Synthesis and Physico-Chemical Characterization of a New Non-Centrosymmetric Organic Cation Iodate

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ABSTRACT

The synthesis, crystal structure and physico-chemical characterization are presented for the piperazinium bis iodate dihydrate. An X-ray investigation has shown that this compound crystallizes in a non-centrosymmetric monoclinic system, space group Pc with the lattice parameters: a = 8.969 (2) Å, b = 6.027 (3) Å, c = 11.958 (2) Å; V = 612.7 (3) Å^3 and Z = 2. The structure was solved from 3546 independent reflexions with R_1 = 0.053 and wR_2 = 0.130. I···O halogen bonds [$R_2^2(4)$ graph-set motif] range between 2.770 (4) and 3.108 (1) Å and connect neighboring IO_3^- anions with each other so as to create a bi-dimensional layer parallel to the (b,c) plane. These layers are interconnected via N−H···O and C−H···O, to the piperazinium dication to generate a three-dimensional network.

Indexing terms/Keywords

Organic-inorganic hybrid; Crystal structure; IR Spectroscopy; DSC analysis; Band-gap.

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1. INTRODUCTION

Kurtz and Coworkers [1] have suggested that molecules or ions of the form BO_x^{n-}, where the B atom has a non bonded pair of electrons, could be appropriate building blocks in order to generate acentric crystals. Thus they considered the iodate ion IO_3^- as a good potential candidate. Organic iodates are of considerable interest because many of these materials exhibit pyroelectric or ferroelectric behavior and they may have potential application in nonlinear optical materials [2,3]. On the other hand, piperazine is a very interesting ligand because of its good bridging ability [4-6] and its biologically activity such as antifungal, antibacterial, antipsychotic [7]. In this paper, we report the crystal structure and the physico-chemical results of a non-centrosymmetric $(C_4H_{12}N_2)(IO_3)_2.2H_2O$ phase.

2. EXPERIMENTAL

2.1 Material Preparation

Crystals of piperazinium bisiodate dihydrate were obtained by mixing, in stoichiometric ratio, a solution of iodic acid (1 M) with an aqueous solution of piperazine (0.86 g). The mixture was stirred for 1 hour, and then the precipitated was filtered. The obtained solution was slowly evaporated at room temperature. After 2 weeks of evaporation at 278 K, colorless cube shaped crystals appear in the solution. Annal. Calc. for the $(C_4H_{12}N_2)(IO_3)_2.2H_2O$: C, 10.135 %; N, 5.911 %; Found: C, 11.118 %; N. 5.347 %.

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 [8] 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 $R_1= 0.053$ and $wR_2= 0.130$.

Elemental analyses were performed on a thermo flash EA 1112 elemental analyzer.

The infrared spectrum of the $(C_4H_{12}N_2)(IO_3)_2.2H_2O$ was recorded on a Nicolet IR200 FT-IR Spectrometer at ambient temperature.

The differential scanning calorimetric 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.

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 final atomic coordinates and U_{eq} or U_{iso} are given in Table 2.

Table 1. Crystal data and structure refinement

Empirical formula	$C_4H_{16}I_2N_2O_8$
Formula weight(g.mol^{-1})	473.99
Temperature (K)	293
Wavelength (Å)	0.56087
Crystal system	monoclinic
Space group	Pc
a (Å)	8.969 (2)
b (Å)	6.027 (3)
c (Å)	11.958 (2)
β (°)	108.567 (2)
Volume (Å^3)	612.7 (3)
Z	2

D_{calc} (g.cm^{-3})	2.569
Absorption coefficient (mm^{-1})	2.74
F(000)	448
Crystal size (mm^3)	0.35 × 0.30 × 0.20
Reflections collected	4552
Independent reflections parameters	3290
Goodness-of-fit on F²	1.12
Final R indices [I > 2 sigma (I)]	R_1=0.053 and wR_2= 0.130
Flack parameter	-0.11 (2)
Largest diff. peak and hole (e. Å^{-3})	0.431 and -2.95

Table 2. Atomic coordinates and equivalent isotropic thermal parameters

Atoms	X(σ)	Y(σ)	Z(σ)	U_{eq}.or U^*_{iso}
I1	0.00078 (3)	0.21035 (7)	0.00006 (2)	0.01665 (1)
I2	0.20231 (3)	0.28938 (8)	0.31696 (2)	0.01740 (1)
O1	0.0973 (1)	0.0536 (1)	0.3455 (7)	0.0322 (2)
O2	0.2670 (1)	0.1839 (1)	0.2011 (7)	0.0211 (1)
O3	0.3893 (1)	0.2845 (1)	0.4369 (8)	0.039 (2)
O4	−0.0718 (9)	0.3434 (1)	0.1135 (7)	0.0205 (1)
O5	−0.1779 (1)	0.2112 (1)	−0.1163 (9)	0.0321 (2)
O6	0.0923 (1)	0.4539 (1)	−0.0339 (8)	0.043 (2)
O7	0.285 (2)	−0.3029 (2)	0.1886 (2)	0.052 (4)
O8	−0.0759 (1)	0.8052 (1)	0.1260 (2)	0.030 (2)
N1	−0.2754 (9)	0.1134 (1)	0.2157 (8)	0.0213 (1)
N2	−0.5339 (8)	0.3986 (1)	0.1051 (6)	0.0179 (1)
C1	−0.4071 (1)	0.0269 (2)	0.1147 (1)	0.029 (2)
C2	−0.4795 (1)	0.2173 (1)	0.0389 (9)	0.0143 (1)
C3	−0.315 (2)	0.2812 (2)	0.2937 (1)	0.038 (4)
C4	−0.3950 (1)	0.4725 (1)	0.2034 (8)	0.0214 (2)
H10	−0.067 (11)	0.664 (4)	0.119 (6)	0.019 (2)*
H11	−0.015 (6)	0.840 (9)	0.194 (3)	0.000 (1)*

H12	0.219 (11)	−0.235 (1)	0.214 (1)	0.03 (2)*
H13	0.29 (3)	−0.437 (12)	0.21 (2)	0.18 (12)*
H1A	−0.2037	0.1739	0.1867	0.026*
H2A	−0.5744	0.5130	0.0566	0.021*
H3A	−0.2214	0.3341	0.3539	0.046*
H4A	−0.4270	0.5907	0.2459	0.026*
H1B	−0.2292	−0.0027	0.2608	0.026*
H2B	−0.6087	0.3461	0.1335	0.021*
H3B	−0.3875	0.2210	0.3313	0.046*
H4B	−0.3176	0.5332	0.1707	0.026*
H1C	−0.3678	−0.0799	0.0703	0.035*
H2C	−0.5688	0.1650	−0.0254	0.017*
H1D	−0.4844	−0.0460	0.1433	0.035*
H2D	−0.4037	0.2792	0.0050	0.017*

The asymmetric unit of the title compound, $(C_4H_{12}N_2)(IO_3)_2 \cdot 2H_2O$ (Figure 1), contains two independent iodate anions, one piperazinium dication and two water molecules. Each of the I atoms in the iodate adopts a trigonal pyramidal geometry with the lone pair of electrons (LEP) of iodine pointing at the fourth vertex of a tetrahedron. The bond angles at the I atoms vary in the range from 95.95 (1) to 100.76 (1) ° for I(1) and 99.19 (1) to 104.10 (1) ° for I(2). The I-O bond lengths (in the range from 1.757 (2) to 1.781 (1) Å) and the O-I-O bond angles (Table 3) are comparable to those in similar compounds like $C_{12}H_{14}N_2^{2+} \cdot 2IO_3^-$ [9], $(C_6H_{16}N_2O_2)^{2+}(HI_2O_6)^-(IO_3)^-$ [10].
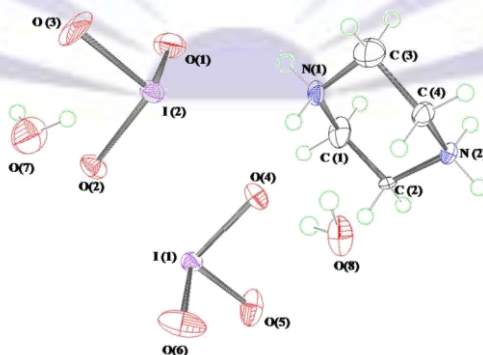

Figure 1. ORTEP view of $(C_4H_{12}N_2)(IO_3)_2 \cdot 2H_2O$, showing 50% probability ellipsoids

Table 3. Selected bond distances (Å) and angles (°) for $(C_4H_{12}N_2)(IO_3)_2.2H_2O$

I(1)O$_6$ octahedron

Atoms	Distances (Å)	Atoms	Angles (°)
I(1)−O(4)	1.863 (1)	O(4)−I(1)−O(5)	97.69 (1)
I(1)−O(5)	1.757 (2)	O(4)−I(1)−O(6)	95.95 (1)
I(1)−O(6)	1.790 (1)	O(5)−I(1)−O(6)	100.76 (1)
I(1)···O(1)	2.777 (1)	O(2)−I(1)−O(8)	78.23 (1)
I(1)···O(2)	2.802 (4)	O(2)−I(1)−O(1)	100.2 (1)
I(1)···O(8)	3.060 (1)	O(8)−I(1)−O(1)	92.1 (1)

I(2)O$_6$ octahedron

Atoms	Distances (Å)	Atoms	Angles (°)
I(2)−O(1)	1.796 (1)	O(1)−I(2)−O(2)	100.72 (1)
I(2)−O(2)	1.781 (1)	O(1)−I(2)−O(3)	104.10 (1)
I(2)−O(3)	1.827 (3)	O(2)−I(2)−O(3)	99.19 (1)
I(2)···O(4)	2.874 (4)	O(4)−I(2)−O(6)	95.61 (1)
I(2)···O(6)	2.770 (1)	O(4)−I(2)−O(7)	100.2 (1)
I(2)···O(7)	3.108 (1)	O(6)−I(2)−O(7)	92.1 (1)

Organic group

Atoms	Distances (Å)	Atoms	Angles (°)
C2−C1	1.478 (1)	N1−C3−C4	102.3 (1)
C3−C4	1.586 (2)	C4−N2−C2	107.5 (7)
N2−C2	1.519 (1)	N2−C4−C3	113.9 (8)
N2−C4	1.483 (1)	C2−C1−N1	107.8 (7)
N1−C1	1.489 (1)		
N1−C3	1.493 (2)		

In the title compound the anions are packed so that the two iodine atoms face each other, favoring the formation of two weak I···O contacts per anion, one through the iodine atom and one through an oxygen atom, giving rise to a dimeric anion $R_2^2(4)$ rings. These I···O contacts (I(1)···O(2)= 2.802 Å and I(2)···O(4)= 2.874 Å) are shorter than the sum of the van der Waals radii (3.50 Å), however, they are comparable to I···O contacts found in other organic iodate having a similar dimeric anion. [8] The usual motif found for iodate salts, is a 4-membered ring containing two O and two I atoms and four I-O halogen bonds, however, a few other motifs are also found for crystal packing based an halogen bonds [11]. These dimeric anions $(I_2O_6)^{2-}$ are interconnected by O(1) and O(6) oxygen atoms to built up an undulating layers parallel to the (b,c) planes (Figure 2). Taking into account these long bonds, all the iodine atoms become pseudo-octahedral coordinated with the I atom displaced off center along the threefold axis [12].
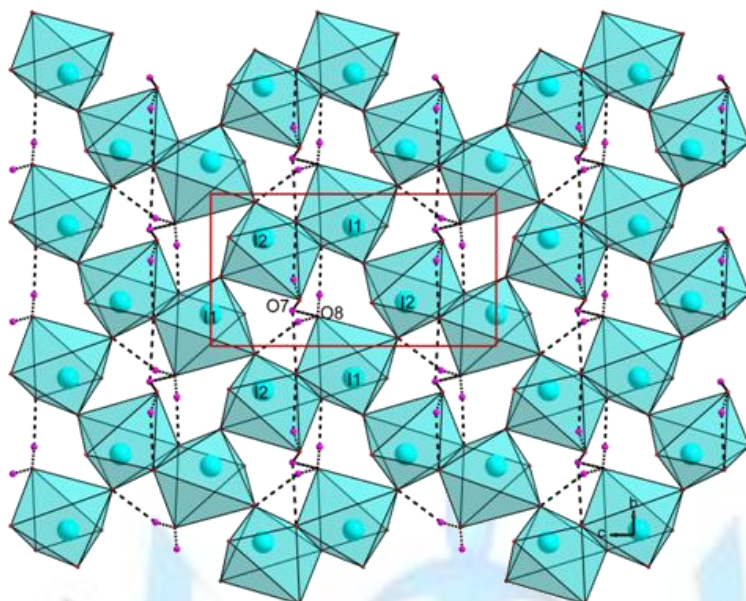
Figure 2. Two dimensional (2D) layer composed of iodates anions with hydrogen bonds as dotted lines

The I-I distances between two IO$_3^-$ anions are 6.027 and 6.496 Å for I(1) and I(2) respectively and the shortest I(1)···I(2) distance is 3.673(1) Å. By taking into account the six fold coordination of the iodine atoms, we have proceeded to calculate the bond valence sum of this halogenide given by Brown [13]. This calculation, reported in Table 4, shows the correspondence between the expected and the experimental valence (I^{5+}).

Table 4. Bond-valence distribution of the iodine atom in IO$_3^-$ anions

	S1	S2	S3	S4	S5	S6	$V = \sum_{I=1}^{6} Si$
I(1) O$_3$	1.459	1.944	1.778	0.123	0.115	0.057	5.476
I(2) O$_3$	1.749	1.822	1.609	0.094	0.125	0.050	5.449
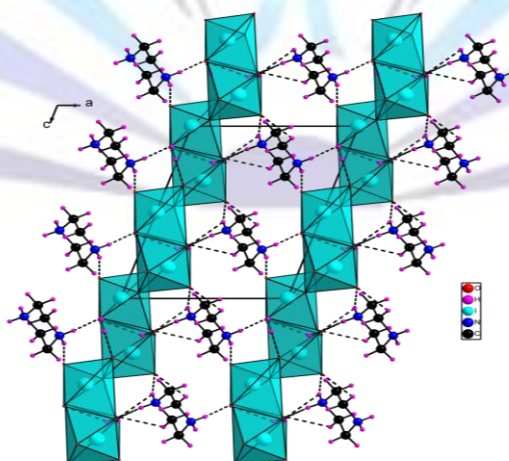
Figure 3. Crystal packing with hydrogen bonds as dotted lines

Table 5. Principal intermolecular distances (Å) and bond angles (°) of the hydrogen bonding scheme

Donor-H···Acceptor	D−H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)
N(1)−H(1A)···O(4)	0.90	1.97	2.859 (12)	171
N(1)−H(1B)···O(5)	0.90	1.88	2.741 (12)	160
N(2)−H(2A)···O(3)	0.90	1.83	2.699 (11)	162
N(2)−H(2B)···O(2)	0.90	1.85	2.736 (11)	167
N(2)−H(2B)···O(7)	0.90	2.49	2.812 (18)	101
O(8)−H(10)···O(4)	0.86 (3)	1.93 (3)	2.788 (10)	172 (9)
O(8)−H(11)···O(1)	0.85 (4)	2.19 (4)	2.992 (15)	158 (5)
O(7)−H(12)···O(2)	0.85 (11)	2.57 (9)	2.945 (12)	108 (8)
O(7)−H(12)···O(8)	0.85 (11)	2.53 (11)	3.15 (2)	131 (10)
O(7)−H(13)···O(2)	0.84 (12)	2.29 (8)	3.103 (12)	161
C(1)−H(1C)···O(8)	0.97	2.58	3.221 (15)	123
C(1)−H(1C)···O(3)	0.97	2.57	2.985 (14)	106
C(4)−H(4A)···O(7)	0.97	2.53	3.13 (2)	119

In this non-centrosymmetric unit-cell, there is one piperazin-1.4-dium dication with a chair conformation. These cations are located between the iodates layers at x = 1/2 through N−H···O ($d_{N···O}$ = 2.758 Å) and C−H···O ($d_{C···O}$ = 2.985 Å) hydrogen bonds (Table 5), van der Waals interaction and electrostatic forces, to generate a three-dimensional network (Figure 3). The table 3 reports the principal geometrical features of the piperazinium cation. The C−C and C−N bond lengths are similar to those reported in related compound such as $(C_4H_{12}N_2(H_2PO_4)_2)$ [14], $(B_3O_4(OH)·0.5(C_4H_{10}N_2))$ [15], $((C_4H_{12}N_2)^{2+}.2(H_2AsO_4)^-)$ [16].

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 [17].

- Frequencies in the range 3600 and 2300 cm^{-1} are attributed to the stretching of the organic group ν(N−H), ν(C−H) and ν(O−H) of H_2O molecules.

- Bands in the 1600-1200 cm^{-1} region correspond to the valence of C−N group and the bending vibrations of N−H and O−H groups.

- The symmetric v_1 and antisymmetric v_3 iodate stretching bonds appear in the range 691-833 cm^{-1} and the bonds of its bending mode are observed between 463 and 506 cm^{-1} [18].
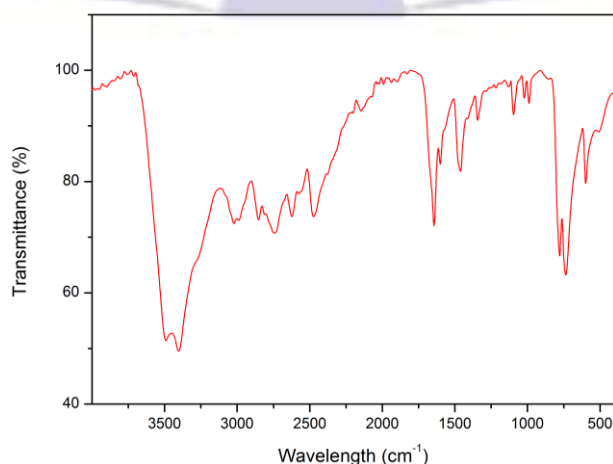
Figure 4. IR absorption spectrum of $(C_4H_{12}N_2)(IO_3)_2.2H_2O$

3.3 UV Absorption and Diffuse Reflectance

The UV absorption spectrum revealed one little intensity band at 273.29 nm. These band indicates the n→π* transition of the iodate IO_3^- anions. Optical diffuse reflectance spectrum (Figure 5) indicates an optical band gap of 4.37 eV, hence, $(C_4H_{12}N_2)(IO_3)_2.2H_2O$ is a wide-band-gap of dielectric material. A similar high gap energy value was observed in glycine potassium iodate and lies at 5.92 eV [17].

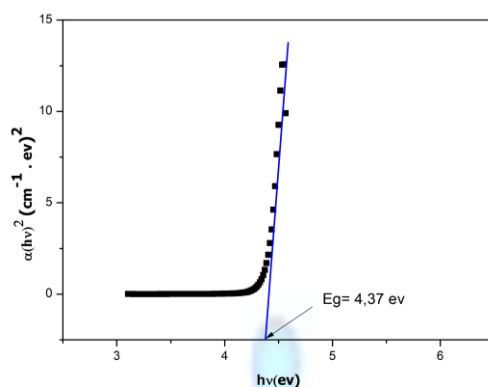**Figure 5. UV diffuse reflectance spectrum for $(C_4H_{12}N_2)(IO_3)_2.2H_2O$**

3.4 DSC analysis

DSC curve reveals series of endothermic peaks (Figure 6). The first peak, at 130°C, corresponds to an elimination of the two crystallization water molecules. After the dehydration, the organic entity of the anhydrous compound begins to decompose in a wide temperature range to release I_2, O_2 molecules and a black residue of carbon.

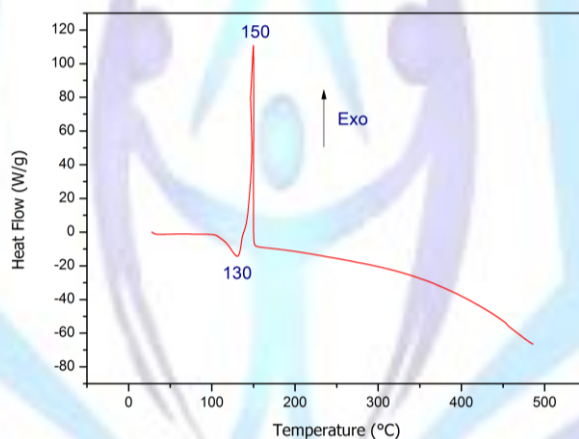**Figure 6. DSC diagram for $(C_4H_{12}N_2)(IO_3)_2.2H_2O$**

3.5 Conclusion

A non-centrosymmetric material, $(C_4H_{12}N_2)(IO_3)_2.2H_2O$, with Pc space group symmetry has been prepared and structurally characterized. The atomic arrangement of this iodate consists of a three-dimensional network of $R_2^2(4)$ graph-set motifs of

iodate anions and piperazinium dication connected by 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 4.37 eV which is a typical of dielectric material. This compound may be potentially a good candidate for application as new second-order non linear optical (NLO) materials.

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