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Preparation and characterization of a new halo chromate nanoparticle: Triphenylphosphonium trifluoroiodochromate (III)[P(C₆H₅)₃H]⁺[CrF₃I]⁻

ABSTRACT

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A new mixed halo chromate nanoparticle compound was synthesised and characterized. Triphenylphosphonium trifluoroiodochromate (III)[P(C₆H₅)₃H]⁺[CrF₃I]⁻ nanoparticle was synthesized by using triphenylphosphonium iodide reaction with CrF₃, in the presence of 3-mercaptopropionic acid. This method is a simple and direct method. The product was characterized by spectroscopic and analytical methods such as ³¹P-NMR, FT-IR, XRD, SEM. 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 98 package of programs. The comparison between theory and experiment is made. On the base of application of scanning electron microscopy (SEM) is showed about 54 nm particle sizes.

Keywords: [P(C₆H₅)₃H]⁺[CrF₃I]⁻; Mixed halochromate; Nanoparticles; Preparation; Characterization.

INTRODUCTION

Synthesis of inorganic materials with specific size and morphology has recently attracted a lot of interest because of the potential to design new materials and devices in various fields such as catalysis, medicine, electronics, ceramics, pigments and cosmetics. Nanoparticles are the end products of a wide variety of physical, chemical and biological processes some of which are novel and radically different, others of which are quite common place. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed.

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Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.

On the other hand Chromium (Cr) is an important industrial metal used in the fabrication of a wide range of products and applications including alloys, leather tanning, textile processing, electroplating, printing inks, refractories and several other industries [1]. Due to its widespread use in industry, chromate and chromium has become a pervasive contaminant in the environment, making it a serious public health and environmental concern [2]. Cr is readily soluble in alkaline environments [3-5], posing a threat to ground water quality as it can mobilize and spread quickly and has designated as a "priority pollutant" and considerable measures have been taken to effectively remediate and safely detoxify chromium-polluted soil and aquatic environments. Bioremediation is a promising approach for cheap, effective, and rapid in situ remediation of polluted environments [6]. Bioremediation offers multiple advantages over competing technologies by way of in situ decontamination, utilization of natural processes that are specific to the target contaminant [7], and significant reduction of additional environmental stresses [8]. Although bioremediation has vast potential in dealing with intractable environmental problems, much of this promise has yet to be realized. Specifically, much needs to be learned about what drives remediating microorganisms and their interactions with their surrounding chemical and biological environment [7]. New class of chromium 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 [9]. Many biological processes such as energy transfer, bone synthesis, amino acid synthesis, and metabolism require phosphorus and phosphate esters [10-11].

For the hydrolysis of RNA and phospholipids, cyclic phosphate esters are of biological significance [12]. In this work, a multidisciplinary compound between three above categories, $[P(C_6H_5)_3H]^+[CrF_3I]^-$ nanoparticles has been synthesized by a simple method with the starting materials $P(C_6H_5)_3$, HI, CrF_3 and a surfactant 3-mercaptopropionic 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. The molecular geometry and vibrational frequencies, energies, molecular orbitals and ground state calculated. This compound can be used as chromium, phosphorous and halid scavengers and delivery systems.

EXPERIMENTAL

Materials and Instruments

Triphenylphosphine, Hydrogen iodide, chromium trifluoride, 3-mercaptopropionic 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-K α 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.

Preparation of Triphenylphosphonium iodide

To a 500 ml flask equipped with a magnetic stirrer was added hydrogen iodide (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.

**Synthesis of Triphenylphosphonium
trifluoroiodochromate(III)[P(C₆H₅)₃H]⁺[CrF₃I]⁻)**

Triphenylphosphonium
trifluoroiodochromate (III)[P(C₆H₅)₃H]⁺[CrF₃I]⁻,
TPPTFIC prepared by two methods:

First: To chromium trifluoride (0.44 g, 3.64 mmol) in acetonitrile (200mL) was added at room temperature a solution of triphenylphosphonium iodide (1.0g, 2.56 mmol) in acetonitrile (100 mL). 3-mercaptopropionic acid in excess amount (2.06 g) was added as surfactant. After 50 min, a green 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 (0.5g, 1.9mmol) was dissolved in acetonitrile (10 ml) and stirred for 0.5 h. (0.24 g, 1.87mmol) HI was added to this mixture and stirring continued for 5 minutes. 3-mercaptopropionic acid (MPA), (1.4g) was added to the materials and stirring continued for another 5 minutes. CrF₃ (0.22 g, 1.82mmol) in acetonitrile added to this mixture as the last of starting materials and stirring was continued for 4 h to precipitate a green solid. Precipitate was filtered and washed with ether and hexane. M.P.: 120-121°C; Anal. Calc. for [P(C₆H₅)₃H]⁺[CrF₃I]⁻: Calculated C, 43.28; H, 3.20. Found: C, 43.93; H, 3.45. IR (KBr) (cm⁻¹): 3415, 1660, 980, 595, 458, 620 cm⁻¹. ³¹P NMR (135 MHz, CDCl₃): δ= 26.06ppm (Figure 1, 2).

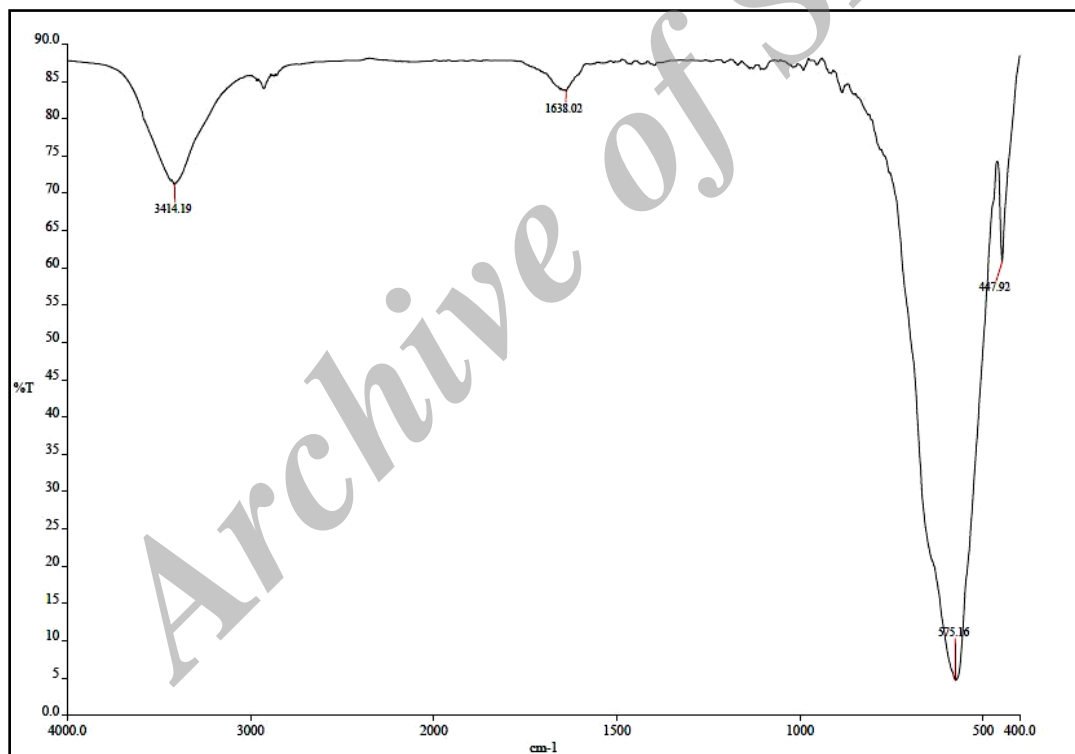
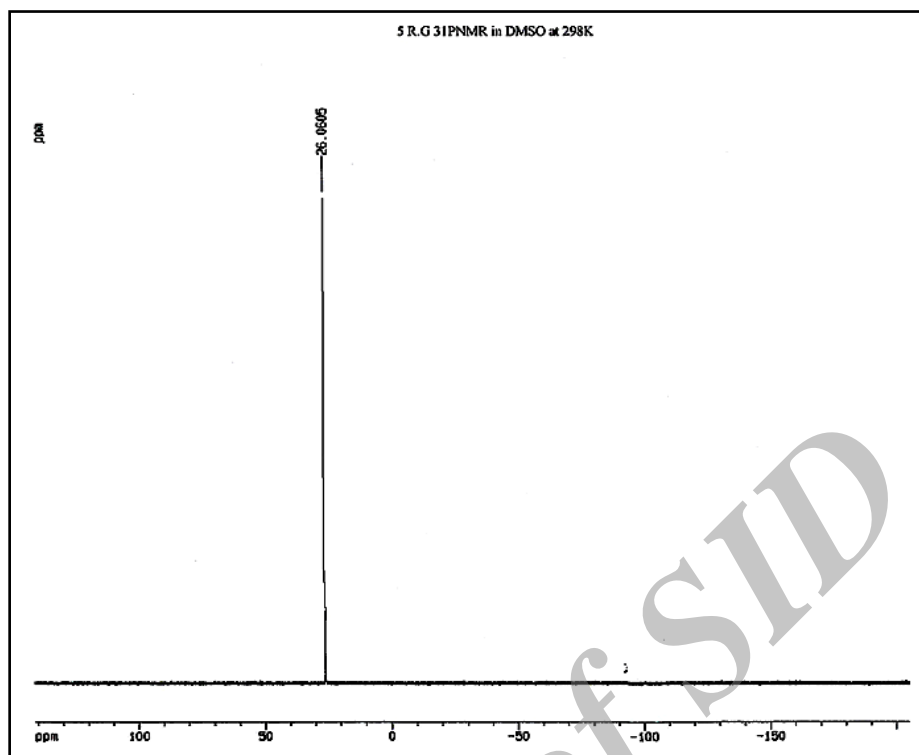


Fig. 1. IR spectrum of [P(C₆H₅)₃H]⁺[CrF₃I]⁻

Fig. 2. ^{31}P -NMR Spectrum of $[\text{P}(\text{C}_6\text{H}_5)_3\text{H}]^+[\text{CrF}_3\text{I}]^-$

RESULTS AND DISCUSSION

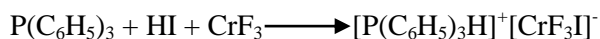
Preparation

Salts containing large organic cations, such as butylpyridinium chloride or 1, 3-dialkylimidazolium chloride, interact with CrF_3 to form ionically conducting liquids at room temperature. CrF_3 consists primarily of discrete Cr_2F_6 dimers, and appears as a molecular liquid with high vapor pressure. It is well known that the melting point of CrF_3 can be lowered upon mixing with RI (R denotes such as an alkali metal or organic cation), which is believed to originate from the Lewis acid–base interactions of CrF_3 with RI and the formation of large-sized complex anions.

Triphenylphosphonium trifluoroiodochromate (III) (TPPTFIC) easily obtained by the addition of triphenylphosphonium iodide to an acetonitrile solution of chromium trifluoride. The 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.

This paper describes some initial work on the characterization of nanoparticles investigated the processing of preparation a novel nanoparticle with formula $[\text{P}(\text{C}_6\text{H}_5)_3\text{H}]^+[\text{CrF}_3\text{I}]^-$. This goal was happened by reacting triphenylphosphonium iodide added to acetonitrile and CrF_3 . Then 3-mercaptopropionic acid was added to the starter materials. Reporting the synthesis of the (TPPTFIC) has been shown that chromate was useful for organic chemists. That is analog of the above chromate compounds.

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



This production method can be defined as a bottom-up production of nanoparticles in the liquid phase. By use of 3-mercaptopropionic 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.

Ab initio calculations method

In this manuscript, we report the synthesis, spectroscopic characterization, density functional theory calculation 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.

All ab initio calculations were done by using the Gaussian-98 suite of programs [13]. 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 $[P(C_6H_5)_3H]^+[CrF_3I]^-$ in this product are depicted in (Figure 3, 4). The Cr atom in anion is coordinated by three F and one I atoms as ligands in tetrahedral geometry.

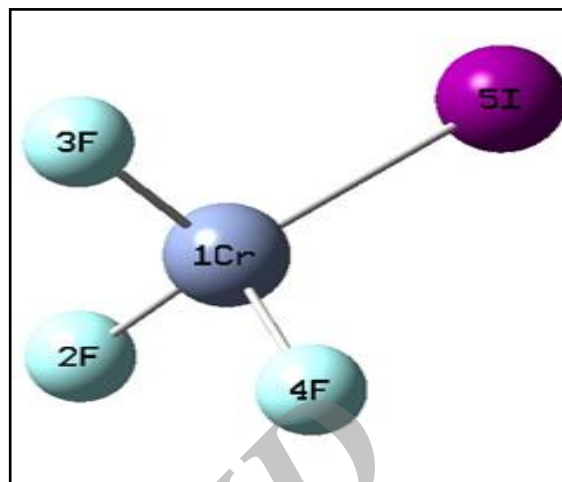


Fig. 3. Optimized structure of $[CrF_3I]^-$ anion

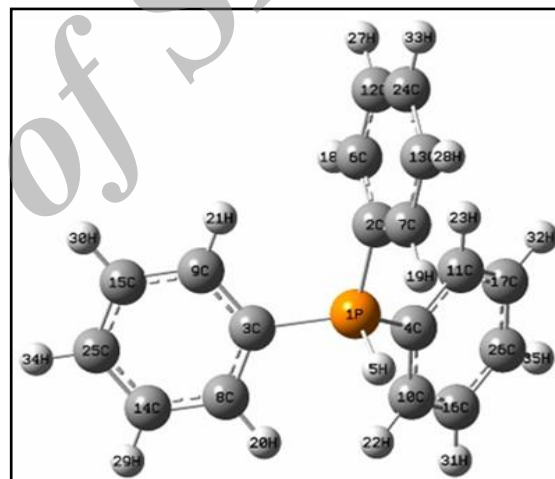


Fig. 4. Optimized structure of $[P(C_6H_5)_3H]^+$ cation

Table 1. Calculated and experimental frequencies of $[P(C_6H_5)_3H]^+[CrF_3I]^-$ (cm^{-1})

$[P(C_6H_5)_3H]^+[CrF_3I]^-$		
	Expt.	B3LYP/6311G
ν P-H	980	965
ν C6H6	1660	1638
ν =C-H(str)	3415	3414
Cr-F	595	576
Cr-F	458	446
Cr-I	620	619

XRD and SEM Data

Powder X ray diffraction (XRD) of TPPTFIC has shown (Figure 5). The size of the nano particles can be calculated from Scherrer equation used for this purpose:

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

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 (TPPTFIC) has nano size about 50 nm and produced in nano scale.

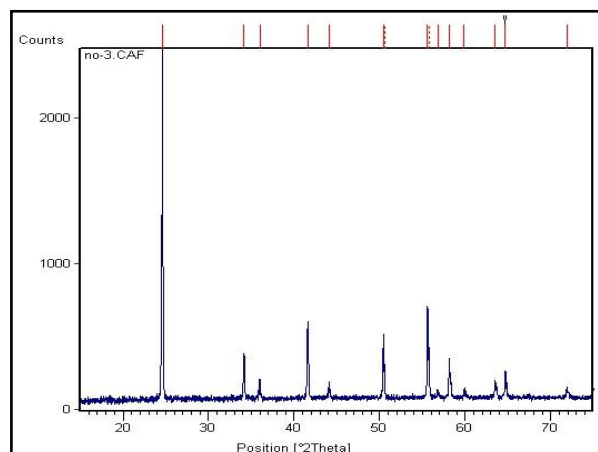


Fig. 5. XRD pattern of $[P(C_6H_5)_3H]^+[CrF_3I]^-$

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 show agglomeration of particles and multifarious texture. SEM shows the size of nanoparticles about 54 nm that confirm the predicted size range by XRD. (Figure 6) The morphology of this nanoparticle as seen in SEM pictures is semi spherical. As known, the morphologies sometimes arise spontaneously as an effect of a templating or directing agent present in the synthesis such as micellar emulsions or anodized alumina pores, or from the innate crystallographic growth patterns of the materials themselves. 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 small 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.



Fig. 6. SEM graph of $[P(C_6H_5)_3H]^+[CrF_3I]^-$

CONCLUSIONS

In this work, a novel halochromate compound with formula $[P(C_6H_5)_3H]^+[CrF_3I]^-$ was synthesized from the reaction of triphenylphosphonium iodide with CrF_3 in acetonitrile. By some modification in preparation method such as addition of 3-mercaptopropionic acid, the product changed to nano scale. The ^{31}P NMR spectrum of this compound indicates a signal at 26.06 ppm. The structure of the compound has been calculated and optimized by the density functional theory (DFT) based method at

B3LYP/6-311G levels of theory, using the Gaussian 98 package of programs. The comparison between theory and experiment is made. The nano form of this compound was synthesized and measured by FTIR, XRD and SEM (Figure 1-6).

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