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Synthesis, Crystal Structure, and Characterization of the first Organic Cation Hexaoxoperiodate

I. Wacharine, W. Smirani Sta*, M. Rzaigui

Laboratoire de chimie des matériaux, Faculté des sciences de Bizerte, 7021,
Zarzouna, Tunisia
*Corresponding author: wajda_sta@yahoo.fr

ABSTRACT

The title compound is an organic-inorganic hybrid material. The single crystal X-ray diffraction investigation reveals that the studied compound crystallizes in the monoclinic system, space group $P2_1/c$ with the following lattice parameters: a = 7.551 (2) Å, b = 6.694 (3) Å, c = 14.783 (2) Å, β = 97.61 (2)° and Z = 2. The crystal lattice is composed of a discrete $(H_4IO_6)^-$ anions surrounded by piperazinium cations and water molecules. Complex hydrogen bonding interactions between the different chemical spices form a three-dimensional network. Room temperature IR, ^{13}C NMR spectroscopy, thermogravimetric analysis and optical absorption of the title compound were recorded and analyzed.

Indexing terms/Keywords

First organic cation periodate; Crystal structure; IR Spectroscopy; Thermogravimetric analysis; ^{13}C NMR.

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1. INTRODUCTION

The chemistry of periodic acid is rather complex as a great number of periodate oxo-anions $H_XIO_6^{(5-x)-}$ have been elaborated and structurally investigated [1-2]. IO_4^- anion is called metaperiodate, $H_4IO_6^-$, $H_3IO_6^{2-}$, $H_2IO_6^{3-}$, HIO_6^{4-} and IO_6^{5-} anions are called orthoperiodates. $H_4IO_6^-$ anion is known only with a limited number of cations. Sebert characterized some compounds containing anions by IR and Raman spectroscopy, but no detailed structural analysis can be found due to twining of the crystals. Recently, $Sr(H_4IO_6)_2.3H_2O$ [1] and $Be(H_4IO_6)_2.4H_2O$ [2] are structurally characterized on single crystals. In literature, there are some organic cations metaperiodates [3]. Up to now, there is no organic cation orthoperiodate structurally well characterised. At our acknowledgement the title compound, $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$, is the first one of this family. We report here its synthesis and crystal structure. Piperazine and some derivates are biologically active across a number of different therapeutic areas [4] such as antifungal, antibacterial, antimalarial, antipsychotic, antidepressant and antitumour activity against colon, prostate, breast, lung and leukemia tumors [5].

2. EXPERIMENTAL

2.1 Material Preparation

Crystals of piperazinium bis-tetrahydrogen-hexaoxoperiodate dihydrate were obtained by mixing, in stoichiometric ratio, a solution of periodic acid (1 M) with an aqueous solution of piperazine (0,4g). The mixture was stirred for 5 hours, and then the precipitated was filtered. The obtained solution was slowly evaporated at room temperature. After 2 weeks of evaporation at 278 K, colorless prism shaped crystals appear in the solution.

2.2 Physical measurement

X-ray diffraction measurements were collected using CAD4 diffractometer MACH III, (graphite-monochromated Ag. Kα radiation λ = 0.56087 Å). All calculations were performed using SHELXL97 [6] for structure determination and refinement. The positional parameters of the iodine atoms were obtained from the three-dimensional Patterson map, whereas the remaining atoms were found from successive refinement and difference-Fourier synthesis. After introducing anisotropic thermal factors for the non hydrogen atoms and isotropic ones for H atoms [O−H bond distances and distances between two atoms from each water molecule were restrained to be 0.85(2) and 1.37(2) Å, with $U_{iso}(H)= 1.5\ U_{eq}\ (O)$], the final refinement cycles led to $R_1 = 0.062$ and $wR_2 = 0.156$.

The infrared spectrum of the $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$ was recorded on a Nicolet IR200 FT-IR Spectrometer at ambient temperature.

The thermogravimetric measurements were performed with the use of the multimodule 92 Setaram analyzer apparatus in the 25-500 °C temperature range in the argon flow. The rate of heating was 5°C / min; the mass of the sample was 13.83 mg.

The UV adsorption and optical diffuse reflectance spectra were measured at room temperature with a Perkin Elmer Lambda 11 UV/Vis spectrophotometer in the range of 200-800 nm.

The ^{13}C NMR spectra was measured with a Bruker ULTRASHIELD PLUS 500 spectrometer

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

Crystal data summary of intensity data collection and structure refinement are reported in Table 1.

The piperazinium bis-tetrahydrogen-hexaoxoperiodate dihydrate (I) has an asymmetric unit built of one $H_4IO_6^-$ anion, one half of piperazinium cation and one water molecule (Figure 1). $H_4IO_6^-$ anions are coupled into pairs through H-bonds O2-H7…O3. The formed dimmers are connected by O4-H4…O1 to built layers parallel to (b,c) plane at x = 0. These layers are interconnected with the water molecules and piperazinium dications via Ow-H…O, N-H…O and C-H…O hydrogen bonds (Figure 2). In this hydrogen bonding, the water molecules play a double role, acceptor in O5-H5…O7 and donor in O7-H15…O5 and O7-H14…O3. In the IO_6 octahedra, there are two groups of distances (I-O) short distances ranging from 1.807(4) and 1.820(3)Å and four longer distances between 1.891(3) and 1.916(3)Å. The longer distances I-O correspond to oxygen atoms O(2), O(4), O(5) and O(6) carry hydrogen in $H_4IO_6^-$ anion (Table 2).

Table 1. Crystal data and structure refinement

Empirical formula	$C_4 H_{24} I_2N_2O_{14}$
Formula weight(g.mol^{-1})	578.04
Temperature (K)	293
Wavelength (Å)	0.5688
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	7.551(2)
b (Å)	6.694 (4)
c (Å)	14.783 (2)
β (°)	97.61 (2)
Volume (Å^3)	770.6(4) (3)
Z	2
D_{calc} (g.cm^{-3})	2.491
Absorption coefficient (mm^{-1})	0.22
F(000)	560
Crystal size (mm^3)	0.22×0.20×0.20
Reflections collected	5940
Independent reflections parameters	3771
Goodness-of-fit on F²	1.05
Final R indices [I > 2 sigma (I)]	R_1=0.062 and wR_2= 0.156

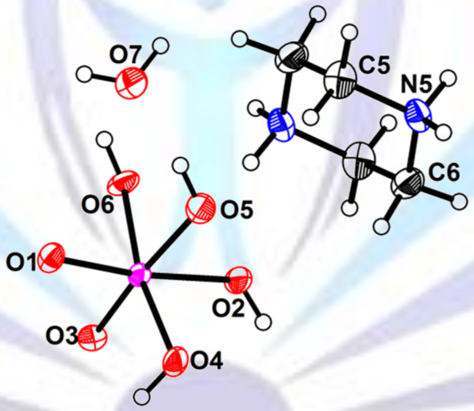

Figure 1. ORTEP view of $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$ showing 50% probability ellipsoids

Hydrogen bonds originating from the $H_4IO_6^-$ anions are expected to be much stronger than those originating from the water molecules. Relatively short distances (2.657 and 2.623Å) are found between the oxygen atoms O2 and O3 and O4 and O1 respectively, of the periodate ions (Table 3). Similar bonding are observed in inorganic compounds $Sr(H_4IO_6)_2.3H_2O$ [2]. So, in this case we expect strong hydrogen bonds which link periodate anions to built layers parallel to (b, c) planes (Figure 3). In these latter the tetrahydrogenperiodate anions are associated so as to create R_1^6 (18) and R_1^2(8) graph-set motif.

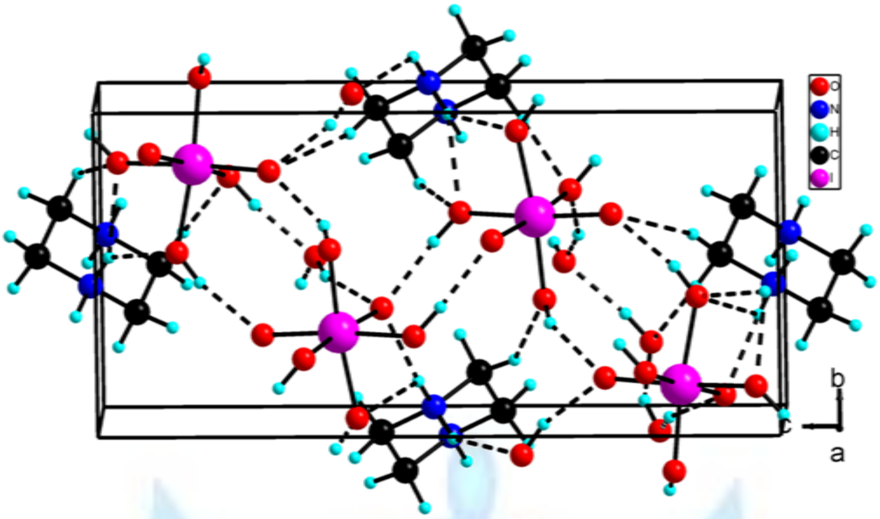

Figure 2. Crystal packing of $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$ with hydrogen bonds as dotted lines

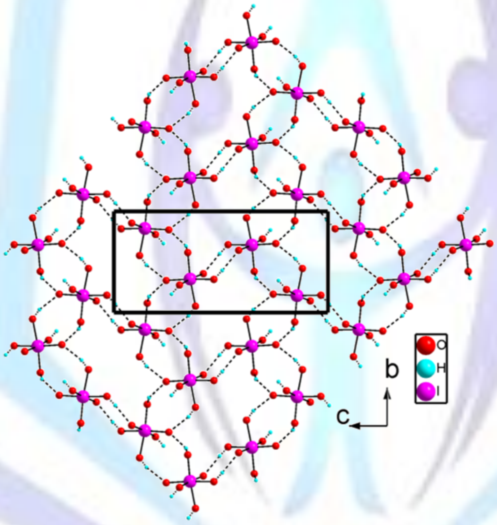

Figure 3. Two dimensional network of periodate anions

Table 2. Selected bond distances (Å) and angles (°) for $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$

I	O_1	O_2	O_3	O_4	O_5	O_6
O_1	1.806(4)	3.702	2.698	2.627	2.656	2.724
O_2	172.22(17)	1.904(4)	7.617	7.617	2.49(2)	2.538
O_3	96.17(17)	91.16(18)	1.820(3)	2.716	3.726	2.648
O_4	94.91(15)	87.16(15)	94.04(17)	1.891(3)	2.609	3.792
O_5	91.16(18)	81.46(18)	172.55(16)	86.61(17)	1.912(3)	2.657
O_6	94.06(14)	83.26(15)	90.25(16)	169.18(14)	87.91(17)	1.916(3)

The organic piperazinium dication lies at an inversion centre and adopts a typical chair geometry, as evidenced by the mean deviation (± 0.038) from the least square plane, with normal valence bond lengths and angles [7], as observed in the structures of piperazinediium tetrachloridozincate [8] and piperazinediium tetrachloridozincate monohydrate [9].

Table 3. Principal intermolecular distances (Å) and bond angles (°) of the hydrogen bonding scheme

D - H....A	D - H	H...A	D...A	D - H... A
O (4) -H(4) ...O(1)	0.82	1.90	2.626(5)	147
N (5) -H (5A)...O(2)	0.90	2.13	2.947(5)	150
N (5) -H (5A)...O(6)	0.90	2.26	3.004(6)	140
N (5) -H (5B)...O(3)	0.90	1.95	2.822(5)	162
N (5) -H (5B)...O(6)	0.90	2.51	3.099(6)	124
O (2) -H (7) ...O(3)	0.85(5)	1.83(6)	2.656(5)	162(7)
O (5) -H (10)...O(7)	0.83(7)	1.72(7)	2.546(7)	172(9)
O (6) -H (11)...O(1)	0.81(6)	1.98(7)	2.680(5)	145(7)
O (7) -H (14)...O(3)	0.84(5)	1.95(6)	2.740(6)	156(7)
O (7) -H (15)...O(5)	0.85(9)	2.01(8)	2.767(6)	148(10)
C (5) -H (5C)...O(1)	0.97	2.60	3.536(7)	163
C (5) -H (5D)...O(5)	0.97	2.47	3.384(7)	157
C (6) -H (6A)...O(2)	0.97	2.58	3.301(7)	132
C (6) -H (6B)...O(4)	0.97	2.43	3.262(7)	144

3.2 Infrared Spectroscopy

The infrared absorption spectrum of crystalline iodate is shown in Figure 4. To assign the IR peaks to vibrational modes, we examined the modes and frequencies observed in similar compounds [1]. The bands between 3758 cm^{-1} and 2843 cm^{-1} correspond to the stretching vibrations of groups (-NH$_2^+$) and (-CH$_2$-) [10] and to the bending vibration of group (H$_2$O) [11]. Bands appearing between 1592 and 1406 cm^{-1} are attributed to the bending vibrations of (-NH$_2^+$), (CH$_2$), (OH) and (H$_2$O) groups. The area between 1216-1090 cm^{-1} corresponds to the stretching vibrations ν (C-N) and ν (C-C).

Bands that lie between 1324 and 1142 cm^{-1} correspond to the bending of IOH group. The two strong bands at 635 and 761 cm^{-1} correspond to the stretching vibrations of IO(H). The area between 860 and 720 cm^{-1} is characteristic of the stretching vibration of I = O and the area of fréqeunces ν <566 cm^{-1}, corresponds to the bending vibration of I = O.

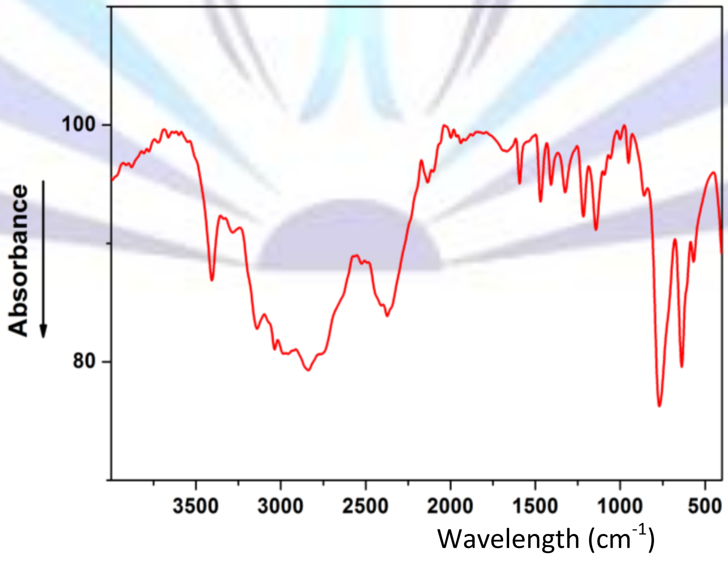

Figure 4. IR absorption spectrum of ($C_4H_{12}N_2$)(H_4IO_6)$_2$.2H_2O

3.3 UV Absorption and Diffuse Reflectance

The UV absorption spectrum revealed one little intensity band at 274 nm. These band indicates the n→π* transition of the periodate IO6 anions. Optical diffuse reflectance spectrum (Figure 5) indicates an optical band gap of 4neV, hence,

$(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$ is a wide-band-gap of dielectric material. This value suggests that this compound could be used for optical applications in far UV region [12].

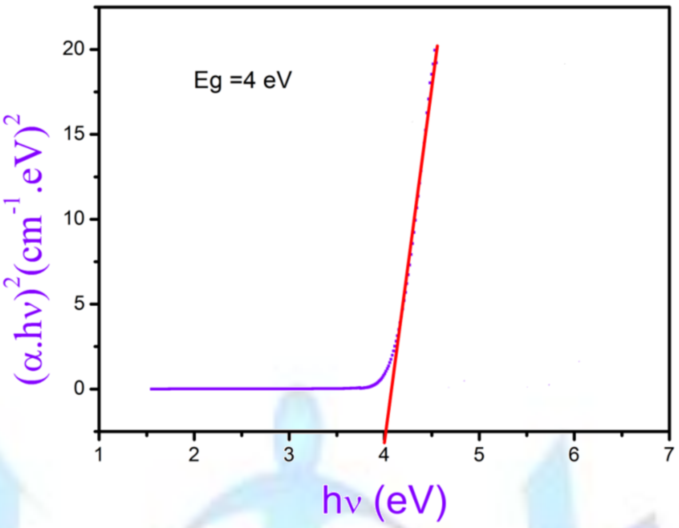

Figure 5. UV diffuse reflectance spectrum for $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$

3.4 Thermogravimetric analysis

The simulations TG-DTA analysis curves (Figure 6) of the title compound show that this material is thermally stable up to 364K where it begins to dehydrate. In fact, the series of endothermic peaks, observed in the temperature range [363-403 K] in DTA curve correspond to the dehydratation of the periodate to give a new phase of diperiodate to give a new phaseof diperiodate to diperiodate of piperazinium. This reaction is confirmed by the first weight loss (12%) in the TG curve. This weight loss is very close to the percentage of four water molecules in the title compound

$$[C_4N_2H_{12}](IO_2(OH)_4)_2.2H_2O \longrightarrow [C_4N_2H_{12}](H_4I_2O_{10}) + 4H_2O$$

The obtained anhydrous phase undergoes, in a wide temperature range [403-773 K]. Several phenomena represented by a series of peaks in the DTA curve and by two successive weight losses on the TG curve. The sum of these weight losses (86%) corresponds to the percentage of the organic molecule in the studied compound (87, 2%). The organic molecules has suffered a pyrolysis and a combustion which give a gaseous release (NH_3 , CO_2 , CO, H_2O) and which leave a liquid of diode contaminated of residue of carbon.

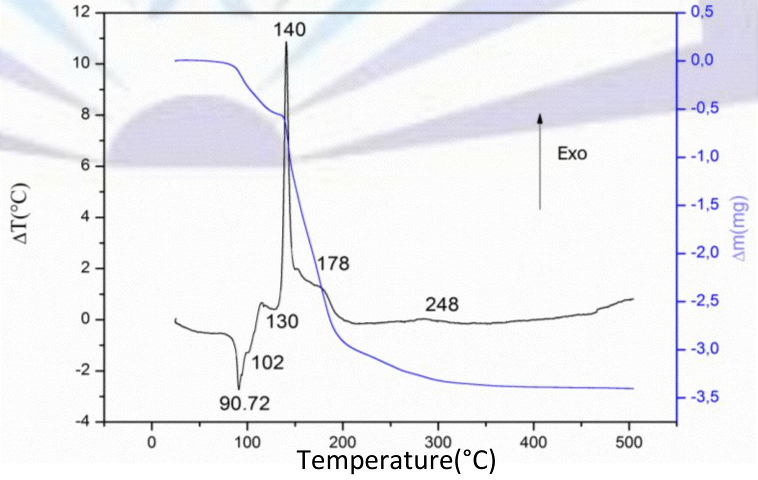

Figure 6. DTA-TGA diagram for $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$

3.4 ^{13}C MAS-NMR analysis

Figure 7 shows the ^{13}C MAS-NMR Spectrum of crystalline orthoperiodate $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$. This Spectrum is in good agreement with the X-ray structure. Indeed, it exhibits tow resonnance peaks at 43.57 and 41.05 ppm, with their corresponding satellite spinning side bands. These NMR components are related to the tow cristallographicallly inequivalent carbon which exist in the assymetric unit

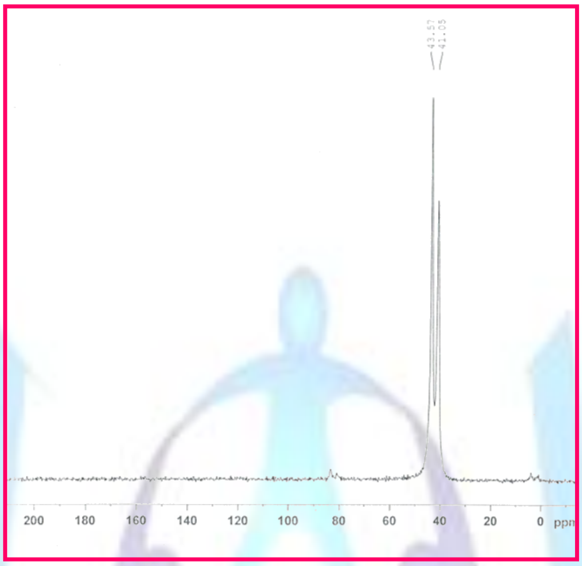

Figure 7. ^{13}C MAS-NMR Spectrum for $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$

3.6 Conclusion

The first organic cation periodate, $(C_4H_{12}N_2)(H_4IO_6)_2.2H_2O$, has been prepared and structurally characterized. The atomic arrangement of this periodate consists of a three-dimensional network of tetrahydrogenperiodate anions, water molecules and piperazinium dication connected by Ow-H…O, N−H···O and C−H···O hydrogen bonding interactions. Upon heating, this salt lost the crystallization water molecules then begins to degrade. The UV cut of wavelength indicates an energy gap 4 eV, a value indicating that this material could be used for optical applications in far UV region.

REFERENCES

[1] M. Alexandrova, H. Heuseler, Journal of molecular structure, (2004), 706,7

[2] T. Kraft, M. Jansen, Zeitschrift für anorganische und allgemeine Chemie, (1994), 620, 805

[3] J.G. Hu, Acta cristallographica, (2011), 67, 0472

[4] H.K.Fun, C.S.Yeap, C.S.Chidan Kumar, H.S.Yathirayan et B. Narayana, Acta Cristallographica, (2010), 66, 0361.

[5] H.R.Girisha, S. Naveen, K. Vinaya, M.A.Sridhar et K. S. Rangappa, Acta cristallographica,(2008),64, 0358.

[6] G.M. Sheldrick, Acta crystallographica, (2008), 64,112.

[7] F.H. Allen, O.Kennard, D.G. Watson, L. Brammer, et R. Taylor, journal of the Chemical Society, Perkin Transactions2, (1987), 1.

[8] A. V.Polishchuk, E.T. Karaserva et M. A. Pushilin, Acta crystallographica, (2009), 65, 1377

[9] R.Kefi, C.B.Nasr, Zeitschrift für Kristallographie - New Crystal Structures,(2005), 220,241

[10] Z.H.Liu, J.JZhang, W.J.Zhang, Inorganica chimica Acta, (2006), 69, 359

[11] Z. Liu, L. Li, J. Li, M. Hu, Journal of Alloysand compounds, (2005), 394, 277

[12] K.P.Blwvana, S.R Jeabas, materials letters journals, (2007),61,1489