



Synthetic and structural investigations of mercurous and mercuric organophosphonates and phenylarsonates



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ARTICLE INFO

Article history:

Received 1 June 2016

Received in revised form

5 August 2016

Accepted 9 August 2016

Available online 9 August 2016

Keywords:

Mercurous phosphonates

Mercuric phosphonates

Mercuric phenylarsonates

Synthesis

Crystal structure

Raman spectroscopy

ABSTRACT

The following twelve mercurous and mercuric organophosphonates, bis/diphosphonates and phenylarsonates have been isolated and structurally characterized by single crystal X-ray diffraction, ^{13}C - and ^{31}P NMR, infrared and Raman spectroscopic methods: $\text{Hg}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2$ (**1**), $\text{Hg}_2(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H})_2$ (**2**), $\text{Hg}_2(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3\text{H})$ (**3**), $\text{Hg}_2(\text{HO}_3\text{P}(\text{CH}_2)_4\text{PO}_3\text{H})$ (**4**), $\text{Hg}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}$ (**5**), $(\text{Hg}_2)_2(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3)$ (**6**), $(\text{Hg}_2)_2(\text{O}_3\text{P}(\text{CH}_2)_3\text{PO}_3)$ (**7**), $\text{Hg}(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}$ (**8**), $\text{Hg}(\text{O}_3\text{PCH}_2\text{C}_6\text{H}_5) \cdot \text{H}_2\text{O}$ (**9**), $\text{Hg}(\text{O}_3\text{AsC}_6\text{H}_5) \cdot \text{H}_2\text{O}$ (**10**), $\text{Hg}_3(\text{O}_3\text{AsC}_6\text{H}_5)_2(\text{HO}_3\text{AsC}_6\text{H}_5)_2$ (**11**) and $(\text{Hg}_2)\text{Hg}_3(\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**12**). Compounds **1–7** are the first examples of mercurous phosphonates and di/bisphosphonates. They contain Hg_2O_6 units, which consist of Hg_2^{2+} cations with Hg–Hg bond of ~ 2.5 Å length. Phenylphosphonates **1** and **5** are layered compounds, whereas bis/diphosphonates **2**, **3**, **4**, **6** and **7** have pillared-layered and three-dimensional structures. Compounds **8–11** are layered mercuric phosphonates and phenylarsonates. Compound **12** is a three-dimensional mixed-valent mercury phenylenebisphosphonate.

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1. Introduction

The solid-state chemistry of inorganic-organic hybrid materials is an active and important research arena. Metal organophosphonates are a class of inorganic-organic hybrid materials that started [1], way back in 1978, when zirconium phenylphosphonate, $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$ was synthesized for the first time. Thereafter, a large number of metal organophosphonates and organobisphosphonates with or without additional functional groups were reported [2]. They find various applications [3], such as gas storage, intercalation reactions, proton conductivity, metal ion absorption and corrosion inhibition.

The organophosphonates of di- to hexa-valent metals were predominantly reported in the literature. The monovalent metal organophosphonate chemistry remained largely unknown until $A(\text{HO}_3\text{PPh})(\text{H}_2\text{O}_3\text{PPh})$ ($A = \text{Li, Na, K, Rb, Cs, Tl, NH}_4$) phenylphosphonates were reported [4]. Prior to this, only $\text{Ag}_4(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3)$ compound was known [5]. Subsequently reported [6–10] were the diphosphonates, $\text{Ag}_2(\text{HO}_3\text{P}(\text{CH}_2)_4\text{PO}_3\text{H})$, $\text{Ag}_4(\text{O}_3\text{P}(\text{CH}_2)_4\text{PO}_3)$ and $\text{Ag}_4(\text{O}_3\text{P}(\text{CH}_2)_3\text{PO}_3) \cdot \text{H}_2\text{O}$, $\text{Na}(\text{HO}_3\text{P}(\text{CH}_2)\text{PO}_3\text{H}_2)$, $A(\text{HO}_3\text{P}(\text{CH}_2)_2\text{PO}_3\text{H}_2)$ ($A = \text{Li, Na, K, Rb, Cs, Tl and NH}_4$), $\text{Na}(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}_2)$, $A(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3\text{H}_2)$ ($A = \text{Li, Na, K, Rb and Cs}$) and $\text{Na}_2(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3\text{H})$. Silver phenylphosphonates, $\text{Ag}_x\text{H}_{4-x}(\text{O}_3\text{PPh})_2$ ($x = 1–4$) and monovalent ion 1,4-phenylenebisphosphonates, $A(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}_2)$ ($A = \text{Li, K, Rb, Cs, Tl, NH}_4$ and Ag) are recent additions [11,12] to the literature.

$A(\text{HO}_3\text{PPh})(\text{H}_2\text{O}_3\text{PPh})$ ($A = \text{Li, Na, K, Rb, Cs, Tl, NH}_4$) phenylphosphonates have 1:2 ratio of A^+ ion to phosphonate moiety. They are divided into four structure types [13], namely, chain-like one-dimensional lithium compound, two-dimensional sodium compound, layered cesium compound and ladder-like potassium, rubidium, thallium and ammonium compounds. The lamellar framework and the three acidic hydrogen atoms of $A(\text{HO}_3\text{PPh})(\text{H}_2\text{O}_3\text{PPh})$ ($A = \text{Li, Na, K, Rb, Cs, Tl}$) compounds render them to behave as solid Brønsted acids. They undergo, at room temperature, acid-base intercalation reactions with ammonia and primary n -alkyl amines, which occupy the interlamellar region. These reactions are topotactic because they involve minimum structural reorganization of the reactant metal phosphonate. Similarly $A(\text{HO}_3\text{P}(\text{CH}_2)_2\text{PO}_3\text{H}_2)$ ($A = \text{Li, Na, K, Rb, Cs, Tl and NH}_4$) ethylene-diphosphonates also undergo topotactic intercalation with ammonia and the ammonia intercalates, upon heating, undergo topotactic deintercalation. Hydroxyphosphonoacetates [14] of lithium, sodium, potassium and cesium are monovalent metal phosphonates having additional functional groups such as hydroxyl and carboxyl groups. These functional groups establish hydrogen bonds with water of crystallization and hence these compounds were reported to be proton conductors.

Organophosphonates/di(bis)phosphonates and phenylarsonates of other monovalent ions such as mercurous Hg_2^{2+} and cuprous Cu^+ are not reported yet. In continuation of research on monovalent metal phosphonates, an exploratory synthetic research work on organophosphonates and organobisphosphonates

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of Hg_2^{2+} ion was considered worthwhile and, therefore, undertaken. Some metal phenylarsonates are isostructural with their phenylphosphonate analogues. Their structural elucidation is necessary and immensely useful, when the structural characterization of their phenylphosphonate analogues is elusive for want of good quality crystals. Therefore, a worthy investigation of metal phenylarsonates, along with phenylphosphonates, has been taken up.

Unintended mercuric organophosphonates and phenylarsonates were also obtained in the synthetic and crystal growth attempts for the mercurous compounds. Therefore, the synthesis and crystal structures of mercuric compounds are also included in this paper. Furthermore, only three non-molecular mercuric phosphonates, namely, $\text{Hg}(\text{PC}_5\text{H}_5\text{N}) \cdot \text{H}_2\text{O}$, $\text{Hg}(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}$ and $\text{Hg}_2(\text{O}_3\text{PCH}_2\text{NH}_2)(\text{HO}_3\text{PCH}_2\text{NH}_2)(\text{H}_2\text{O})_2(\text{NO}_3)$ are known in the literature [15–17].

The results of this synthetic and structural investigation of phosphonates and arsonates of mercury pertain to twelve compounds listed in Table 1. The values of ratio of mercury to phosphonate/arsonate moiety are 1:1 and 2:1 in mercurous compounds 1–7, 1:1 and 3:4 in mercuric compounds 8–11 and 5:4 in the mixed-valent mercury compound 12. All of them were isolated and structurally characterized by single crystal X-ray diffraction. This paper is the first report on mercurous phosphonates and bis/diphosphonates, which represent the first examples of metal organophosphonates containing metal-metal bond.

2. Experimental

2.1. Syntheses

Phenylphosphonic acid ($\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$), benzylphosphonic acid ($\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H}_2$), phenylarsonic acid ($\text{C}_6\text{H}_5\text{AsO}_3\text{H}_2$), 1,4-phenylenebisphosphonic acid ($\text{H}_2\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}_2$), 4,4'-biphenylenebisphosphonic acid ($\text{H}_2\text{O}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3\text{H}_2$), 1,2-ethylenediphosphonic acid ($\text{H}_2\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3\text{H}_2$), 1,3-propylenediphosphonic acid ($\text{H}_2\text{O}_3\text{P}(\text{CH}_2)_3\text{PO}_3\text{H}_2$), 1,4-butylenediphosphonic acid ($\text{H}_2\text{O}_3\text{P}(\text{CH}_2)_4\text{PO}_3\text{H}_2$), mercurous perchlorate tetrahydrate ($\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$), mercuric acetate ($\text{Hg}(\text{OCOCH}_3)_2$) and mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$) were used as purchased.

$\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, when dissolved in water or 3:1 triethylorthoformate-methanol (TEOF-MeOH) solvent mixture, led to some insoluble yellow solid residue. The yellow residue was filtered and the clear filtrate was the aqueous/non-aqueous solution of $\text{Hg}_2(\text{ClO}_4)_2$ employed for the syntheses and crystal growth of mercurous compound 1. $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, dissolved completely in perchloric acid, was used for the crystal growth of other mercurous compounds, 2–7. $\text{Hg}(\text{NO}_3)_2$ in dilute nitric acid and $\text{Hg}(\text{OAc})_2$ in aqueous medium were employed for the syntheses and

crystal growth of mercuric compounds, 8–12. Diphosphonic acids, benzylphosphonic acid, phenylarsonic acid and phenylphosphonic acid were dissolved respectively in methanol, diethyl ether, *n*-butanol and TEOF-MeOH mixture. Diethyl ether or water was also used as a solvent for phenylphosphonic acid.

A white polycrystalline mixture of $\text{Hg}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\mathbf{1})$, $\text{Hg}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{5})$ and $\text{Hg}(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{8})$ was formed instantaneously, when a 10 mL aqueous solution of $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.480 g, 0.714 mmol) was added to an aqueous 10 mL solution of $\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$ (0.226 g, 1.429 mmol). In a similar synthetic procedure, TEOF-MeOH was employed as the solvent; when a clear 10 mL solution of $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.630 g, 0.937 mmol) was added to $\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$ (0.148 g (0.937 mmol), a white solid precipitated instantaneously. The container was covered with a perforated film and left overnight for evaporation of the solvent at room temperature. The solid contents were washed with distilled water and air-dried. Polycrystalline $\text{Hg}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\mathbf{1})$ was obtained in 40% yield.

Polycrystalline samples of three mercuric compounds, 8, 9 and 11 were obtained as white precipitates, when a 10 mL aqueous solution of mercuric acetate/nitrate was added each to 25 mL aqueous solutions of phenylphosphonic acid, benzylphosphonic acid and phenylarsonic acid respectively. The yield of the product and the quantities of reactants are as follows. For compound 8 (0.3776 g, 75% yield), 0.4467 g (1.40 mmol) $\text{Hg}(\text{OCOCH}_3)_2$ and 0.2216 g (1.40 mmol) $\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$; for compound 9 (0.1470 g, 74% yield), 0.1751 g (0.54 mmol) $\text{Hg}(\text{NO}_3)_2$ and 0.0928 g (0.54 mmol) $\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H}_2$; and for compound 11 (0.3806 g, 76% yield), 0.3405 g (1.06 mmol) $\text{Hg}(\text{OCOCH}_3)_2$ and 0.2878 g (1.42 mmol) $\text{C}_6\text{H}_5\text{AsO}_3\text{H}_2$.

2.2. Single crystal growth

A clear 10 mL dilute perchloric acid solution of $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.2069 g, 0.308 mmol) was taken in a narrow Schlenk tube and layered with 10 mL diethyl ether first and then followed by 5 mL ether solution of $\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$ (0.0973 g, 0.615 mmol), without disturbing the ether-water interphase. After about two weeks, a mixture of plate-like crystals of $\text{Hg}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\mathbf{1})$, $\text{Hg}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{5})$, $\text{Hg}(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{8})$ and other unidentified compounds was formed at the interphase. The aqueous layer was syringed out and the crystals were filtered off and air-dried. The single crystal of compound 1 was hand-picked for X-ray diffraction (XRD) study.

A crystal of $\text{Hg}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{5})$ was hand-picked from a similar mixture of plate-like crystals obtained, at the ether-water interphase, when $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.102 g, 0.152 mmol) and $\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$ (0.048 g, 0.304 mmol) and no perchloric acid were employed.

For $\text{Hg}_2(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H})_2(\mathbf{2})$ compound, $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.2254 g, 0.335 mmol), was dissolved in 2 mL of concentrated

Table 1
List of mercurous and mercuric compounds isolated and structurally characterized.

Sr. no.	Compound	Formula	Hg: P/As ratio
1	Mercurous phenylphosphonate	$\text{Hg}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\mathbf{1})$	1:1
2	Mercurous 1,4-phenylenebisphosphonate	$\text{Hg}_2(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H})_2(\mathbf{2})$	1:1
3	Mercurous 4,4'-biphenylenebisphosphonate	$\text{Hg}_2(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3\text{H})_2(\mathbf{3})$	1:1
4	Mercurous 1,4-butylenediphosphonate	$\text{Hg}_2(\text{HO}_3\text{P}(\text{CH}_2)_4\text{PO}_3\text{H})_2(\mathbf{4})$	1:1
5	Mercurous phenylphosphonate	$\text{Hg}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{5})$	2:1
6	Mercurous 1,2-ethylenediphosphonate	$(\text{Hg}_2)_2(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3)_2(\mathbf{6})$	2:1
7	Mercurous 1,3-propylenediphosphonate	$(\text{Hg}_2)_2(\text{O}_3\text{P}(\text{CH}_2)_3\text{PO}_3)_2(\mathbf{7})$	2:1
8	Mercuric phenylphosphonate	$\text{Hg}(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{8})$	1:1
9	Mercuric benzylphosphonate	$\text{Hg}_2(\text{O}_3\text{PCH}_2\text{C}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{9})$	1:1
10	Mercuric phenylarsonate	$\text{Hg}(\text{O}_3\text{AsC}_6\text{H}_5) \cdot \text{H}_2\text{O}(\mathbf{10})$	1:1
11	Mercuric phenylarsonate	$\text{Hg}_3(\text{O}_3\text{AsC}_6\text{H}_5)_2(\text{HO}_3\text{AsC}_6\text{H}_5)_2(\mathbf{11})$	3:4
12	Mercurous-mercuric 1,4-phenylenebisphosphonate	$(\text{Hg}_2)\text{Hg}_3(\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}(\mathbf{12})$	5:4

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