

HYDROTHERMAL SYNTHESIS AND CHARACTERISATION OF AMINE-TEMPLATED METAL PHOSPHATE FRAMEWORK

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ABSTRACT

Two coordination polymers $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{M}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$ (M = Ni for compound I and M = Zn for compound II) incorporating ethylammonium-4-aminobenzoate, were hydrothermally synthesized (autogeneous 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 $-\text{NH}_3^+$. The broad band at 3914cm^{-1} (I) and $3926 - 3760\text{cm}^{-1}$ (II) is due to the presence of water molecule in the structure. The bands at $3542 - 3401\text{cm}^{-1}$ (I) and 3434cm^{-1} are associated with stretching vibration of $\nu(\text{-NH}_2)$. The strong absorption bands at $1108 - 1014\text{cm}^{-1}$ (I) and $1108 - 1018\text{cm}^{-1}$ (II) are associated with the asymmetric stretching vibration of $\nu(\text{PO}_4)$ groups, whereas those at $936 - 629\text{cm}^{-1}$ (I) and $934 - 718\text{cm}^{-1}$ (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-, tetrapic 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 $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2 - \text{I}$

The resultant mixture with molar composition $3\text{C}_2\text{H}_5\text{NH}_2 + 2\text{NH}_2\text{C}_6\text{H}_4\text{COOH} + 3\text{H}_3\text{PO}_4 + 3\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5 + 278\text{H}_2\text{O} + 3\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

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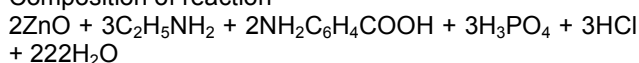
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Procedure

In the synthesis of compound I, 1.785g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 5ml of distilled water and poured into 50ml beaker. To the solution, 0.5ml of H_3PO_4 was added under effective stirring for 7 minutes before 1ml of ethylacetate, 0.5ml of $\text{C}_2\text{H}_5\text{NH}_2$ and 0.685g of p-aminobenzoic 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 $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Zn}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2 - \text{II}$

Composition of reaction



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 H_3PO_4 was added under effective stirring for 7 minutes before 0.3ml of $\text{C}_2\text{H}_5\text{NH}_2$ and 0.411g of p-aminobenzoic acid was added and stirred for 30 minutes for complete homogeneity. The resultant mixture with pH of 4 was sealed in a 13ml 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 $4000 - 350\text{cm}^{-1}$ on Perkin Elmer FTIR spectrophotometer. The compounds were prepared on KBr disc at the Multidisciplinary Central Research Laboratory, University of Ibadan.

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 $50\mu\text{m}$. The SEM images revealed a greenish rectangular block for compound I and colourless square plate for compound II.

Table 1: Infrared Vibrational Frequencies for the Compounds I and II (All measurements are in cm^{-1})

Complexes	$\nu(\text{H}_2\text{O})$	$\nu(-\text{N-H})$	$\nu(-\text{COO})$	$\nu(\text{P-O})$	$\delta(\text{P-O})$	$\nu(\text{N-M})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
$[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$	3914	3401	1647	1108	936	2371	569	410
$[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Zn}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$	3926	3434	1644	1108	934	2377	606	435

Infrared spectroscopy of Ethyl ammonium bis(4-carboxyphenyl) amino Ni(II) dihydrogen phosphate $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2 - \text{I}$ and Ethyl ammonium bis(4-carboxyphenyl) amino Zn(II) dihydrogen phosphate $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Zn}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2 - \text{II}$

The infrared spectra of the complexes were recorded in the range of $4000 - 350\text{cm}^{-1}$. 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

associated with stretching vibration of NH_2 (Silverstein, Bassler and Morrill, 1981) and the band at 1647cm^{-1} (I) and 1644cm^{-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 2371cm^{-1} (I) and 2377cm^{-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 1014cm^{-1} are associated with the asymmetric stretching vibration of $\nu(\text{PO})$ groups whereas those at 936 and 629cm^{-1} (I) and 934cm^{-1} and 718cm^{-1} (II) correspond to its bending mode (Ayi, 2006). The band at 569cm^{-1} (I) and 606cm^{-1} (II) is due to metal-nitrogen vibrations while the one at 410cm^{-1} (I) and 435cm^{-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
$[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$	25.92	Ni = 18.31	12.89	22.45	3.95	5.82	36.59
$[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Zn}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$	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.

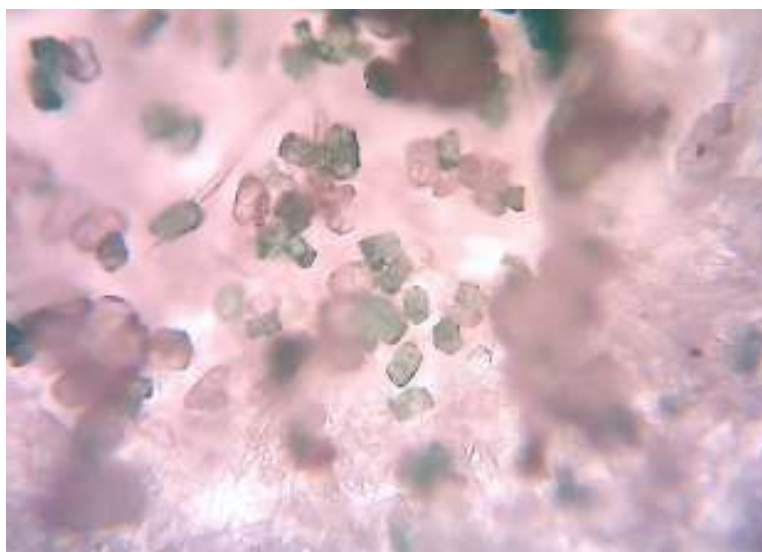


Fig. 1: SEM Image of $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$



Fig. 2: SEM Image of $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Zn}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$

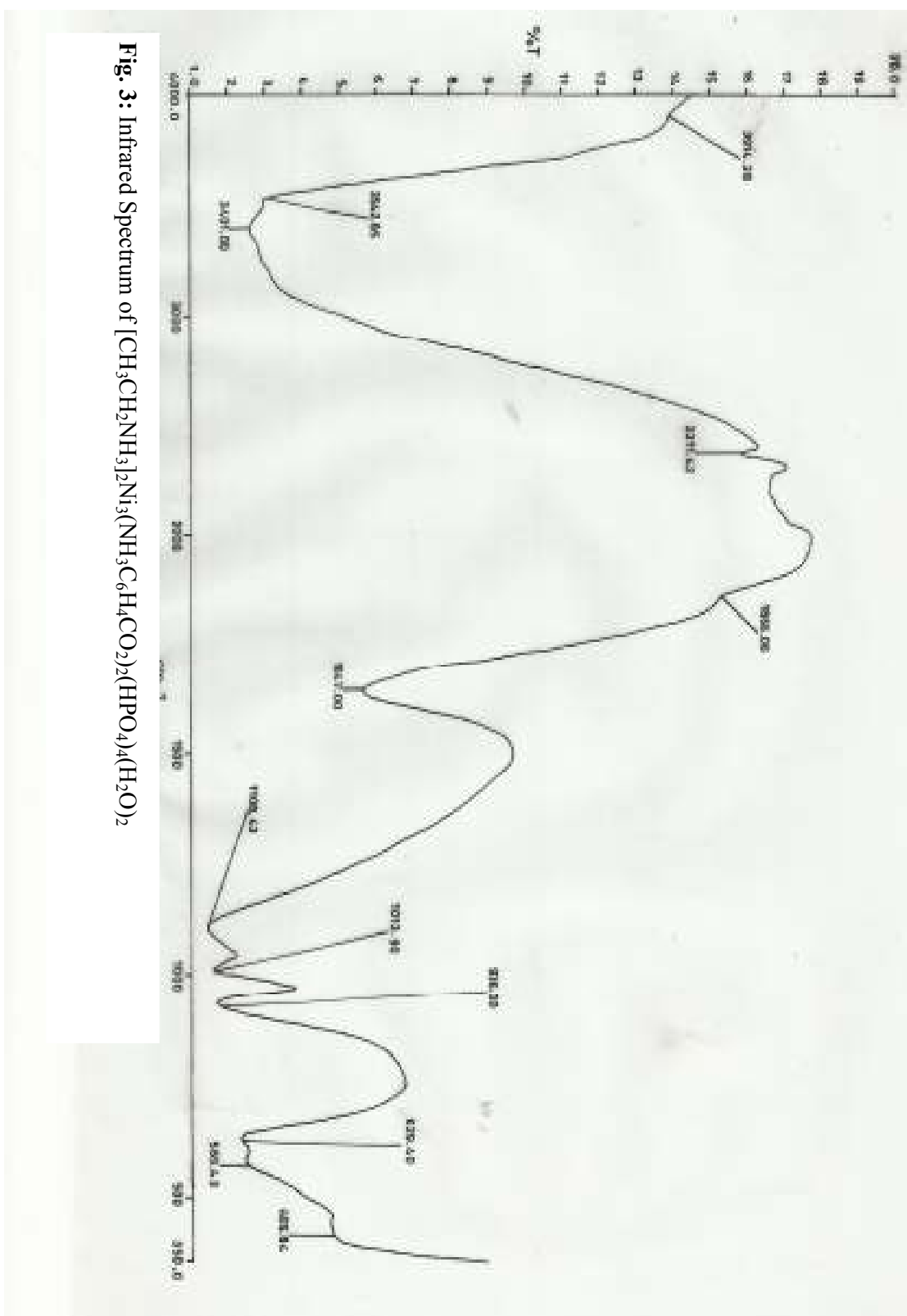


Fig. 3: Infrared Spectrum of $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$

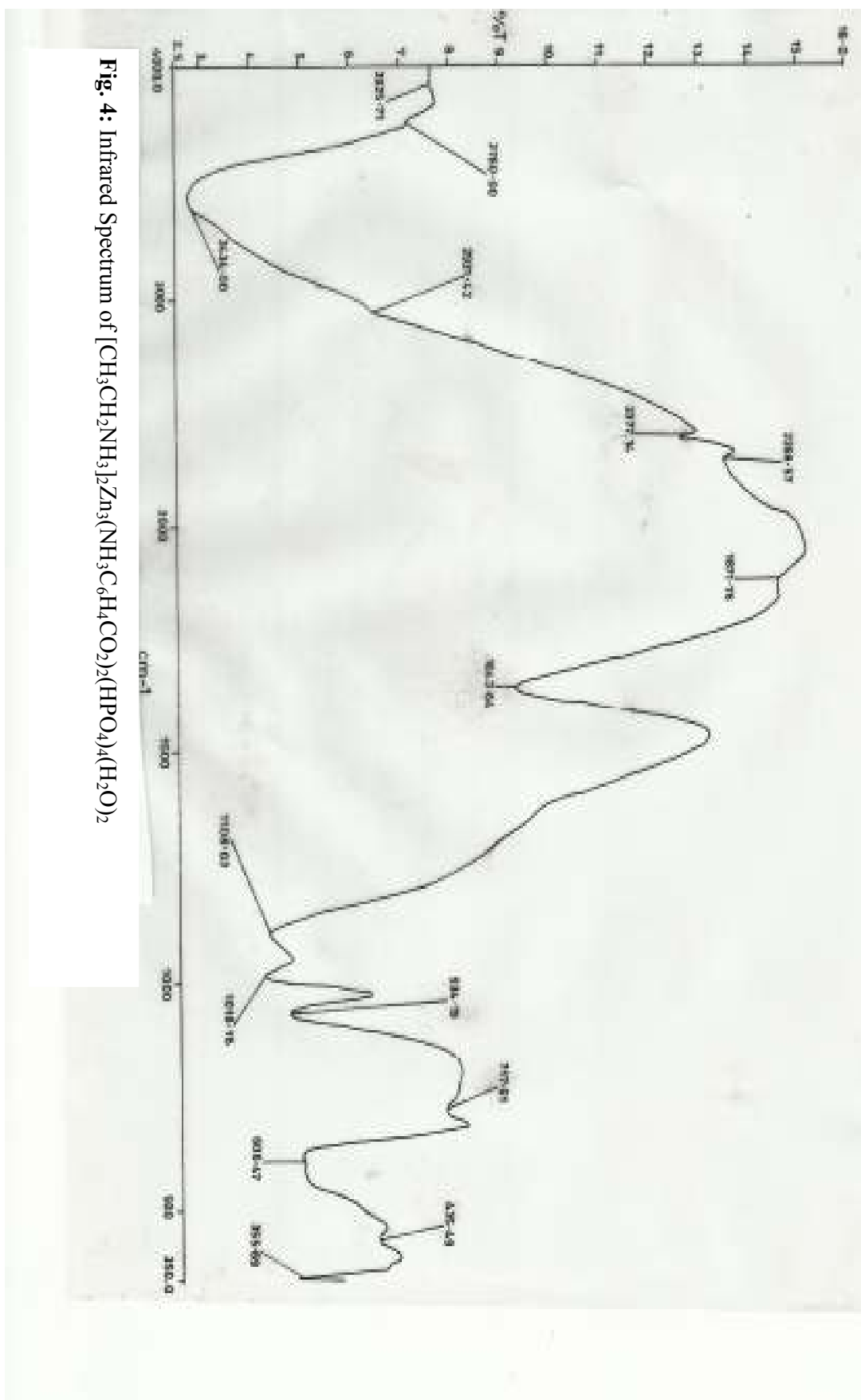


Fig. 4: Infrared Spectrum of $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Zn}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$

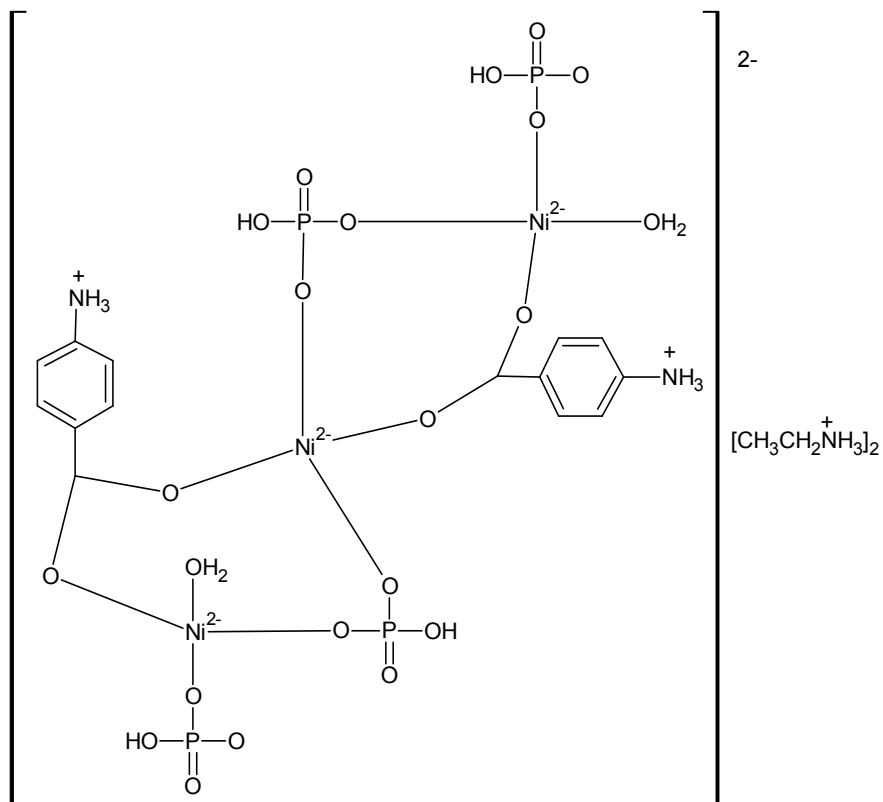


Fig. 5: Proposed structure of $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Ni}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$

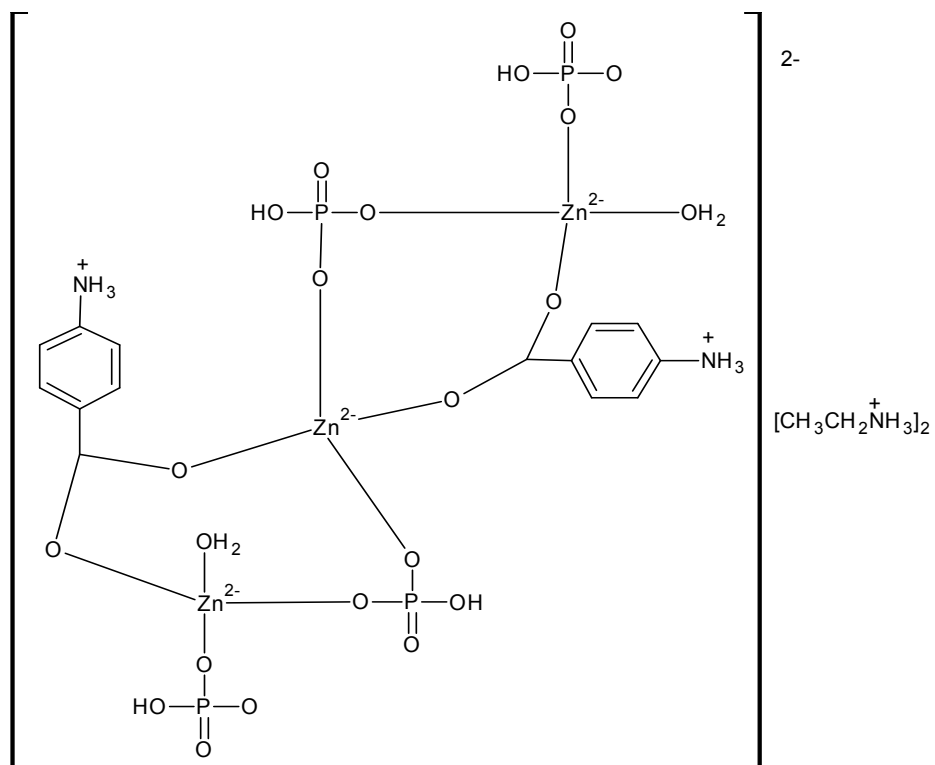


Fig. 6: Proposed structure of $[\text{CH}_3\text{CH}_2\text{NH}_3]_2\text{Zn}_3(\text{NH}_3\text{C}_6\text{H}_4\text{CO}_2)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$

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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