



Journal Homepage: [-www.journalijar.com](http://www.journalijar.com)

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI: 10.21474/IJAR01/19886

DOI URL: <http://dx.doi.org/10.21474/IJAR01/19886>



RESEARCH ARTICLE

CHARACTERIZATION OF NEW MIXED AND HYBRID INORGANIC-ORGANIC MATERIALS BASED ON PHOSPHATES BY INFRARED SPECTROSCOPY

Dame Seye^{1,3}, Lamine Yaffa³, Momath Lo², Assane Toure³, Diadioly Gassama³ and Cheikh Abdoul Khadir Diop³

1. Département Physique - Chimie, UFR Science et Technologie, Université Iba Der THIAM de Thiès, Sénégal.
2. Laboratoire de Chimie Physique Organique et d'Analyses Environnementales, Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal.
3. Laboratoire de Chimie Minérale et Analytique (LA.CH.MIA), Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal.

Manuscript Info

Manuscript History

Received: 10 September 2024

Final Accepted: 19 October 2024

Published: November 2024

Key words:-

Phosphato, Monomer, Supramolecular Architecture Infinite Band, Infinite Layer Double Metallic Component Structures

Abstract

In this work we synthesized three inorganic-organic hybrid organic phosphate compounds of current interest due to their fascinating architectures and potential applications in supramolecular chemistry engineering. These compounds were characterized mainly by elementary analysis and IR spectroscopies. They were synthesized from a reaction carried out in a common organic solvent between the monocyclohexylamine phosphate and SnBu_2Cl_2 ; $\text{Y}(\text{CH}_3\text{CO}_2)_3$ or D_yCl_3 . Structures involving complex anions have been proposed. Structures involving complex anions have been proposed. In phosphate compounds, the anion is present in the form of HPO_4^{2-} and H_2PO_4^- . The structures obtained are of the infinite type, monomer or with double metallic components. Phosphato compounds with rare earths gave new monomeric or double metallic component structures. The nine coordination (9) found in one of the metallic components is a coordination that we find with rare earths. The structural study of its complexes has shown that these coordination complexes can present promising catalytic activity for the oxidation and degradation of compounds such as methylene blue.

Copyright, IJAR, 2024., All rights reserved.

Introduction:-

The discovery of a new class of porous crystalline solids in the early 2000s constituted a major advance in materials chemistry [1]. The assembly of organic ligands and inorganic clusters allowed the formation of three-dimensional networks called MOFs (Metal-Organic Frameworks). These are porous compounds made up of an organic framework linked, via strong and/or weak coordination bonds, to metallic base units [2-4]. These materials differ from each other, on the one hand, by their constitution which gives the skeletons formed distinct physical properties and on the other hand, by the pore sizes which define their storage and gas separation capacities. MOFs have great structural flexibility and offer the possibility of adjusting the pore size as well as the chemical properties based on the choice of precursors. The diversity of metal centers and ligands gives access to a panel of structures each having intrinsic physicochemical properties which allow them to consider more advanced industrial applications such as:

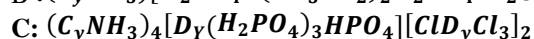
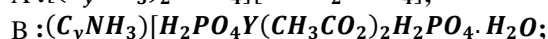
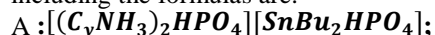
Corresponding Author:- Dame Seye

Address:- Université Iba Der THIAM de Thiès, Sénégal.

catalysis, magnetism, selective adsorption of gases, filtration, ion exchange, energy storage, agriculture and biology [5-16]. Among the hybrid compounds explored, organic phosphates formed following the reaction with inorganic oxyacids such as orthophosphoric acid (H_3PO_4) and organic amines and amides are of particular interest.

In fact, the classification panel of these applications potentially depends on the distinct routes of development of these systems (at low or high temperature) and on the different types of matrices that can be synthesized (simple, mixed or hybrid). Inorganic-organic hybrid compounds are of current interest due to their fascinating architectures and potential applications in crystal engineering and supramolecular chemistry [17–18]. These organic compounds of monohydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate ($H_2PO_4^-$), constitute a class of materials with multiple practical and potential uses in various fields such as biomolecular sciences, catalysis, development of liquid crystal materials, ferroelectrics, nonlinear and supramolecular optics [19-21].

In this dynamic, we prepared the diacid salt between monocyclohexylamine and phosphoric acid ($CyNH_3$)[H_2PO_4] we reacted with $SnBu_2Cl_2$, $Y(CH_3(CO_2))_3$ and $DyCl_3$ and were able to obtain three compounds including the formulas are:



Experimental section: -

Procedure for synthesis of monocyclohexylamine phosphate: $(C_yNH_3)[H_2PO_4]$

The phosphoric acid salt was recovered in the form of a white powder after evaporation in an oven at 60°C by reacting phosphoric acid and monocyclohexylamine in the ratio 1:1 in water according to the following reaction:



Procedure for synthesis of $[(C_yNH_3)_2HPO_4][SnBu_2HPO_4]$

A mixture of $CyNH_3H_2PO_4$ (1.6 mmol) with $SnBu_2Cl_2$ (1.6 mmol) in 20 mL of ethanol solution gives a clear solution. A white powder was recovered after a week of slow evaporation.

Procedure for synthesis of $(C_yNH_3)[H_2PO_4Y(CH_3CO_2)_2H_2PO_4 \cdot H_2O]$;

A mixture of $CyNH_3H_2PO_4$ (1.6 mmol) with $Y(CH_3CO_2)_2$ (1.6 mmol) in 20 mL of ethanol solution gives a clear solution. A white powder was recovered after a week of slow evaporation.

Procedure for synthesis of $(C_yNH_3)_4[D_Y(H_2PO_4)_3HPO_4][ClD_YCl_3]_2$

A mixture of $CyNH_3H_2PO_4$ (1.6 mmol) with $DyCl_3$ (1.6 mmol) in 20 mL of ethanol solution gives a clear solution. A white powder was recovered after a week of slow evaporation.

The solutions obtained were stirred for approximately two hours (2h) in order to obtain stable compounds; we obtained either precipitates or clear solutions. The precipitates are filtered and the powders are dried in an oven at 60°C. The crystals obtained are recovered after a few days.

The chemicals were purchased from Aldrich Company-Germany- without any further purification.

The elemental analyses have been obtained from the Analytical Laboratory-Padua University, Padua, Italy. The IR spectra were performed at Padua University and University de Bourgogne Dijon-France with a PerkinElmer 180 spectrometer as Nujol mulls using CsI as optical windows.

We report, in Table 1 which follows, for the complexes obtained, and the results of the elemental analyses.

Table 1:- Results of the elemental analyses of compounds A-C.

Compound	Chemical formula	Elemental analysis [%]		
		C	H	N

		Calc.	Found	Calc.	Found	Calc.	Found
A	$[(C_yNH_3)_2HPO_4][SnBu_2HPO_4]$	31,12	32,06	6,00	6,45	0,6	0,65
B	$(C_yNH_3)[H_2PO_4Y(CH_3CO_2)_2H_2PO_4 \cdot H_2O]$	4,49	4,34	1,86	1,68	0,96	0,92
C	$(C_yNH_3)_4[D_Y(H_2PO_4)_3HPO_4][Cl_3]_2$	31,12	31,06	4,13	4,45	0,6	0,65

Infrared spectra were recorded on a Bruker Vector 22 spectrometer equipped with a Specac Golden Gate™ ATR device. Infrared data are given in cm^{-1} [IR abbreviations: (vs) very strong, (s) strong, (m) medium, (vw) very weak]. Elemental analyses were performed at the “Institut de Chimie Moléculaire”, University of Bourgundy, Dijon (France). All chemicals were purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and used without any further purification.

Results and Discussion:-

Table 2 shows the allocations of the main infrared bands(A– C).

Table 2:-Assignments of the main bands of the infrared spectra(A–C).

Complexes	vPO4	vNH3	δNH_3	$\nu SnBu_2$	$\nu_{as}SnBu_2$
A	1106(m)	2930(m) 2880(m)	1603(s) 1517(m)	620(s)	684(s)
B	1119(m)	2945(m) 2855(m)	1559(m)
C	1198(m)	2998(F) 2865(F)	1656(m)

On all infrared spectra (A – C), we observe the antisymmetric valence vibration bands of the phosphate which appear on each spectrum in the form of a strong and broad band around 1100 cm^{-1} .

In the deformation vibration region of the phosphate ion, we observe two bands on the spectra of the compounds yttrium $(C_yNH_3)[H_2PO_4Y(CH_3CO_2)_2H_2PO_4 \cdot H_2O]$ (B) and dysprosium $(C_yNH_3)_4[D_Y(H_2PO_4)_3HPO_4][Cl_3]_2$ (C) while on the spectrum of $SnBu_2HPO_4$ (A), we no longer observe two bands.

We thus attribute on the spectrum of the compound $[(C_yNH_3)_2HPO_4][SnBu_2HPO_4]$ (A), the band at 684 cm^{-1} to $\nu(SnBu_2)$ and one of the shoulders around 620 cm^{-1} to $\nu_{as}(SnBu_2)$. The weakness of the $\nu_{as}(SnBu_2)$ band allows us to say that the $SnBu_2$ skeleton is almost linear.

- The structure proposed for $[(C_yNH_3)_2HPO_4][SnBu_2HPO_4]$, is an infinite chain with a bichelating hydrogen phosphate, the environment around the tin being trans octahedral (Fig. 1a).
- The OH group is involved in chelation through its oxygen atom and the hydrogen atom through which the chain associates with the neighboring chain to give a three-dimensional supramolecular architecture (Fig. 1b).
- For the yttrium complex $(C_yNH_3)[H_2PO_4Y(CH_3CO_2)_2H_2PO_4 \cdot H_2O]$, the proposed structure consists of a Y^{3+} ion coordinated by a water molecule then monochelated by the $H_2PO_4^-$ and acetate ions, which gives yttrium has a coordination of nine (9) (Fig.3).

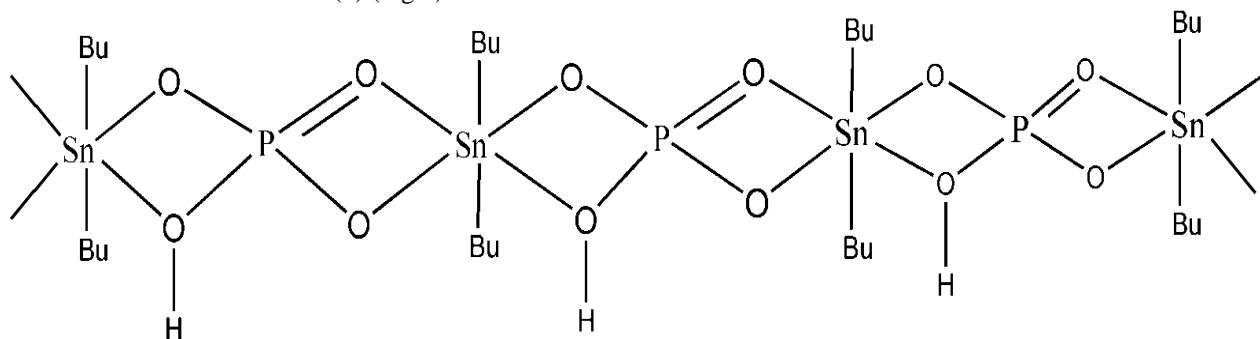


Figure 1a: infinite band of $[(C_yNH_3)_2HPO_4][SnBu_2HPO_4]$

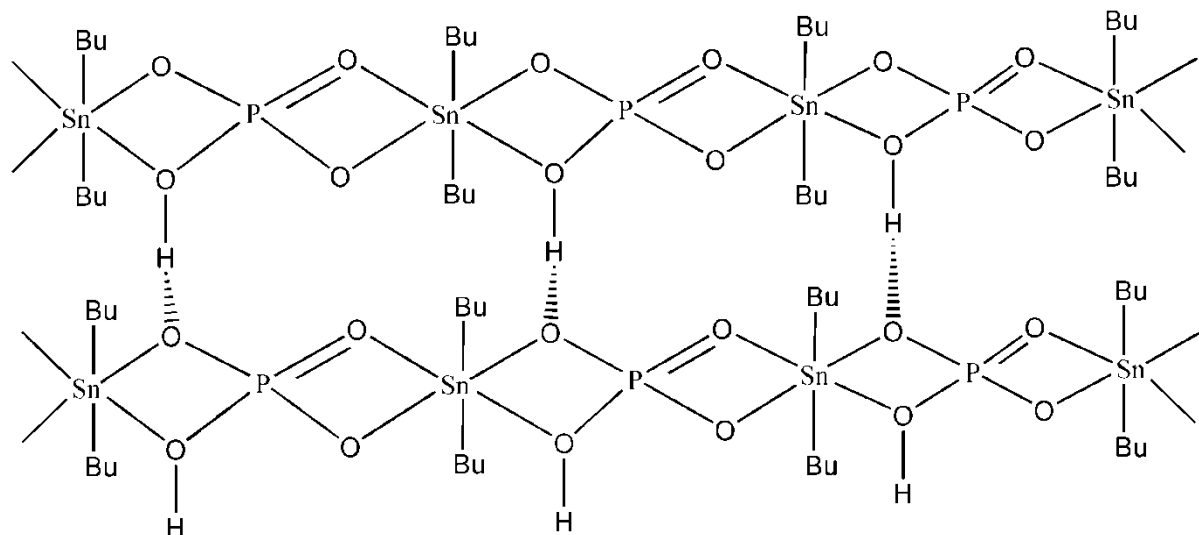


Figure1b:- Infinite layer of $[(C_yNH_3)_2HPO_4][SnBu_2HPO_4]$.

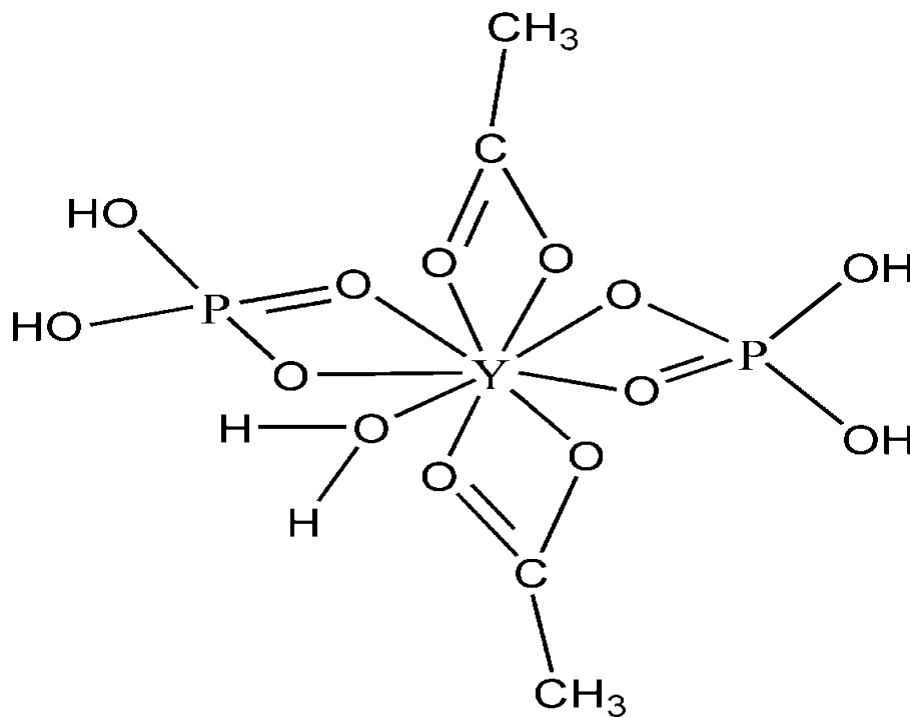


Figure2:- Structure of the anion of the compound $(C_yNH_3)[H_2PO_4Y(CH_3CO_2)_2H_2PO_4 \cdot H_2O]$

The dysprosium complex $[CyNH_3PO_4H_2]_3[DyHPO_4ClDyCl_3]_2$ is similar to the two dysprosium compounds already obtained with phenylsulfonate and maleate. Its structure has a double metallic component (Fig. 3).

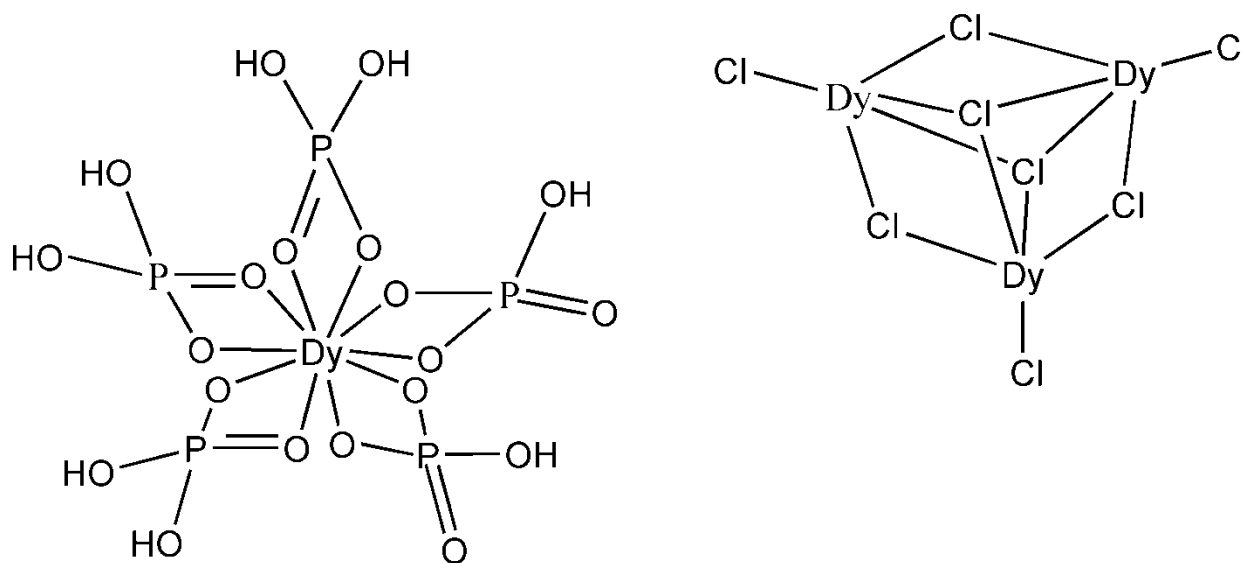


Figure3:- Structure of the anion of the compound $(C_yNH_3)_4[Dy(H_2PO_4)_3HPO_4][ClDyCl_3]_2$

Conclusion:-

In phosphate compounds, the anion is present in the form of HPO_4^{2-} and $H_2PO_4^-$. The structures obtained are of the infinite, monomeric or double metallic component type. Phosphato compounds with rare earths have given new monomeric or double metallic component structures. The study of the structural types showed very high coordination which can present promising catalytic activity for the oxidation and degradation of compounds like methylene blue.

As a precautionary measure, we intend to carry out the crystallization of these compounds in suitable solvents to possibly

1. Perform antioxidant activity tests
2. Evaluate the catalytic activity of systems prepared on other types of organic dyes.
3. Establish electrochemical corrosion tests for the hybrid phases of phosphite and sulfate in order to evaluate their corrosion inhibition power.
4. Study the energy storage capacity of open-frame phosphate systems and measure the electrochemical performance of the lithiated vanado-phosphate system to evaluate its insertion behavior among host-guest molecule networks.

Acknowledgments:-

Dakar group thanks are gratefully acknowledged Dr Laurent Plasseraud (University de Bourgogne Dijon-France) for performing elemental analyses and for the equipment support.

References:-

- [1] Hailian, Li., Eddaoudi, M., O'Keeffe, M., Yaghi, O.M., Nature, 1999, 402, 276-279.
- [2] Brenden, F.A., Hoskins, B.F., Robson, R., Journal of the American Chemical Society, 1991, 113, 3606-3607.
- [3] Kitagawa, S., Kitaura, R., Noro, S., Angewandte Chemie International Edition, 2004, 43, 2334-2375.
- [4] Batten, S. R., Champness, N. R., Chen, X.-M., Garcia-Martinez, J., Kitagawa, S., Öhrström, L., O'Keeffe, M., Paik Suh, M., Reedijk, J., Pure and Applied Chemistry, 2013, 85, 1715-1724.
- [5] Jing, X., Zhang, L., Gong, S., Li, G., Bi, M., Huo, Q., Liu, Y., Microporous and Mesoporous Materials., 2008, 116, 101-107.
- [6] Mandal, S., Green, M A., Natarajan, S., Current Science, 2005, 89, 1899-1903.
- [7] Wang, Q., Tang, k-Z., Liu, W-S., Tang, Y., Tan, M-Y., Journal of Solid-State Chemistry, 2009, 182, 3118-3124.
- [8] Fernandez, S., Pizarro, J L., Mesa, J L., Lezama, L., Arriortua, M I, Olazcuaga, R., Rojo, T., Inorganic Chemistry, 2001, 40, 3476-3483.
- [9] Zhan, C-H., Feng, Y-L., Journal of Solid-State Chemistry, 2010, 183, 1226-1230.
- [10] Qui, L-G., Gu, L-N., Hu, G., Zhang, L-D., Journal of Solid-State Chemistry, 2009, 182, 502-508.
- [11] Zhu, Y-P., Ren, T-Z., Yuan, Z-Y., Catalysis Science & Technology., 2015, 5, 4258-4279.

- [12] Cheng, C-C., Chang, W.K., Chiang, R.K., Wang, S.L., Journal of Solid-State Chemistry, 2010, 183, 304-309.
- [13] Kim, M.K., Lee, D.W., Ok, M.K., Journal of Solid-State Chemistry, 2010, 183, 2406-2410.
- [14] Mandal, S., Natarajan, S., Journal of Solid-State Chemistry, 2005, 178, 2376-2382.
- [15] Khandar, A.A., Klein, A., Bakhtiari, A., Mahjoub, A.R., Pohl, R.W.H., Journal of SolidState Chemistry, 2011, 184, 379-386.
- [16] Nettleman, J.H., Supkowski, R.M., LaDuca, R.L., Journal of Solid-State Chemistry, 2010, 183, 291-303.
- [17] Davies, A. G., Milledge, H. J., Puxley, .D. C. et Smith, P.J., (1970). Chem. Soc., A, 2862
- [18] Tordjman, I., Boudjada A., Guitel, J.-C. et Masse, R., (1978). Acta. Cryst., B34, 3723- 3725.
- [19] Zhou, K. , Fan, X., Li, Y., Zhang, C. et Jin, T. (2018). Acta. Cryst., F74, 236-244.
- [20] Ittyachan, R., Ahigna, M. S. et Jagan, R. Acta. Cryst. (2016). E72, 530-533.
- [21] Vavra. M., Potočník. I., Marhefková. M., Boča. R. et Dlháň. L'ubor. (2012). Polyhedron., 48(1), 227-236.