Trans. Phenom. Nano Micro Scales, 3(2): 129-134, Summer – Autumn 2015
DOI: 10.7508/tpnms.2015.02.007

ORIGINAL RESEARCH PAPER

Synthesis and Characterization of a New Halomercurate Nanoparticles: Triphenylphosphonium Trichloromercurate (II) $[P(C_6H_5)_3H]^+[Hgcl_3]^-$

Sh. Ghamami[1,*], R. Ghahremani Gavineh Roudi[1], S. Kazem Zadeh Anari[1]
[1] *Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, I.R. Iran*

ARTICLE INFO.

Article history
Received 20 December 2014
Accepted 25 May 2015

Keywords
$[P(C_6H_5)_3H]^+[HgCl_3]^-$
Halomercurate
Nanoparticles
SEM
Synthesis
X-ray diffraction

Abstract

That particles are of less than 100nm in diameter called nano particles (NPS) and there are in the world naturally like volcanic activity. In the present investigation a new mixed halomercurate nano particle compound was synthesised and characterized. Triphenylphosphonium trichloromercorate (II) $[P(C_6H_5)_3H]^+[HgCl_3]^-$ nanoparticle was synthesi -zed by using triphenylphosphonium chloride reaction with $HgCl_2$, in the presence of trimercaptopropionic acid. This method is a simple and direct method. The product was characterized by spectroscopic and analytical methods such as ^{31}P-NMR, scanning electron microscopy (SEM), infrared spectroscopy (IR) and also size of nanoparticles were calculated by X-ray diffraction (XRD). Average particles size of nano is showed about 89.83 nm Theoretical calculations were applied 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 09 package of programs. Finally, the comparison between theory and experiments are done.

1. Introduction

That particles are of less than 100nm in diameter called nano particles (NPS) and there are in the world naturally like volcanic activity. Algaenanoparticles were examind for their size dependent physical and chemical properties [1]. Widely in the world many method have been applied to prepared the nano particles like a electrochemical reduction[2-3], sono chemical method[4], micro emulision method[5], heat evaporation[6,7], sol-gel[8], laser vaporization[9], hydrothermal[10], ionized beam deposition[11]. Nanoparticles are as bridge between bulk materials and atomic structures. Nano-scale physical properties depend on the particle size, but large-scale material properties are constant regardless of the particle size [12].

Mercury has attracted people from previous years, as a heavy liquid metal.

However, because of its toxicity, many application of mercury are being Useless. It is now mainly used in the chemical industry as catalysts. It is also used in some electrical switches and rectifiers. Main group elements have unique coordination preferences and

[*]Corresponding author
Email address: nanochemistry.inorganic@gmail.com

electronic properties, and as results present opportunities for the preparation of novel structures with new and interesting characteristics [1, 3, 5]. Mercury poisoning (also known as hydrargyria or mercurialism) is a disease caused by exposure to mercury or its compounds. Toxic effects include damage to the brain, kidney, and lungs [12]. Mercury poisoning can result in several diseases, including acrodynia (pink disease) [13], Hunter-Russell syndrome, and Minamata disease [14]. New class of mercury compounds specially nano particles and nano compounds were investigated.

In the other side the phosphorus chemistry has been developed in two recent years as one of the most important branches of science [15-16]. In this work, Triphenyl phosphonium trichloromercorate. $[P(C_6H_5)_3H]^+[HgCl_3]^-$ nanoparticles were synthesized by a simple method with the starting materials $P(C_6H_5)_3$, HCl, $HgCl_2$ and a surfactant that is trimercaptopropionic acid (MPA), respectively. In addition to the spectroscopic techniques such as ^{31}P-NMR, FT-IR, XRD, SEM theoretical calculations were used for this compound by using B3LYP method with the 6-311G* basis set and two methods were compared. The molecular geometry and vibrational frequencies, molecular, energies orbitals and ground state calculated. This compound can be used as mercury, phosphorous and halide scavengers and delivery systems

2. Experimental

2.1. Materials and Instruments

Triphenylphosphine, Hydrogen chloride (Hydro chloridric acid), mercuric chloride, trimercaptopropionic acid and other all materials were prepared from Merck Company 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. XRD diffractions were studied with X-ray diffraction device Siemens D500 Diffractometer model. In all phases of Cu-Kα radiation with a wavelength of 1.5404 Å was used.

The morphological studies by scanning electron microscopy (SEM) were performed. NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer. All the chemical shifts are quoted in ppm using the high frequency positive convention. The percent composition of elements was obtained from the Micro analytical Laboratories, Department of Chemistry, OIRC, Tehran.

2.2. preparation of Triphenylphosphonium chloride

To a 500 ml flask equipped with a magnetic stirrer was added hydrogen chloride (100 mmol) and triphenylphosphine (100 mmol, 26.2g) 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.

2.3. Triphenylphosphonium trichloromercorate (II) [P (C6H5)3H] + [HgCl3]-

Triphenylphosphonium trichloromercorate (II) $[P(C_6H_5)_3H]^+[HgCl_3]^-$, prepared by two methods:
First: To mercuric chloride (0.92 g, 3.38 mmol) in acetonitrile (200mL) was added at room temperature a solution of triphenylphosphonium chloride (1.00 g, 3.35 mmol) in acetonitrile (100 mL). Trimercaptopropionic acid in excess amount (2.06 g) was added as surfactant. After 50 min, a white precipitate formed, diethyl ether (100 mL) was added to the mixture, cooled and filtered. The solid product was washed with ether and hexane.

Second: Triphenylphosphine (0.44g, 1.67 mmol) was dissolved in acetonitrile (10 ml) and stirred for 0.5 h. (0.06 g, 1.64 mmol) HCl was added to this mixture and stirring continued for 5 minutes. Trimercaptopropionic acid (MPA), (1.84g) was added to the materials and stirring continued for another 5 minutes. $HgCl_2$ (0.46 g, 1.69 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. A fine white Precipitate was filtered and washed with ether and hexane. M.P.: 210-211°; Anal. Calc. for $[P(C_6H_5)_3H]^+[HgCl_3]^-$: Calculated C, 37.88; H, 2.80. Found: C, 37.97; H, 2.95. IR (KBr) (cm^{-1}): 3129, 1480, 1636, 1101, 750, 523, 505, 467 cm^{-1}. ^{31}P NMR (135 MHz, $CDCl_3$): δ= 23.28ppm.

3. Results and Discussion

3.1. Preparation

Mercury (II) chloride or mercuric chloride used as a treatment for syphilis, it is no longer used for medicinal purposes because it is highly toxic and

superior treatments have become available. Preparation of new mercuric compounds specially nano scale was demanded and interested this time.

Triphenylphosphonium trichloromercorate (II) (TPPTCM) can be easily obtained by the addition of triphenylphosphonium chloride to an acetonitrile solution of mercuric chloride.

The processing of preparation a novel nanoparticle with formula $[P(C_6H_5)_3H]^+[HgCl_3]^-$. This goal was happened by reacting triphenylphosphonium chloride added to acetonitrile and $HgCl_2$ then trimercaptopropionic acid was added to the starter materials. The reported methods for their preparation involved non-mild or hard conditions such as high temperatures.

$$P(C_6H_5)_3 + HCl + HgCl_2 \longrightarrow [P(C_6H_5)_3H]^+[HgCl_3]^-$$

This production method can be defined as a bottom-up production of nanoparticles in the liquid phase. By use of trimercaptopropionic acid that added to the starter materials, particle size, chemical composition, and surface and charge properties occurs mainly through controlled chemical reactions, and self-limiting self-assembly processes have evolved by controlling growth conditions.

In this paper, the synthesis, spectroscopic characterization, density functional theory
Calculation of a compound was reported 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.

3.2. 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 $[P(C_6H_5)_3H]^+[HgCl_3]^-$ in this product are depicted in (Figure 3-4) The Hg atom in anion is coordinated by three Cl atoms as ligands in trigonal geometry.

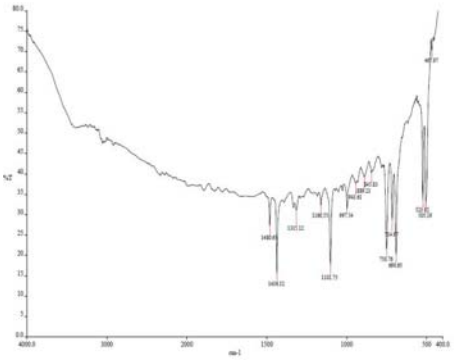

Fig. 1. IR spectrum of $[P(C_6H_5)_3H]^+[HgCl_3]^-$

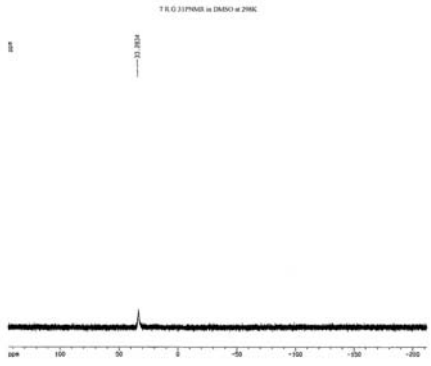

Fig. 2. ^{31}P-NMR Spectrum of $[P(C_6H_5)_3H]^+[HgCl_3]^-$

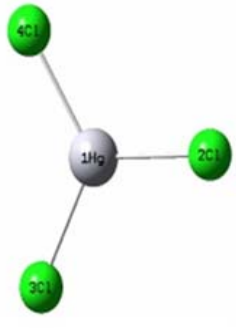

Fig. 3. Optimized structure of $[HgCl_3]^-$ anion

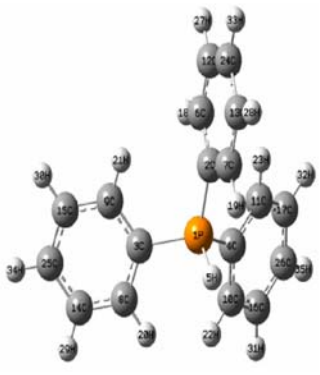

Fig. 4. Optimized structure of $[P(C_6H_5)_3H]^+$ cation

Table 1
Calculated and experimental frequencies of $[P(C_6H_5)_3H]^+[HgCl_3]^-$ (cm^{-1}).

$[P(C_6H_5)_3H]^+[HgCl_3]^-$		
Expt.		**B3LYP/6311G**
υ P-H	775	750
υ P(C6H5)	1493	1480
υ C6H6	1112	1101
υ =C-H(str)	3137	3129
υ c=c	1445	1436
υ =C-H	540	523
Hg-Cl	516	505
Hg-Cl	481	467

3.3. XRD and SEM Data

Powder X ray diffraction (XRD) of TPPTCM shown in Figure 5 The particle size can be calculated. The average particle size of the Sample was also calculated using the Debye–Scherrer formula from the full width at half maximum (FWHM) approximately 89.83nm.

$$D=0.9\,\lambda/\,B\,Cos\theta \qquad (1)$$

In the above equation D in terms of particle diameter Å, B corresponds to 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 (TPPTCM) has nano size about 83.8 nm and produced in nano scale. Smaller particles are expose to risk of aggregation of particles during storage and transportation of nanoparticle dispersion.

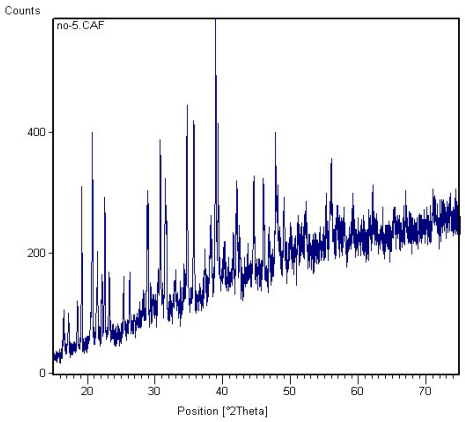

Fig. 5. XRD patent of $[P(C_6H_5)_3H]^+[HgCl_3]^-$

It is because always a effort to formulate nanoparticles with the smallest size possible but maximum stability.

photon-correlation spectroscopy or dynamic light scattering is the fastest and most routine method of determining particle size.

Photon-correlation spectroscopy needs the viscosity of the medium To be identified and determines the diameter of the particle with light scattering and Brownian motion properties needs the viscosity of the medium.

The results obtained by photon-correlation spectroscopy are usually confirmed by scanning or transmission electron microscopy. Scanning electron microscopy (SEM) of the sample was done in order to estimate the shape and surface morphology of the sample ,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 show nanoparticles were similar to Spherical shape with agglomeration of particles and multiform of texture. SEM shows the size of nanoparticles about 85-89 nm that confirm the predicted size range by XRD. (Figure 6).

The morphology of this nanoparticle as seen in SEM pictures is semi spherical. The morphologies sometimes are spontaneously as an effect of a modeling or directing agent present in the synthesis like miscellar emulsions or anodized alumina pores, or from the innate crystallographic growth patterns of the materials themselves.

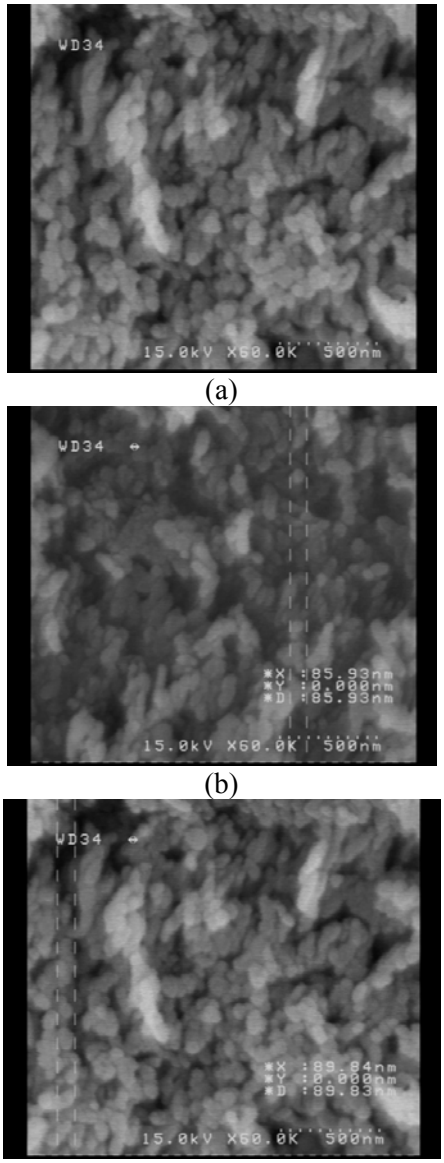

Fig. 6 . SEM graph of $[P(C_6H_5)_3H]^+[HgCl_3]^-$

Amorphous particles usually adopt a spherical shape (due to their microstructural isotropy) – whereas the shape of anisotropic microcrystalline whiskers corresponds to their particular crystal habit. At the end of the size range, nanoparticles are often referred to as clusters. Spheres, rods, fibers, and cups are just a few of the shapes that have been grown.

4. Conclusions

In this work, a novel mercurate compound with formula $[P(C_6H_5)_3H]^+[HgCl_3]^-$ was synthesized from the reaction of Triphenylphosphonium with acetonitrile. The ^{31}PNMR spectrum of this compound indicates a signal at δ= 23.28 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 FT-IR, XRD, and SEM techniques (Figure 1-6). The average particle size of the Sample was calculated using the X-ray diffraction. SEM images show that the particles were similar to Spherical shape with agglomeration of particles and average particles size of nano is showed about 89.83 nm

Acknowledgements

The authors wish to express their thanks to Dr. Shahriar Ghammamy for his valuable discussions. This work was supported by Imam Khomeini International University, Qazvin.

References

[1] C.B. Murray, C.R. Kagan, M.G. Bawendi, Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies, Ann Rev Mater Sci 30 (2000) 545-610.

[2] Y.C. Liu, L.H. Lin, New pathway for the synthesis of ultrafine silver nanoparticles from bulk silver substrates in aqueous solutions by sonoelectrochemical methods, Electrochem. Commun 6 (2004) 1163-1168.

[3] G. Sandmann, H. Dietz, W. Plieth, Preparation of silver nanoparticles on ITO surfaces by a double-pulse method, J. Electroanal. Chem 491 (2000) 78-86.

[4] Y. Mizukoshi, K. Okitsu, Y. Maeda, T.A. Yamamoto, R. Oshima, Y. Nagata, Sonochemical Preparation of Bimetallic Nanoparticles of Gold/Palladium in Aqueous Solution, J. Phys. Chem B 101 (1997) 7033-7037.

[5] L.K. Kurihara, G.M. Chow, P.E. Schoen, NANOSTRUCTURED Ni FILMS BY POLYOL ELECTROLESS DEPOSITION, Nanostruct. Mater 5 (1995) 607.

[6] C.H. Bae, S.H. Nam, S.M. Park, Formation of Silver nano Particles by Laser Ablation of a Silver Target in NaCl Solution, Appl. Surf. Sci 197 (2002) 628.

[7] A.B. Smetana, K.J. Klabunde, Synthesis of spherical silver nanoparticles by digestive ripening, stabilization with various agents, and their 3-D and 2-D superlattice formation, S J. Colloid Interface Sci 284 (2005) 521.

[8] S. Devarajan, P. Bera, S. Sampath, Bimetallic nanoparticles: A single step synthesis, stabilization, and characterization of Au–Ag, Au–Pd, and Au–Pt in sol–gel derived silicates, J.Colloid Interface Sci 117 (2005) 290.

[9] K. LaiHing, R.G. Wheeler, W.L. Wilson, M.A. Duncan, Photoionization dynamics and abundance patterns in laser vaporized tin and lead clusters, J Chem Phys 87 (1987) 3401.

[10] M. Wu, G. Lin, D. Chen, G. Wang, D. He, S. Feng, R. Xu, Sol-hydrothermal synthesis and hydrothermally structural evolution of nanocrystal titanium dioxide, Chem Mater 14 (2002) 1974-1980.

[11] Y. Li, X. Duan, Y. Qian, L. Yang, M. Ji, C. Li, Solvothermal Co-reduction Route to the Nanocrystalline III−V Semiconductor, InAs. J Am Chem Soc 119 (1997) 7869-7870.

[12] J.C. Clifton, Mercury exposure and public health, Pediatr Clin North Am 54 (2007) 237-269.

[13] G. Bjørklund, Mercury and acrodynia, Journal of Orthomolecular Medicine 10 (1995) 145-146.

[14] P.W. Davidson, G. J. Myers, B. Weiss, Mercury exposure and child development outcomes, Pediatrics 113 (2004) 1023-1029. Journal of Crystal Growth, 243 (2002) 224-229.

[15] M. Valls, V. de Lorenzo: Exploiting the genetic and biochemical capacities of bacteria for the remediation of heavy metal pollution, FEMS Microbiology Reviews 26 (2002) 327-338.

[16] T.W. Clarkson, L. Magos: he toxicology of mercury and its chemical compounds, T. Crit Rev Toxicol 36(2006) 609.

[17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelti, C.S. Adamo, J. Clifford, O. chterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. MoroKuma, D.K. Malick, D.K. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W.M.W. Chen, J.L. Wong, M. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople: (1998), GASSIAN 98 (Revision A. 3) Gaussian Inc. Pittsburgh, USA PA