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Rinaldo Poli, John Gordon, Raj Khanna, Phillip Fanwick. The first discrete structure for the heptaiodide ion. *Inorganic Chemistry*, 1992, 31 (14), pp.3165-3167. 10.1021/ic00040a032 . hal-03534713

HAL Id: hal-03534713

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Submitted on 19 Jan 2022

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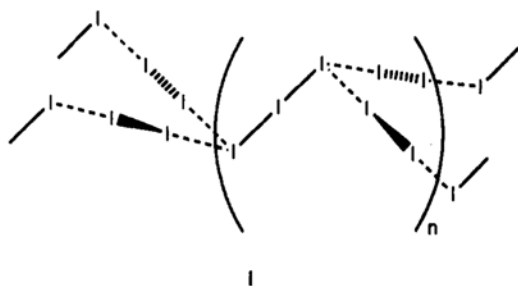
The First Discrete Structure for the I_7^- Ion

Rinaldo Poli,^{a,1a} John C. Gordon,^{1a} Raj K. Khanna,^{1a} and Phillip E. Fanwick^{1b}

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received February 5, 1992

Polyiodides constitute a class of long known, yet relatively poorly understood, materials.² Only two solid-state structures, $[NEt_4]^+I_7^-$ ³ and $[(py)_2I]^+I_7^-$,⁴ have been reported for the hepta-iodide ion, I_7^- , both showing the same two-dimensional network of symmetrical I_3^- ions joined by I_2 units at close contacts (see I), thus corresponding to the formulation $[Cat]^+(I_3)^- \cdot 2I_2$. Infrared



and Raman studies of several polycrystalline I_7^- salts have been carried out,⁵⁻⁸ one of them suggesting a different formulation, i.e. $I_5^- \cdot I_2$.⁸ Here we report the crystal structure of $[PPh_4]^+I_7^-$, which is only the third hepta-iodide salt to have been crystallographically characterized and the first one to exhibit discrete I_7^- ions.

Experimental Section

All operations were carried out under dinitrogen by using standard Schlenk-line and glovebox techniques. The solvents CH_2Cl_2 and 1,1,2- $C_2H_3Cl_3$ were distilled from P_2O_5 . The MoI_3 starting material was prepared according to the published procedure.⁹ Low-energy IR spectra were recorded on a Perkin-Elmer 1800 spectrometer by using Nujol as dispersant and polyethylene plates as transparent support. Raman spectra were recorded on a SPEX 1401 spectrometer equipped with a Krypton laser. The sample, in the form of a pressed pellet of the microcrystalline solid in dry KBr, was kept spinning during the measurements to avoid decomposition by overheating. No change in the appearance of the solid or in the resulting spectrum was noticed after repetitive scans.

Preparation of $PPh_4^+I_7^-$. Method 1. To a suspension of MoI_3 (0.827 g, 1.83 mmol) in freshly distilled CH_2Cl_2 (20 mL) was added a solution of $PPh_4^+I^-$ (0.852 g, 1.83 mmol) in CH_2Cl_2 (20 mL). Since no reaction appeared to occur at room temperature overnight, the solvent was removed under vacuum and replaced with Cl_2CHCH_2Cl (20 mL). The mixture was refluxed for approximately 3.5 days to produce a brown solution with

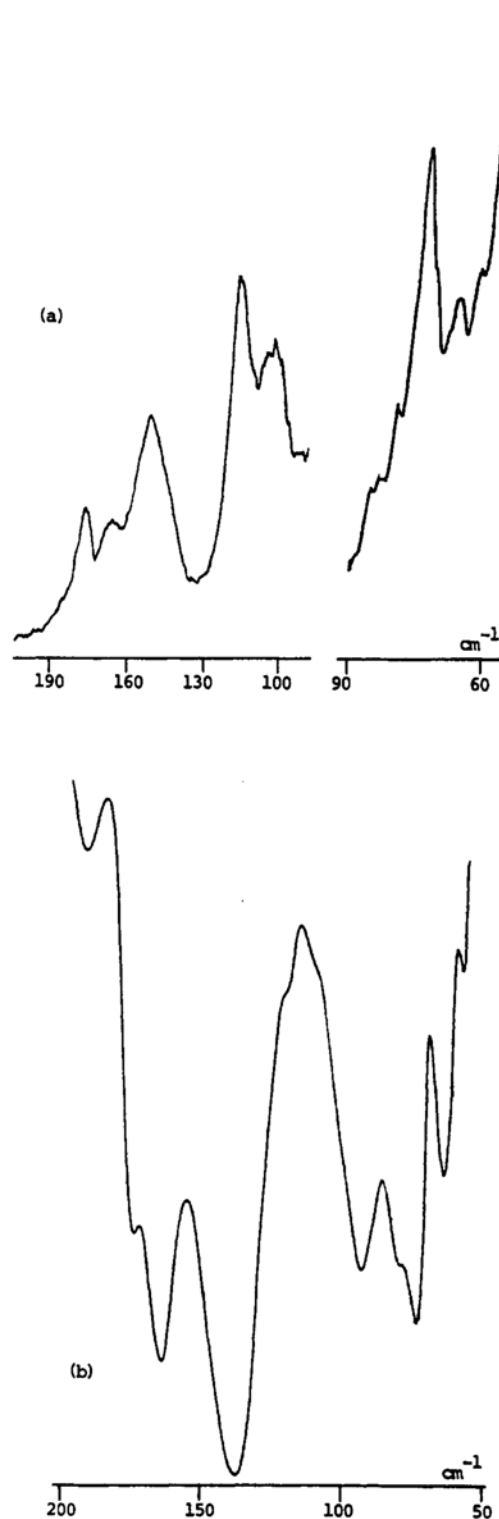


Figure 1. Low-energy Raman (a) and IR (b) spectra of $PPh_4^+I_7^-$.

some residual precipitate. Filtration and cooling to $-20^\circ C$ led to the formation of dark crystals, which were separated from the solution, washed with heptanes (10 mL), and dried under vacuum. Concentration of the mother liquor to approximately half the original volume and cooling to $-20^\circ C$ led to the isolation of an additional batch of crystalline material; total yield 1.030 g. This material was heterogeneous, showing two different types of crystal habits (see Results and Discussion). A single crystal from this batch was used for the X-ray analysis. The Raman spectrum of this material contains the same resonances observed for pure PPh_4I_7 , prepared as described below.

Method 2. I_2 (0.816 g, 3.21 mmol) was added to a solution of $PPh_4^+I^-$ (0.500 g, 1.07 mmol) in CH_2Cl_2 (30 mL) and the mixture allowed to stir for 2 h. During this period, the I_2 dissolved and the solution became

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Table I. Crystal Data for $\text{PPh}_4^+\text{I}_7^-$

formula	$\text{C}_{24}\text{H}_{20}\text{I}_7\text{P}$
fw	1227.73
space group	$P2_1/c$
a , Å	10.197 (2)
b , Å	18.558 (4)
c , Å	16.936 (3)
β , deg	94.65 (1)
V , Å ³	3194 (2)
Z	4
d_{calc} , g/cm ³	2.553
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	67.93
radiation (monochromated in incident beam)	Mo K α ($\lambda = 0.71073$ Å)
temp, °C	20
transm factors: max-min	1.000-0.424
R^a	0.040
R_w^b	0.048

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

brown. Filtration and concentration to approximately one-third of the original volume, followed by cooling to -20 °C overnight, led to the formation of the product, which was separated from the mixture, washed with 50 mL of heptanes, and dried under vacuum; yield 1.085 g. Concentration of the mother liquor and repetition of the above procedure led to the isolation of a further crop of 0.024 g; total yield 1.109 g (84.3%). Anal. Calcd for $\text{PPh}_4^+\text{I}_7^-$: C, 23.48; H, 1.64. Found: C, 23.85; H, 1.66. The low-energy Raman and IR spectra of this material are shown in Figure 1.

X-ray Analysis. A dark red crystal was mounted in a glass capillary in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 25 reflections in the range $18 < \theta < 22^\circ$. From the systematic absences, the space group was uniquely determined as monoclinic $P2_1/c$. Lorentz and polarization corrections were applied to the data. The structure was solved with the direct methods of SHELXS-86,¹⁰ which revealed the positions of the iodine atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. At the end of the isotropic refinement, an empirical absorption correction was applied.¹¹ Selected crystal and refinement parameters are collected in Table I, atomic coordinates are listed in Table II, and the bond distances and angles of the I_7^- ion are shown in Figure 2, together with an ORTEP view of the ion.

Results and Discussion

The PPh_4I_7 compound was first obtained from the reaction of MoI_3 with PPh_4I in an attempt to form an iodomolybdate ion. The crystals obtained from this solution were a mixture of $[\text{PPh}_4]\text{I}_3$ ¹² and the new heptaiodide salt. The molybdenum is presumably in a reduced form in the insoluble material that was observed at the end of the reaction, and which was not investigated further. The I_7^- compound has since been obtained more selectively by interaction of PPh_4I and I_2 in a 1:3 molar ratio. Single crystals were obtained from 1,1,2- $\text{C}_2\text{H}_3\text{Cl}_3$ at -20 °C.

The anion can be described as an isolated portion of the extended three-dimensional structure found for the other two salts (compare Figure 1 with structure I), including the description as a Lewis base I_3^- (I-I21-I22) interacting with two I_2 acceptors (I11-I12 and I31-I32). The I-I21 distance is shorter than the I-I11 and I-I31 distances, and correspondingly, the I21-I22 bond is longer than the I11-I12 and I31-I32 bonds. The latter distances are much closer to the bond length of 2.68 Å found in crystalline I_2 .¹³ All bond angles at the central iodine atom are close to 90°, and the bond angles at the atoms I11, I21, and I31 are all close to

Table II. Positional Parameters and Their Estimated Standard Deviations for PPh_4I_7

atom	x	y	z	B_i^a , Å ²
I	-0.37887 (9)	0.10109 (5)	-0.03648 (5)	5.89 (2)
I11	-0.05870 (9)	0.11229 (5)	0.00710 (5)	5.49 (2)
I12	0.2073 (1)	0.10722 (6)	0.04507 (6)	6.96 (2)
I21	-0.44364 (7)	0.25892 (5)	-0.00746 (4)	4.72 (2)
I22	-0.4820 (1)	0.40583 (5)	0.02463 (6)	7.17 (2)
I31	-0.39634 (8)	0.06949 (5)	0.15301 (6)	5.58 (2)
I32	-0.40351 (9)	0.05032 (7)	0.31242 (6)	8.10 (3)
P	0.0717 (2)	0.1641 (2)	0.3307 (2)	3.35 (5)
C11	0.0896 (9)	0.0781 (5)	0.2868 (6)	3.4 (2)
C12	-0.009 (1)	0.0502 (6)	0.2318 (6)	4.5 (3)
C13	0.009 (1)	-0.0167 (6)	0.1995 (6)	4.6 (3)
C14	0.120 (1)	-0.0567 (6)	0.2200 (7)	5.2 (3)
C15	0.213 (1)	-0.0295 (6)	0.2744 (7)	5.3 (3)
C16	0.198 (1)	0.0365 (6)	0.3075 (7)	4.5 (3)
C21	-0.0706 (8)	0.2084 (5)	0.2861 (5)	3.1 (2)
C22	-0.0702 (9)	0.2261 (6)	0.2060 (6)	4.4 (2)
C23	-0.1755 (9)	0.2620 (6)	0.1686 (6)	4.2 (2)
C24	-0.2796 (9)	0.2804 (6)	0.2105 (7)	4.1 (2)
C25	-0.2798 (9)	0.2644 (6)	0.2888 (6)	4.3 (2)
C26	-0.1762 (9)	0.2274 (6)	0.2271 (6)	4.0 (2)
C31	0.2057 (9)	0.2218 (5)	0.3100 (6)	3.3 (2)
C32	0.2953 (9)	0.2010 (6)	0.2583 (6)	4.4 (2)
C33	0.382 (1)	0.2520 (6)	0.2331 (7)	4.9 (3)
C34	0.383 (1)	0.3212 (7)	0.2614 (7)	5.2 (3)
C35	0.295 (1)	0.3416 (6)	0.3139 (8)	5.4 (3)
C36	0.206 (1)	0.2919 (6)	0.3378 (7)	5.0 (3)
C41	0.0628 (9)	0.1493 (6)	0.4343 (6)	3.8 (2)
C42	0.156 (1)	0.1765 (8)	0.4904 (7)	5.6 (3)
C43	0.149 (1)	0.1598 (9)	0.5691 (7)	7.3 (4)
C44	0.049 (1)	0.1165 (8)	0.5923 (7)	7.2 (4)
C45	-0.041 (1)	0.0891 (8)	0.5376 (7)	6.4 (3)
C46	-0.037 (1)	0.1063 (7)	0.4585 (7)	5.4 (3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

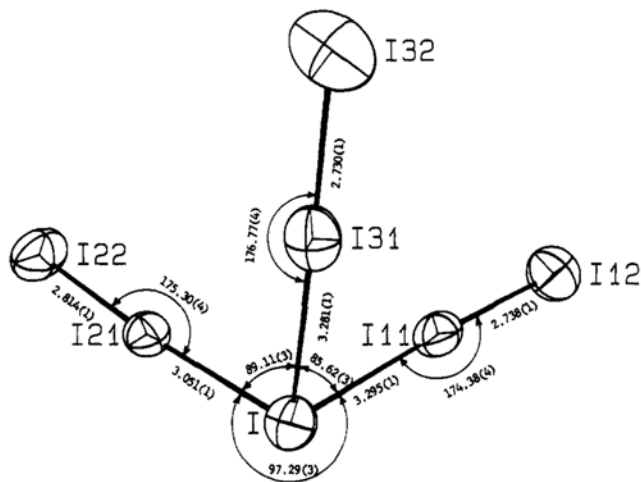


Figure 2. ORTEP view of the I_7^- anion with the atomic numbering scheme and bond distances (Å) and angles (deg).

180°. The relative spatial arrangement is different from that shown in structure I, as can be appreciated from the packing diagram in Figure 3. Thus, the crystal packing of the PPh_4^+ salt is not simply the result of a volume expansion of the packing in the other two salts as a consequence of the larger size of the cation. The closest interionic I...I contact is 3.605 (1) Å between I22 and its symmetry-related counterpart. Compared with the extended I_7^- structures mentioned above,^{3,4} the anion in the PPh_4^+ salt shows substantially the same I-I distance for the two " I_2 " units, although these are substantially closer to the central, tri-coordinated I atom. The " I_3 " unit, however, is significantly distorted in the present structure whereas this is perfectly symmetrical in the previously reported extended structures. The average of the two I-I distances in the " I_3 " unit (2.93 Å) is about

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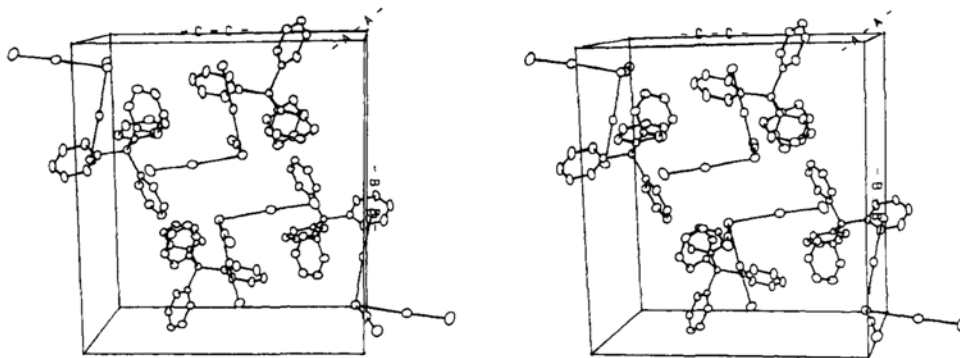


Figure 3. Stereoscopic view of the unit cell for $\text{PPh}_4^+\text{I}_7^-$.

the same as the values found for the Et_4N^+ and $(\text{py})_2\text{I}^+$ salts (2.904 (3) and 2.93 Å, respectively), the outer distance being significantly shorter and the inner one significantly longer. By comparison with the structure of the L-shaped I_5^- unit, which shows outer and inner I–I distances of 2.81 and 3.17 Å, respectively, for the NMe_4^+ salt,¹⁴ one can conclude that the effect of more loosely binding two I_2 Lewis acids to the same end of the I_3^- unit is similar to the effect of binding a single I_2 Lewis acid more strongly.

The observed structural parameters are consistent with the observed Raman and IR spectra of the compound (Figure 1), in the light of previous Raman and IR studies for polyiodide anions.^{5–8} First, we point out that the low symmetry (C_s) of the molecule in the crystal makes all molecular modes both IR and Raman active. However, given the centrosymmetric space group and the presence of four molecules per unit cell, normal modes from different molecules combine to give Raman-active “g-type” modes and IR-active “u-type” modes that do not necessarily have the same frequencies. The observed spectra for the PPh_4^+ salt (Figure 1) are very different from those observed for the extended I_7^- structure in the Et_4N^+ salt⁷ and different also from those reported for the *N*-butylurotropinium salt.⁸ The modes at 178 and 166 cm^{-1} (Raman) and at 175 and 166 cm^{-1} (IR) can be assigned to the asymmetric stretches of the “I...I–I” units, with a larger component from the strong I–I interaction. The frequencies of

these vibrations compare favorably with those reported for other weakly bound I_2 units, and the higher relative intensity in the IR spectrum is consistent with their having an asymmetric character. The modes at 152 cm^{-1} (Raman) and 139 cm^{-1} (IR) are assigned to the asymmetric stretch of the “ I_3^- ” unit. These are in the same range found for other asymmetric stretches for I_3^- salts and for polyiodides containing the I_3^- unit.^{5,7} The stronger relative intensity in the IR spectrum is consistent with an asymmetric mode. The Raman band at 118 cm^{-1} is in the typical range found for I_3^- salts and can thus be assigned to the symmetric mode of the “ I_3^- ” unit. This mode should have a very low intensity in the IR spectrum, and we assign it to the small shoulder visible at ca. 113 cm^{-1} . The assignment of the remaining bands in the 110–70- cm^{-1} region is not clear-cut, but we observe that bands due to the stretching vibration of inner, weaker I...I bonds have previously been reported in this region.^{6,7} The strong Raman band at 74 cm^{-1} seems to be most consistent with a symmetric mode of the “I...I–I” units which has a greater contribution from the weak I...I interaction.

Acknowledgment is made to the National Science Foundation (PYI Award to R.P., CHE-9058375) for support.

Supplementary Material Available: A detailed textual description of X-ray data collection and structure solution and refinement and tables of crystal data, hydrogen atom positions, anisotropic thermal parameters, bond distances, and bond angles (11 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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