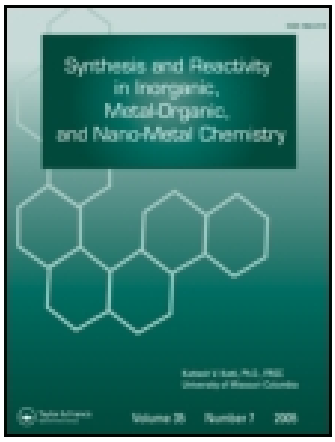

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Preparation, Characterization, and Theoretical Study of Nanoparticles of Triphenylphosphonium Tetrachloroaluminate(III) $[P(C_6H_5)_3H]^+[AlCl_4]^-$

Shahriar Ghammamy [a]

[a] Department of Chemistry, Faculty of Science , Imam Khomeini International University , Qazvin , I. R. Iran

Accepted author version posted online: 04 Dec 2012.Published online: 26 Feb 2013.

To cite this article: Shahriar Ghammamy (2013) Preparation, Characterization, and Theoretical Study of Nanoparticles of Triphenylphosphonium Tetrachloroaluminate(III) $[P(C_6H_5)_3H]^+[AlCl_4]^-$, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:4, 390-394, DOI: 10.1080/15533174.2012.740737

To link to this article: http://dx.doi.org/10.1080/15533174.2012.740737

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:390–394, 2013

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2012.740737

Taylor & Francis
Taylor & Francis Group

Preparation, Characterization, and Theoretical Study of Nanoparticles of Triphenylphosphonium Tetrachloroaluminate(III) $[P(C_6H_5)_3H]^+[AlCl_4]^-$

Shahriar Ghammamy
Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, I. R. Iran

Triphenylphosphonium tetrachloroaluminate(III) $[P(C_6H_5)_3H]^+[AlCl_4]^-$, TPPTCA, nanoparticle was synthesized by using triphenylphosphonium chloride addition to $AlCl_3$ in the presence of surfactant. The product was characterized by spectroscopic and analytical methods such as ^{31}P-NMR, FT-IR, XRD, SEM, and CHN. Theoretical calculations were used for the structural optimization of this compound. The structure of compound has been calculated and optimized by the density functional theory (DFT) based method at B3LYP/6–311G levels of theory, using the Gaussian 03 package of programs. The comparison between theory and experiment is made. On the base of the application of scanning electron microscopy is showed about 54 nm particle sizes.

Keywords characterization, nanoparticles, $[P(C_6H_5)_3H]^+[AlCl_4]^-$, preparation, X-ray diffraction

INTRODUCTION

Transparent ceramics have recently acquired a high degree of interest and notoriety. Basic applications include lasers and cutting tools, transparent armor windows, night vision devices (NVD), and nose cones for heat seeking missiles. Currently available infrared (IR) transparent materials typically exhibit a trade-off between optical performance and mechanical strength. For example, sapphire (crystalline alumina) is very strong, but lacks full transparency throughout the 3–5 μm mid-IR range. Yttria is fully transparent from 3–5 μm, but lacks sufficient strength, hardness, and thermal shock resistance for high-performance aerospace applications. Not surprisingly, a combination of these two materials in the form of the yttria-alumina garnet (YAG) has proven to be one of the top performers in the field. It has been shown fairly recently that laser elements (amplifiers, switches, ion hosts) made from fine-grained ceramic nanomaterials produced by the low-temperature sintering of high-purity nanoparticles and powders can be produced at a relatively low cost. These components are free of internal stress or intrinsic birefringence, and allow relatively large doping levels or optimized custom designed doping profiles. This highlights the use of ceramic nanomaterials as being particularly important for high-energy laser elements and applications. A new class of alumina compounds, specifically nanoparticles and nanocompounds, was investigated. Another side the phosphorus chemistry has been developed in two recent years as one of the most important branches of science.[1] Many biological processes such as energy transfer, bone synthesis, amino acid synthesis, and metabolism require phosphorus and phosphate esters.[2,3] For the hydrolysis of RNA and phospholipids, cyclic phosphate esters are of biological significance.[4] In recent years[5–11] have synthesized a series of aluminates using the sonochemical method, but in the present work, $[P(C_6H_5)_3H]^+[AlCl_4]^-$ nanoparticles was synthesized by a simple method with the starting materials $P(C_6H_5)_3$, HCl, $AlCl_3$, and a surfactant trimercaptopropionic acid (MPA), respectively. In addition to the spectroscopic techniques such as ^{31}P-NMR, FT-IR, powder X-ray diffraction (XRD), and scanning electron microscopy (SEM) theoretical calculations were used for this compound by using B3LYP method with the 6–311G* basis set. The molecular geometry and vibrational frequencies, energies, molecular orbitals, and ground state were calculated.

EXPERIMENTAL

Materials and Instruments

Triphenylphosphine, hydrogen chloride (hydrochloric acid), aluminum trichloride, trimercaptopropionic acid, and other all materials were prepared from Merck Company (Darmstadt, Tehran agent, Germany) and used as received without further treatment. Solvents that were used for reactions purified and dried by standard procedures. Infrared spectra were recorded as KBr disks on a Bruker Tensor model 420 spectrophotometer (Qazuin, IKI University, Iran). XRD diffractions were studied with X-ray diffraction device Siemens D500 Diffractometer

Received 25 January 2012; accepted 13 October 2012.
The authors wish to express their warm thanks to Dr. Gh. RezaeiBehbahani for his valuable discussions. This work was supported by Islamic Azad University, Takestan Branch.
Address correspondence to Shahriar Ghammamy, Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, I. R. Iran. E-mail: shghamami@yahoo.com

model (Tehran University, Iran). In all phases of Cu-Kα radiation with a wavelength of 1.5404 Å was used. The morphological studies by SEM were performed. NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer (Tarbiat Modares University, Iran). All the chemical shifts are quoted in ppm using the high frequency positive convention. The percent composition of elements was obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran (Iran).

Preparation of Triphenylphosphonium Chloride (TPPCl)

To a 500 mL flask equipped with a magnetic stirrer was added hydrogen chloride (100 mmol) and triphenylphosphine (100 mmol, 26.2 g) at 40–50°C. The reaction mixture was stirred for 20 min, cooled to room temperature, and filtered. The filtered solid was washed with ether (2 × 50 ml), crystallized, and identified.

Synthesis of Triphenylphosphonium Tetrachloroaluminate(III), $P(C_6H_5)_3H]^+[AlCl_4]^-$

Triphenylphosphonium tetrachloroaluminate (III), $P(C_6H_5)_3H]^+[AlCl_4]^-$ was prepared by two methods. First, to aluminum trichloride (0.6 g, 4.48 mmol) in acetonitrile (200 mL) was added at room temperature a solution of triphenylphosphonium chloride (1.33 g, 4.48 mmol) in acetonitrile (100 mL). Trimercaptopropionic acid in excess amount (2.06 g) was added as surfactant. After 50 min, a white precipitate formed, and diethyl ether (100 mL) was added to the mixture, cooled, and filtered. The solid product was washed with ether and hexane. Second, triphenylphosphine (0.6 g, 2.28 mmol) was dissolved in acetonitrile (10 mL) and stirred for 0.5 h. (0.08 g, 2.18 mmol) HCl (37%) was added to this mixture and stirring continued for 5 min. Trimercaptopropionic acid (MPA; 0.72 g) was added to the materials and stirring continued for another 5 min. $AlCl_3$ (0.3 g, 2.24 mmol) in acetonitrile added to this mixture as the last of starting materials and stirring was continued for 4 h to precipitate a white solid. Precipitate was filtered and washed with ether and hexane. M.P.: 83–84°; Anal. Calcd. for $P(C_6H_5)_3H]^+[AlCl_4]^-$: C, 50.03; H, 3.73. Found: C, 50.97; H, 3.82. IR (KBr) (cm^{-1}): 3412, 1636, 1477, 1437, 973, 613 cm^{-1}. ^{31}P NMR (135 MHz, $CDCl_3$): $\delta = 31.42$ ppm (Figures 1 and 2).

RESULTS AND DISCUSSION

Preparation

The salt/Lewis acid adducts usually result in either ionic liquids or crystalline materials with low melting points. Salts containing large organic cations, such as butylpyridinium chloride or 1,3-dialkylimidazolium chloride, and interact with $AlCl_3$ to form ionically conducting liquids at room temperature.[12–15] Solid $AlCl_3$ has a melting temperature at 193°C. Upon melting, $AlCl_3$ consists primarily of discrete $Al2Cl_6$ dimers, and appears as a molecular liquid with high vapor pressure. It is well known[16] that the melting point of $AlCl_3$ can be lowered upon

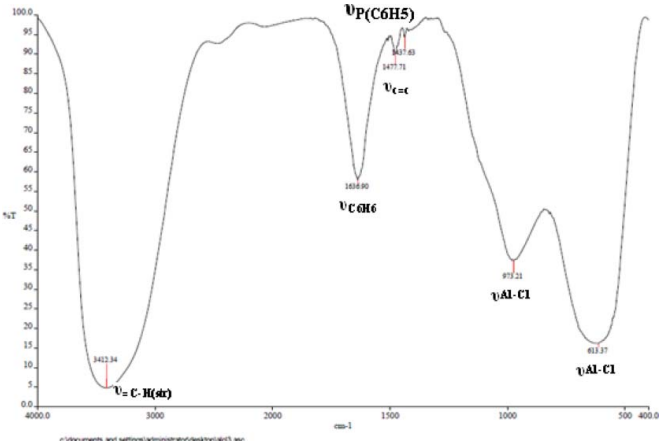

FIG. 1. IR spectrum of $[P(C_6H_5)_3H]^+[AlCl_4]^-$ (color figure available online).

mixing with RCl (R denotes such as an alkali metal or organic cation), which is believed to originate from the Lewis acid–base interactions of $AlCl_3$ with RCl and the formation of large-sized complex anions, such as $AlCl_4^-$, $Al_2Cl_7^-$, and $Al_3Cl_{10}^-$. From the binary phase diagram, it is found that a low-lying eutectic occurs in the 2:1 composition of $AlCl_3$–RCl. Melting temperature of the eutectic is well below that of the $AlCl_3$, representing the minimum liquid us temperature throughout the entire system.

In this letter, we report the synthesis, spectroscopic characterization, and density functional theory calculations of a compound by using B3LYP method with the 6–311G* basis set. The molecular geometry and vibrational frequencies, energies, and molecular orbitals are calculated by using the B3LYP at 6–311G* method.

Triphenylphosphonium trichloroaluminate (TPPTCA) can be easily obtained by the addition of triphenylphosphonium chloride to an acetonitrile solution of aluminum trichloride. The

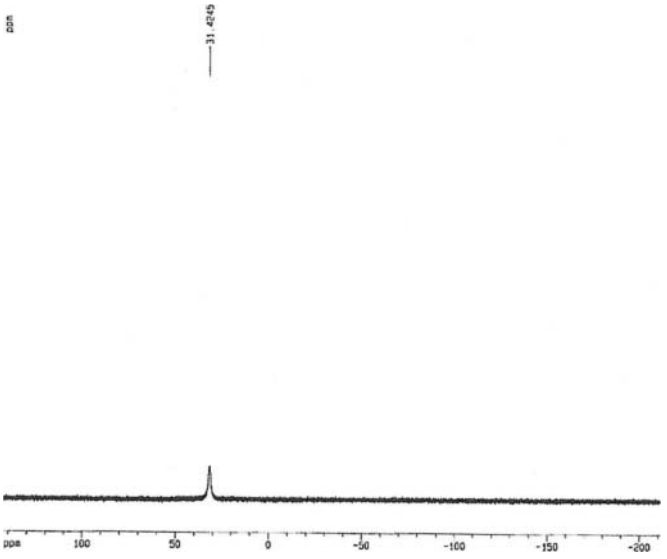

FIG. 2. ^{31}P-NMR Spectrum of $[P(C_6H_5)_3H]^+[AlCl_4]^-$.

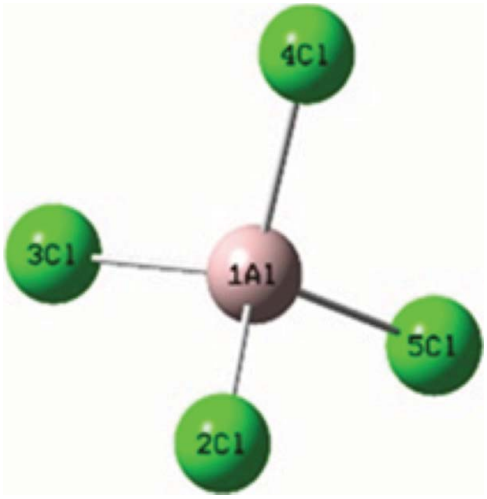

FIG. 3. Optimized structure of $[AlCl_4]^-$ anion (color figure available online).

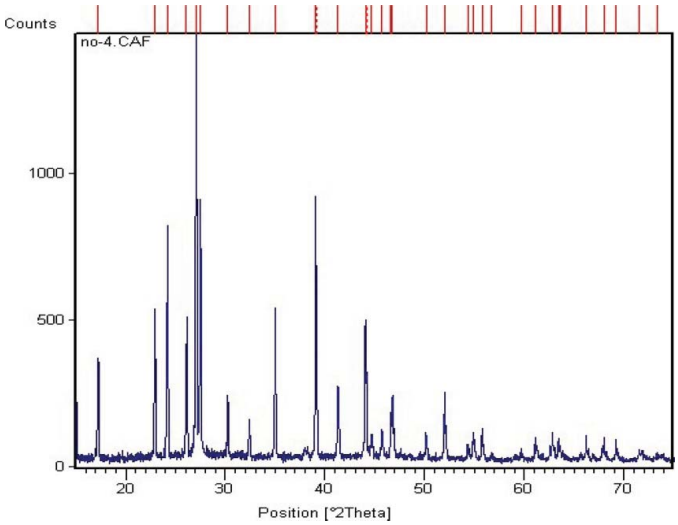

FIG. 5. XRD pattern of $[P(C_6H_5)_3H]^+[AlCl_4]^-$ (color figure available online).

advantages of the new method are the following: (a) there is no side product, (b) the reaction is quite fast, (c) mild conditions, and (d) the accompanied color change, which provides visual means for ascertaining the progress of reaction.

This paper describes some initial work on the characterization of nanoparticles investigated the processing of preparation a novel nanoparticle with formula $[P(C_6H_5)_3H]^+[AlCl_4]^-$. This goal was reached by reacting triphenylphosphonium chloride added to acetonitrile and $AlCl_3$ Then trimercaptopropionic acid was added to the starter materials. Reporting the synthesis of the TPPTCA shows that aluminate was useful for organic chemists, that is, the analog of the previous aluminate compounds.

The reported methods for their preparation involved non-mild or hard conditions such as high temperatures.

$$P(C_6H_5)_3 + HCl + AlCl_3 \longrightarrow [P(C_6H_5)_3H]^+[AlCl_4]^-$$

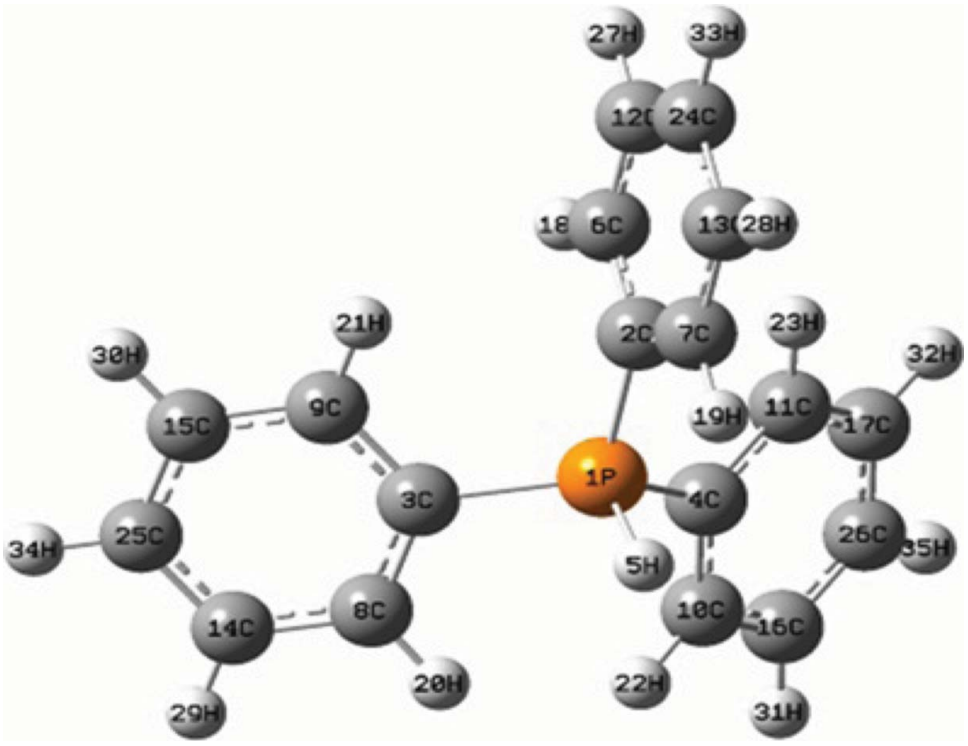

FIG. 4. Optimized structure of $[P(C_6H_5)_3H]^+$ cation (color figure available online).

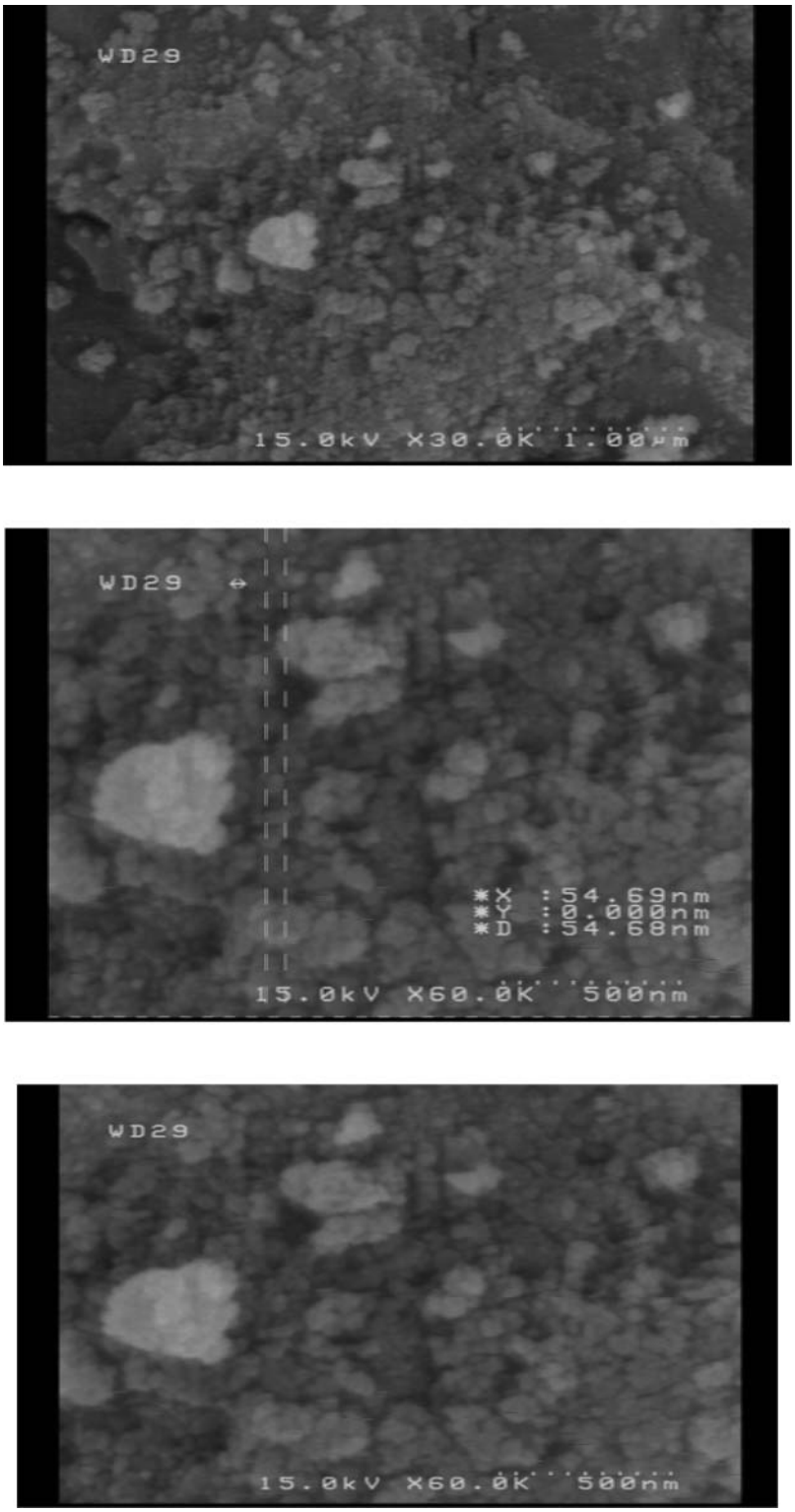

FIG. 6. SEM graphs of nano $[P(C_6H_5)_3H]^+[AlCl_4]^-$.

TABLE 1
Calculated and experimental frequencies of $[P(C_6H_5)_3H]^+[AlCl_4]^-$ (cm^{-1})

	$[P(C_6H_5)_3H]^+[AlCl_4]^-$	
	Expt.	B3LYP/6311G
$\upsilon_{P(C6H5)}$	1485	1477
υ_{C6H6}	1650	1638
υ = C-H(str)	3433	3412
υ c=c	1467	1437
$\upsilon_{Al\text{-}Cl}$	1000	973
$\upsilon_{Al\text{-}Cl}$	620	613

Ab Initio Calculations Method

All *ab initio* calculations were done by using the Gaussian-98 suite of programs.[17] The cations and anions are commonly assumed to be in a hypothetical gaseous free state and without any pre-assumed symmetry, but some calculations also involve better approximations to real systems. After the optimization procedures, giving geometry with a minimum energy, perhaps not a global one, the vibrational frequencies and intensities and the eigenvectors for the normal modes are calculated and displayed on a computer screen, to identify the dominating motions. Then the frequencies (wave numbers) have to be correlated with the results of the IR experiments. The calculated and experimental vibrational spectra are in more or less good agreement (Table 1). The wave number (frequency) scale is often calculated as slightly too high, due to the lack of good modeling of the orbitals and interactions with the surroundings. The structures of the optimized $[P(C_6H_5)_3H]^+[AlCl_4]^-$ in this product are depicted in (Figures 3 and 4) The Al atom in anion is coordinated by four Cl atoms as ligands in tetrahedral geometry.

XRD and SEM Data

XRD of TPPTCA shown in Figure 5. The particle size can be calculated. The size of the nano particles can be calculated from the Scherrer equation used for this purpose.

$$D = 0.9\ \lambda / B\ Cos\theta$$

In the previous equation D is particle diameter (Å), B is the width of the strongest peak at half height in radians, and θ is the angle at which the peak appears. XRD analysis shows that TPPTCA has nanosize about 50 nm and produced in nanoscale.

Currently, the fastest and most routine method of determining particle size is by photon-correlation spectroscopy or dynamic light scattering. Photon-correlation spectroscopy requires the viscosity of the medium to be known and determines the diameter of the particle by Brownian motion and light scattering properties. The results obtained by photon-correlation spectroscopy are usually verified by scanning or transmission electron microscopy. The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the electron-optical system that produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam. SEM pictures shows agglomeration of particles and multiform of texture. SEM shows the size of nanoparticles about 54 nm that confirm the predicted size range by XRD (Figure 6).

CONCLUSIONS

In this work, a novel aluminate compound with formula $[P(C_6H_5)_3H]^+[AlCl_4]^-$ was synthesized from the reaction of triphenylphosphonium with acetonitrile. The ^{31}PNMR spectrum of this compound indicates a signal at 31.42 ppm. The structure of compound has been calculated and optimized by the density functional theory (DFT) based method at B3LYP/6-311G levels of theory, using the Gaussian 03 package of programs. The comparison between theory and experiment is made. This compound was characterized by IR, XRD, and SEM techniques (Figures 1–6). The nanoform of this compound was synthesized and measured by FTIR, XRD, and SEM.

REFERENCES

1. Sengupta, S.K.; Pandey, O.P.; Rao, G.P.; Vishen, P. *Metal Based Drugs* **2002**, *8*, 293.
2. Suarez, P.; Dullius, J.E. L.; Einloft, S.; De Souza, R.R.; Dupont, J. *Inorg. Chim. Acta.* **1997**, *255*, 207–209.
3. Boon, J.A.; Levisky, J.L.; Pflug, L.; Wilkes, J.S. *J. Irg. Chem.* **1986**, *51*, 480–483.
4. Yanes, E.G.; Gratz, S.R.; Baldwin, M.J.; Robinson, S.E.; Stalcup, A.M. *Anal. Chem.* **2001**, *73*, 3838.
5. Lv, W.Z.; Luo, Z.K.; Yang, H. *Ultrason. Sonochem.* **2010**, *17*, 344.
6. Lv, W.Z.; Liu, B.; Qiu, Q. *J. Alloys Compd.* **2009**, *479*, 480.
7. Lv, W.Z.; Liu, B.; Luo, Z.K. *J. Alloys Compd.* **2008**, *465*, 261.
8. Lv, W.Z.; Luo, Z.K.; Liu, B. *Key Eng. Mater.* **2008**,*368*, 604.
9. Lv, W.Z.; Liu, B.; Luo, Z.K. *J. Mater. Sci. Eng.* **2007**, *25*, 686.
10. Lv, W.Z.; Luo, Z.K.; Zhang, P.X. *Inorg. Chem.* Ind. **2007**, *39*, 16.
11. Lv, W.Z.; Liu, B.; Wei, S.H. *J. Shenzhen Univ.* **2006**, *23*, 329.
12. Cooper, E.I.; Sullivan, E.J. M. Proceedings of the 8th International Symposium on Molten Salts, **1992**, 92–16, 386.
13. Chum, H.L.; Koch, V.R.; Miller, L.L.; Osteryoung, R.A. *J. Am. Chem. Soc.* **1975**, *97*, 264–267.
14. Wilkes, J.S.; Levisky, J.A.; Wilson, R.A.; Hussey, C.L. *Inorg. Chem.* **1982**, *21*, 1263–1264.
15. Lee, Y.; Price, D.L.; Curtiss, L.A.; Ratner, M.A.; Shriver, D.F. *J. Chem. Phys.* **2001**, *114*, 4591–4594.
16. Liu, C.; Angell, C.A. *Solid State Ionics* **1996**, *467*, 86–88.
17. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery, J.A. Jr.; Stratmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, A.D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelti, C.; Adamo, C.S.; Clifford, Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; MoroKuma, K.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslowski, J.; Ortiz, J.V.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P.M. W.; Johnson, B.; Chen, W.; Wong, M.W.; Andres, J.L.; Head-Gordon, M.; Replogle, E.S.; Pople, J.A. *GAUSSIAN 98 (Revision A. 3)*; Gaussian Inc., Pittsburgh, PA, **1998**.