Heptacoordination. Synthesis and Characterization of the IOF_5^{2-} Dianion, an XOF_5E Species

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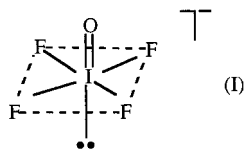
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Abstract: The new IOF_5^{2-} dianion was prepared in the form of its cesium salt by heating stoichiometric amounts of CsF, I_2O_5, and IF_5 to 162 °C for 14 days. The white stable solid was characterized by vibrational spectroscopy. A normal coordinate analysis was carried out with the help of ab initio calculations at the HF/ECP/DZP level of theory and resulted in an excellent agreement between observed and calculated frequencies. The structure of IOF_5^{2-} is that of a pentagonal bipyramid with five equatorial fluorine ligands, and an oxygen atom and one sterically active free valence electron pair occupying the two axial positions. The structure is very similar to that previously established by vibrational spectroscopy and X-ray diffraction for isoelectronic $XeOF_5^-$ and represents only the second example of a heptacoordinated XOF_5E (E = free valence electron pair) main group species. The possible existence of the IOF_6^{3-} trianion is briefly discussed.

Introduction

The existence of the IOF_4^- anion has been known for many years,[1-4] and its pseudo-octahedral structure (I) has been well established by X-ray diffraction[1] and vibrational spectroscopy.[3,4] Furthermore, the isoelectronic species $XeOF_4$ is well-known.[5-9] The recent discoveries that $TeOF_5^-$,[10] $IO_2F_4^-$,[11] IF_6^-,[12] IF_4^-,[13] and even SbF_6^- and BiF_6^- [14] can all add a second F^- ion to form the corresponding dianions and the existence of the isoelectronic $XeOF_5^-$ anion[15] prompted us to explore whether the IOF_5^{2-} anion might also be accessible and stable, and then

to establish its structure. The structure of isoelectronic $XeOF_5^-$ had been controversial and was only recently settled by a combined ab initio vibrational spectroscopy[16] and an X-ray diffraction[17] study.

Experimental Section

Materials and Methods. The I_2O_5 was obtained by heating a commercially available (from Mallinckrodt) sample of "I_2O_5", which based on its Raman spectrum was actually HI_3O_8,[18] in a dynamic vacuum at 210 °C for 12 h. The CsF (KBI) was fused in a platinum crucible, transferred while hot to the drybox, and finely powdered. The IF_5 (Matheson Co.) was treated with ClF_3 (Matheson Co.) at 25 °C until the liquid was colorless, followed by fractional condensation in a dynamic vacuum, using the −64 °C fraction.

Volatile materials were handled in a stainless steel vacuum line equipped with Teflon-FEP U-traps, 316 stainless steel bellows seal valves, and a Heise pressure gauge.[19] Solids were handled in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded on a Mattson Galaxy 5030 spectrometer using AgBr disks, which were prepared by pressing the finely powdered samples between two thin AgBr plates in a Barnes Engineering minipress inside the glovebox. Raman spectra were recorded at room temperature on a Cary Model 83 GT spectrometer using the 488 nm exciting line of an Ar ion laser.

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Preparation of Cs₂IOF₅. On the stainless steel vacuum line, IF₅ (9.255 mmol) was condensed at −196 °C into a prepassivated (with ClF₃) 95 mL Monel cylinder that was closed by a Monel valve. The cylinder was taken to the drybox, cooled to −196 °C, and opened, and preweighed stoichiometric amounts of finely powdered dry CsF (30.92 mmol) and I₂O₅ (3.086 mmol) were added. The cylinder was closed, evacuated at −196 °C, and then heated in an electric oven to 162 °C for 65 h. Inspection of the white loose product by Raman spectroscopy showed only partial conversion to IOF₅²⁻ with large amounts of I₂O₅,[18] CsIOF₄,[3,4] and Cs₂IF₇[12] being present. The product was finely powdered, returned to the cylinder, and heated to 162 °C for an additional 95 h. Examination of the solid product indicated a conversion to Cs₂IOF₅ of about 90% and a substantial decrease in the amounts of I₂O₅, CsIOF₄ and Cs₂IF₇. The product was powdered again and heated to 162 °C for an additional 188 h. At this point, the resulting white loose powder showed essentially complete conversion to Cs₂IOF₅, with a trace of CsIOF₄ being the only impurity detectable by Raman spectroscopy.

Computational Methods. Quantum chemical calculations employing the Hartree−Fock (HF) self-consistent-field method and the program Gaussian 94[20] were performed for the free, C_{5v} symmetry IOF₅²⁻ dianion. A double-ζ plus polarization (DZP) basis set for the oxygen and fluorine atoms[21] and a DZP basis set for the valence shell and an effective core potential (ECP)[22] for the inner shells of iodine were used. This level of calculation has been shown to provide excellent structures and frequencies for hypervalent main group compounds.[10−14] The geometry and vibrational frequencies were calculated using numerical derivative methods.[23] The calculated Hessian matrices (second derivatives of the energy with respect to Cartesian coordinates) were converted to symmetry-adapted internal coordinates for further analysis using the program Bmtrx.[24]

Results and Discussion

Synthesis and Properties of Cs₂IOF₅. The synthesis of Cs₂-IOF₅ was achieved by heating stoichiometric mixtures of I₂O₅, CsF, and IF₅ to 162 °C for extended time periods (eq 1). The

$$10CsF + I_2O_5 + 3IF_5 \xrightarrow[14\ d]{162\ °C} 5Cs_2IOF_5 \qquad (1)$$
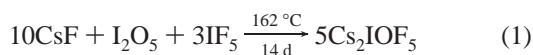
initial reaction products were mainly CsIOF₄[3,4] and Cs₂IF₇,[12] in addition to some Cs₂IOF₅. It was found important to stop the reaction periodically and intimately grind the sample. Two regrinds and a total heating time of 14 days were found sufficient to achieve essentially complete conversion to Cs₂IOF₅, with a trace of CsIOF₄ being the only impurity detectable by Raman spectroscopy. When only half the amount of CsF was used in this reaction, the principal product was CsIOF₄. Our approach of using stoichiometric amounts of I₂O₅ and IF₅ in place of IOF₃ as a starting material is not new. It has been used in the past for the synthesis of IOF₃ itself[25] and of IOF₄⁻ salts.[3] In view of this and the known ease with which IOF₃ can dismutate above 110 °C to IO₂F and IF₅,[25] no attempts were made to isolate

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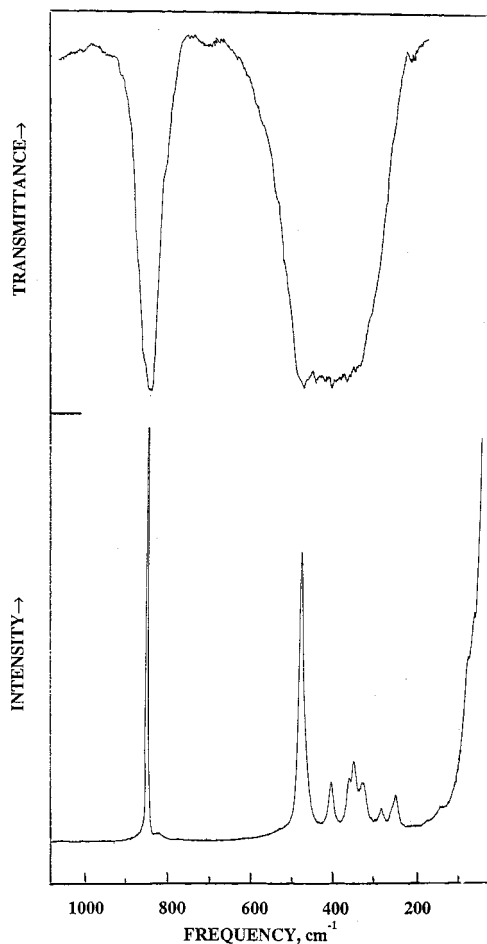

Figure 1. Infrared and Raman spectra of solid Cs₂IOF₅.

first pure IOF₃ and then react it further with CsF to prepare CsIOF₄ and Cs₂IOF₅.

The Cs₂IOF₅ salt is a white stable solid that was characterized by its vibrational spectra (see below). The growing of single crystals for X-ray diffraction or NMR studies was preempted by its poor solubility and ready loss of F⁻ ions in the usual solvents. Multi-fluorine-substituted mononuclear dianions normally lose F⁻ to any solvent, and Cs₂IOF₅ typifies that behavior.

Vibrational Spectra and Computational Results. The Raman and infrared spectra of solid Cs₂IOF₅ are shown in Figure 1, and the observed frequencies and their assignments in point group C_{5v} are summarized in Table 1. As can be seen, the observed spectra are in excellent agreement with the scaled HF/ECP/DZP frequencies and those of the closely related IF₅²⁻ [13] and isoelectronic XeOF₅⁻ [16] anions. The excellent correspondence between the vibrational spectra of XeOF₅⁻ and IOF₅²⁻ leaves no doubt that IOF₅²⁻ also possesses the pseudo-pentagonal bipyramidal C_{5v} structure found for XeOF₅⁻ in NO⁺XeOF₅⁻ by X-ray diffraction.[17] This C_{5v} structure for IOF₅²⁻ was also confirmed by the results of our ab initio calculations, which showed it to be the minimum energy structure with the oxygen atom and a sterically active free valence electron pair of iodine occupying the two axial positions of a pentagonal bipyramid.
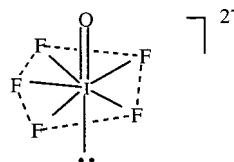
Table 1. Vibrational Spectra of Cs_2IOF_5 and Their Assignments in Point Group C_{4v} Compared to Those Observed for $XeOF_5^-$ and IF_5^{2-}

| assign (activity) | approx mode description | obsd freq, cm^{-1} (intensity) | | calcd freq, cm^{-1} (IR intens)^a | | |
		Ra	IR	HF/ECP/DZP	IF_5^{2-} ^{b}	$XeOF_5^-$ ^{c}
A_1 (IR, Ra)	ν_1 ν I=O	854 (100)	855 s	847 (71)	–	880
	ν_2 ν sym IF$_5$	485 (58)	485 w	488 (0)	474	515
	ν_3 δ umbrella IF$_5$	289 (4)	290 sh	298 (86)	[307]^d	296
E_1 (IR, Ra)	ν_4 antisym comb of ν as IF$_5$ and δ wag I=O	–	415 vs,br	414 (1032)	335	495
	ν_5 sym comb of ν as IF$_5$ and δ wag I=O	334 (5)	330 sh	343 (230)	–	370
	ν_6 δ as in-plane IF$_5$	254 (7)		255 (0)	245	273
E_2 (–, Ra)	ν_7 δ sciss in-plane IF$_5$	409 (11)		385 (0)	396	460
	ν_8 ν as IF$_5$	$\begin{cases} 367\ (2) \\ 355\ (15) \end{cases}$		363 (0)	$\begin{cases} 339 \\ 325 \end{cases}$	397
	ν_9 δ pucker IF$_5$	–		115 (0)	[100]^d	[115]^d

^{a} Empirical scaling factors of 0.9724 and 0.9244 were used for the stretching and the deformation modes, respectively. ^{b} Data from ref 13. ^{c} Data from ref 16. ^{d} Calculated value.

Table 2. Calculated HF/ECP/DZP Geometry for C_{5v} IOF$_5^{2-}$

	unscaled	scaled^a		unscaled	scaled^a
r(I=O), Å	1.722	1.70	∠O=I−F, deg	91.48	91.7
r(I−F), Å	2.041	2.08	∠F−I−F, deg	71.97	72.4

^{a} Predicted values based on scale factors from XeOF$_4$ in ref 16 and a comparison between predicted HF/ECP/DZP values for isoelectronic XeOF$_5^-$ in ref 13 and the experimental data from ref 17.

Table 3. Symmetry Force Constants^a and Potential Energy Distribution^b of C_{5v} IOF$_5^{2-}$ Calculated from the Scaled HF/ECP/DZP Second Derivatives

| | freq, cm^{-1} | | sym force consts | | | |
	obsd	calcd	F_{11}	F_{22}	F_{33}	PED
A_1	854	847	F_{11} 6.006			98.0(1) + 1.6(3) + 0.4(2)
	485	488	F_{22} 0.320	2.655		98.1(2) + 1.0(3) + 0.8(2)
	289	298	F_{33} 0.265	−0.466	2.751	91.7(3) + 8.3(2)

| | freq, cm^{-1} | | sym force consts | | | |
	obsd	calcd	F_{44}	F_{55}	F_{66}	PED
E_1	415	414	F_{44} 1.237			47.7(4) + 43.8(5) + 8.5(6)
	334	343	F_{55} −0.181	2.013		54.4(4) + 45.2(5) + 0.4(6)
	254	255	F_{66} 0.089	−0.262	1.008	63.3(6) + 34.7(5) + 2.0(4)

| | freq, cm^{-1} | | sym force consts | | | |
	obsd	calcd	F_{77}	F_{88}	F_{99}	PED
E_2	409	385	F_{77} 1.375			78.9(7) + 21.1(8)
	367	363	F_{88} 0.143	2.027		82.6(8) + 17.0(7) + 0.3(9)
	355					
	–	115	F_{99} −0.302	0.031	0.685	94.0(9) + 5.9(8) + 0.1(7)

^{a} Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad^2, and stretch−bend interaction constants in mdyn/rad. ^{b} PED in percent; symmetry coordinates: $S_1 = \nu$ I=O; $S_2 = \nu$ sym IF$_5$; $S_3 = \delta$ umbrella IF$_5$; $S_4 = \nu$ as IF$_5$; $S_5 = \delta$ wag I=O; $S_6 = \delta$ as in-plane IF$_5$; $S_7 = \delta$ sciss in-plane IF$_5$; $S_8 = \nu$ as IF$_5$; $S_9 = \delta$ pucker IF$_5$.

The geometry, predicted for IOF$_5^{2-}$ on the basis of the ab initio calculations, is given in Table 2.

Since our evidence for the structure of IOF$_5^{2-}$ rests mainly on the vibrational spectra, a normal coordinate analysis was carried out for this anion. Its symmetry force constants and potential energy distribution (PED) are listed in Table 3, and its internal stretching force constants are compared in Table 4 to those of the closely related IOF$_4^-$,[3] IF$_5^{2-}$,[13] and IF$^-_4$[26] anions and their isoelectronic xenon counterparts.[13,16,26−28]

The PED of Table 3 shows that the vibrations in the A$_1$ block are highly characteristic but that the similarities of the frequencies of the antisymmetric IF$_5$ stretching modes with those of the closest deformation modes result in strong mixing in the E blocks. This similarity is caused by the high ionicity and

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Table 4. Internal Force Constants (mdyn/Å) of IOF$_5^{2-}$, IOF$_4^-$, IF$_5^{2-}$, and IF$_4^-$ Compared to Those of the Isoelectronic Xenon Species

	f X=O	f_r (XF)	f_{rr} (XF)	f_{rr}' (XF)
IOF$_5^{2-}$ ^{a}	6.01	1.84	0.027	0.380
IOF$_4^-$ ^{b}	6.56	2.46	0.16	0.45
IF$_5^{2-}$ ^{c}	–	1.53	0.035	0.423
IF$_4^-$ ^{d}	–	2.22	0.183	0.466
XeOF$_5^-$ ^{e}	6.33	2.25	0.15	0.20
XeOF$_4$ ^{f}	7.08	3.26	0.12	0.10
XeF$_5^-$ ^{g}	–	2.10	0.14	0.26
XeF$_4$ ^{d}	–	3.06	0.12	0.01

^{a} Values from this study. ^{b} Values from ref 3. ^{c} Values from ref 13. ^{d} Values from ref 26. ^{e} Values from ref 16. ^{f} Values from ref 27. ^{g} Values from ref 28.

weakness of the equatorial IF$_5$ bonds which cause, for example, the antisymmetric IF$_5$ stretching frequency, ν_8 (E$_2$), to have a lower frequency than the in-plane IF$_5$ scissoring mode, ν_7 (E$_2$).

Inspection of Table 4 shows the expected trends. The stretching force constants of the IF$_5$ part of IOF$_5^{2-}$ are very similar to those of IF$_5^{2-}$, except for the increase in f_r on going from IF$_5^{2-}$ to IOF$_5^{2-}$, caused by the change in the iodine oxidation state from +III to +V and the concomitant increase in the covalency of the I−F bonds. On going from IOF$_4^-$ to IOF$_5^{2-}$, both the I−O and I−F stretching force constants decrease, as expected for an increased polarity of these bonds due to the additional negative charge in the dianion. The same trends hold for the isoelectronic xenon species of Table 4.

The I−F stretching force constants in IOF$_5^{2-}$ and IF$_5^{2-}$ exhibit very low values of 1.84 and 1.53 mdyn/Å, when compared to the values of 5.60 and 4.68 mdyn/Å for the highly covalent I−F bonds in IF$_6^+$ and F$_{ax}$−IF$_4$, respectively.[29] These low f_r values for IOF$_5^{2-}$ lend strong support to the highly ionic, 6-center 10-electron bond model for the five equatorial fluorine ligands, which was previously proposed and discussed in detail for XeF$_5^-$ [28] and IF$_7$.[30] The value of 6.01 mdyn/Å for the I−O bond in IOF$_5^{2-}$, although on the low side of the usual range for mainly covalent I=O double bonds, confirms that the negative charges in IOF$_5^{2-}$ are concentrated on the fluorine ligands.[31]

Possible Existence of Cs$_3$IOF$_6$. The use of a CsF:I$_2$O$_5$:IF$_5$ stoichiometry of 15:1:3, which corresponds to a final product

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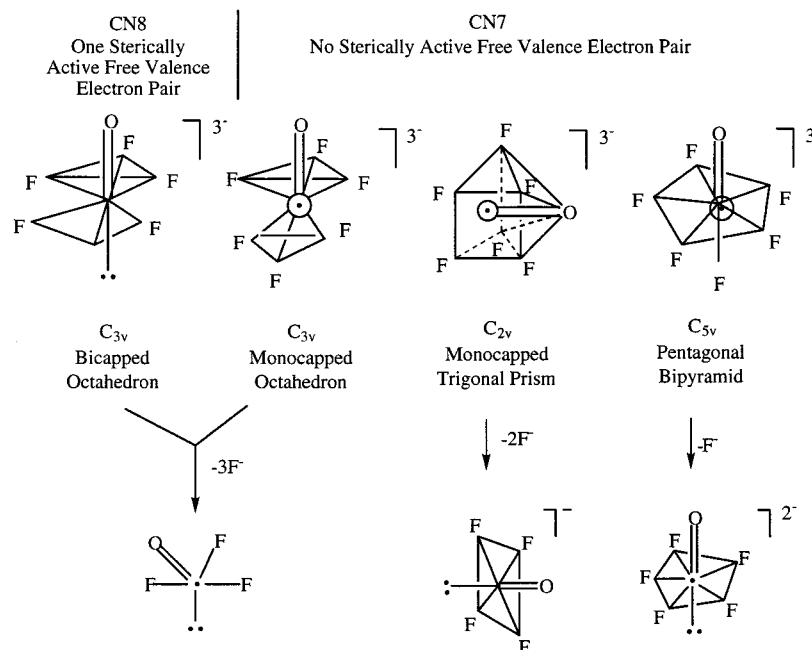
Figure 2. Most likely geometries of the IOF_6^{3-} trianion and their spontaneous decomposition modes.

having a composition of Cs_3IOF_6, resulted in a white solid, the Raman spectrum of which was distinct from that of Cs_2IOF_5. After 83 days of heating to 162 °C and periodic grinding of the sample, a new composition was obtained that gave the following Raman spectrum (cm^{-1}, relative intensity): 865 (100), 468 (100), 372 (2), 327 (24), 265 (1), 246 (7), 177 (7). The IOF_4^- and IOF_5^{2-} anions, observable in the early stages of its synthesis had vanished, and the only impurities detectable by Raman spectroscopy were traces of I_2O_5 and IF_7^{2-}.

Based on the observation of a single band in the I=O stretching mode range, the presence of a dioxo species can be precluded. To judge if this composition could represent the novel IOF_6^{3-} anion, ab initio calculations, similar to those previously used for evaluating the feasibility of IF_6^{3-},[13] were carried out. The most likely structures for IOF_6^{3-}, possessing either a sterically active or a sterically inactive free valence electron pair on iodine, are shown in Figure 2 and were tested for their tendencies to spontaneously lose fluoride ions. In all four calculations, spontaneous fluoride ion loss and no energy minima for the different IOF_6^{3-} structures were found. The C_{5v} IOF_6^{3-} structure lost one F^-, the C_{2v} structure lost two F^-, and the C_{3v} structures lost three F^- to give the stable IOF_5^{2-} and IOF_4^- ions and the IOF_3 molecule, respectively. In view of these calculations, no reliable interpretation can be offered at this time for the Raman spectrum of the "Cs_3IOF_6" composition. The fact that the I=O stretching vibration of "Cs_3IOF_6" is actually 11

cm^{-1} higher than that in IOF_5^{2-} might be interpreted as evidence against the presence of discrete IOF_6^{3-} ions.

Conclusions

This study conclusively demonstrates the existence of the IOF_5^{2-} dianion as its stable cesium salt. This dianion is only the second known example of a pseudo-pentagonal bipyramidal main group species possessing, in addition to the five equatorial fluorine ligands, one doubly bonded oxygen ligand and one sterically active free valence electron pair in the axial positions. The results from a normal coordinate analysis of the vibrational spectra show that the five equatorial ligands are relatively weakly bound through highly ionic 6-center 10-electron bonds, similar to those found for the pentagonal planar XeF_5^{-} [28] and IF_5^{2-} [13] anions. The possible existence of the IOF_6^{3-} trianion was also studied, and the presence of a new composition was indicated by the Raman spectra but ab initio calculations and a slight shift of the I=O stretching mode to higher frequency augur against the presence of IOF_6^{3-}.

(31) The Mulliken charges for IOF_5^{2-} are 2.35 e for I, −0.86 e for O, and −0.70 e for F. Thus, most of the negative charge is found in the ring of the five equatorial fluorines. Even though the oxygen has a slightly larger negative Mulliken charge than fluorine, it is partially compensated by the high positive charge on I.