\)H\(_4\)COOH + 3H\(_3\)PO\(_4\) + 3C\(_6\)H\(_4\)COCH\(_2\)CO\(_2\)C\(_3\)H\(_5\) + 278H\(_2\)O + 3NiCl\(_2\)6H\(_2\)O

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Procedure
In the synthesis of compound I, 1.785g of NiCl₂.6H₂O was dissolved in 5ml of distilled water and poured into 50ml beaker. To the solution, 0.5ml of H₃PO₄ was added under effective stirring for 7 minutes before 1ml of ethylacetocateate, 0.5ml of C₂H₅NH₂ and 0.685g of p-aminoanbenzoic acid were added and stirred for 30 minutes for complete homogeneity. The resultant mixture with pH of 4 was sealed in a 37ml Teflon lined stainless steel autoclave and kept at 105°C for 5 days. The greenish crystals obtained were washed, filtered and dried at ambient temperature. The synthesized compound was characterized by melting point, solubility in different solvents and infrared spectroscopy.

Synthesis of Ethyl ammonium bis(4-carboxyphenyl) amino Zn(II) dihydrogen phosphate

\[\text{[CH₃CH₂NH₃]₂Zn₃(NH₃C₆H₄CO₂)₂(HPO}_4\text{)₄(H}_2\text{O)}_2\text{ – II}\]

Composition of reaction
2ZnO + 3C₂H₅NH₂ + 2NH₃C₆H₄COOH + 3H₃PO₄ + 3HCl + 22H₂O

Procedure
In the synthesis of compound II, 0.367g of ZnO was dispersed in 8ml of distilled water in a 50ml beaker. 0.6ml of conc. HCl was added to the solution as a mineralizing agent and the mixture was stirred for 7 minutes. To the mixture, 0.3ml of H₃PO₄ was added under effective stirring for 7 minutes before 0.3ml of C₂H₅NH₂ and 0.411g of p-aminoanbenzoic acid was added and stirred for 30 minutes for complete homogeneity. The resultant mixture with pH of 4 was sealed in a 37ml Teflon lined stainless steel autoclave and kept at 105°C for 5 days. The colourless single crystals obtained was washed, filtered and dried at ambient temperature. The synthesized compound was characterized by melting point, solubility in different solvents and infrared spectroscopy.

Characterization
Infrared spectroscopy (IR)
The Fourier Transform Infrared (FTIR) spectra of the compounds under investigation were recorded between 4000 – 350cm⁻¹ on Perkin Elmer FTIR spectrophotometer. The compounds were prepared on KBr disc at the Multidisciplinary Central Research Laboratory, University of Ibadan.

Table 1: Infrared Vibrational Frequencies for the Compounds I and II
(All measurements are in cm⁻¹)

| Complexes                                                                 | v(H₂O) | v(-N-H) | v(-COO) | v(P-O) | δ(P-O) | v(N-M) | v(M-N) | v(M-O) |
|--------------------------------------------------------------------------|--------|---------|---------|--------|--------|--------|--------|--------|
| [CH₃CH₂NH₃]₂Ni₃(NH₃C₆H₄CO₂)₂(HPO}_4\text{)₄(H}_2\text{O)}_2\text{ – I} | 3914   | 3401    | 1647    | 1108   | 936    | 2377   | 569    | 410    |
| [CH₃CH₂NH₃]₂Zn₃(NH₃C₆H₄CO₂)₂(HPO}_4\text{)₄(H}_2\text{O)}_2\text{ – II} | 3926   | 3434    | 1644    | 1108   | 934    | 2377   | 606    | 435     |

Infrared spectroscopy of Ethyl ammonium bis(4-carboxyphenyl) amino Ni(II) dihydrogen phosphate

\[\text{[CH₃CH₂NH₃]₂Ni₃(NH₃C₆H₄CO₂)₂(HPO}_4\text{)₄(H}_2\text{O)}_2\text{ – I}}\]
and
\[\text{[CH₃CH₂NH₃]₂Zn₃(NH₃C₆H₄CO₂)₂(HPO}_4\text{)₄(H}_2\text{O)}_2\text{ – II}}\]

The infrared spectra of the complexes were recorded in the range of 4000 – 350cm⁻¹. The infrared spectrum showed the various vibrational modes expected for protonated amine, water molecule, metal-oxygen and metal-nitrogen bonds. The broad band at 3914cm⁻¹(I) and 3926cm⁻¹(II) is due to the presence of water molecule in the structure (Coates, 2000). The bands at 3542 and 3401cm⁻¹(I) and 3434cm⁻¹(II) are

Melting point determination
The melting points of the compounds were measured using melting point apparatus (SMP3, Biocote) and capillary tube. The capillary tube was sealed at one end and the sample was introduced through the open end of the tube. The samples in the tubes were inserted into the melting point instrument and the temperature at which the substances melted was noted.

pH determination
The pH of the reaction medium was measured using pH paper.

Solubility determination
The solubility test of compound I and II were determined in water, ethanol, dimethylformamide (DMF) and dimethylsulphoxide (DMSO) at room temperature.

Elemental Composition
The elemental compositions of compounds I and II were obtained from the proposed structures. The percentage yields of the compounds were low, and as such, there were not enough samples for XRF analysis.

RESULTS AND DISCUSSIONS

The Ni(II) I, and Zn(II) II: phosphates incorporating ethylammonium-4-aminobenzoate, were hydrothermally synthesized (autogeneous pressure for 5 days) at 105°C. A pH value of 4 was maintained for the reaction mixtures in each case, and this resulted in good quality crystals and high yield.

The physical properties for the two compounds showed that the two compounds were thermally stable up to 300°C, after which the organic components starts decomposing. The elemental compositions for the two complexes were calculated based on the proposed structures. The solubility test in a wide spectrum of solvents (at room temperature) showed that the two compounds were insoluble in water, ethanol, DMF and DMSO.

The scanning electron micrographs of compounds I and II are presented in Fig. 1 and Fig. 2 respectively. The scale bar is about 50µm. The SEM images revealed a greenish rectangular block for compound I and colourless square plate for compound II.
associated with stretching vibration of NH$_2$ (Silverstein, Bassler and Morrill, 1981) and the band at 1647 cm$^{-1}$ (I) and 1644 cm$^{-1}$ (II) is attributed to the stretching vibration of COO group (Dong et al., 2011) indicating the involvement of oxygen atom of carboxyl group in bonding with the metal ion. The absorption band at 2371 cm$^{-1}$ (I) and 2377 cm$^{-1}$ (II) indicates that the Nitrogen atom of amino-group was coordinating to the metal (Badawi et al., 2007). The strong absorption bands at 1108 and 1014 cm$^{-1}$ are associated with the asymmetric stretching vibration of $\nu$(PO) groups whereas those at 936 and 629 cm$^{-1}$ (I) and 934 cm$^{-1}$ and 718 cm$^{-1}$ (II) correspond to its bending mode (Ayi, 2006). The band at 569 cm$^{-1}$ (I) and 606 cm$^{-1}$ (II) is due to metal-nitrogen vibrations while the one at 410 cm$^{-1}$ (I) and 435 cm$^{-1}$ (II) is due to metal-oxygen vibrations.

### Table 2: Percentage Yield and Elemental Composition of compounds I and II

| Compounds | % Yield | Elemental compositions (%) | Metal Ion | P | C | H | N | O |
|-----------|---------|---------------------------|-----------|---|---|---|---|---|
| [CH$_3$CH$_2$NH$_3$]$_2$Ni$_3$(NH$_3$C$_6$H$_4$CO$_2$)$_2$(HPO$_4$)$_4$(H$_2$O)$_2$ | 25.92 | Ni = 18.31 | 12.89 | 22.45 | 3.95 | 5.82 | 36.59 |
| [CH$_3$CH$_2$NH$_3$]$_2$Zn$_3$(NH$_3$C$_6$H$_4$CO$_2$)$_2$(HPO$_4$)$_4$(H$_2$O)$_2$ | 39.21 | Zn = 20.00 | 12.63 | 22.00 | 3.87 | 5.76 | 35.84 |

Table 2 shows the percentage yield and elemental compositions (obtained from the proposed structures) of the compounds I and II.

**Fig. 1:** SEM Image of [CH$_3$CH$_2$NH$_3$]$_2$Ni$_3$(NH$_3$C$_6$H$_4$CO$_2$)$_2$(HPO$_4$)$_4$(H$_2$O)$_2$

**Fig. 2:** SEM Image of [CH$_3$CH$_2$NH$_3$]$_2$Zn$_3$(NH$_3$C$_6$H$_4$CO$_2$)$_2$(HPO$_4$)$_4$(H$_2$O)$_2$
Fig. 3: Infrared Spectrum of \( \text{[CH}_3\text{CH}_2\text{NH}_3\text{]}_2\text{Ni[NN(CH}_3\text{)C}_6\text{H}_4\text{CO}_2\text{]}_2\text{HPO}_4\text{]}_2\text{H}_2\text{O} \).
Fig. 4: Infrared Spectrum of [CH$_3$CH$_2$NH$_3$]$_2$Zn$_6$(NH$_3$C$_6$H$_4$CO$_2$)(HPO$_4$)$_2$(H$_2$O)$_2$. 
Fig. 5: Proposed structure of $[\text{CH}_3\text{CH}_2\text{NH}_3]^2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)^2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$

Fig. 6: Proposed structure of $[\text{CH}_3\text{CH}_2\text{NH}_3]^2\text{Zn}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)^2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$
CONCLUSIONS

Using hydrothermal method, two amine-templated metal phosphate frameworks have been synthesized. The IR spectra clearly showed the presence of water molecules in the complexes and terminals NH$_2$ which could be used as linkers to form a network of different topologies. Also, the complexes were insoluble in water, ethanol, DMF and DMSO and thermally stable at 300°C. This shows that the complexes could retain their structures at extreme conditions and this is one of the properties of a MOF material.

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