Synthesis, NMR and Vibrational Spectroscopic Characterization, and Computational Study of the cis-IO$_2$F$_3^{2-}$ Anion (Postprint)

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Synthesis, NMR and Vibrational Spectroscopic Characterization, and Computational Study of the cis-IO$_2$F$_3^{2-}$ Anion

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The N(CH$_3$)$_4^+$ salt of the cis-IO$_2$F$_3^{2-}$ anion was synthesized from [N(CH$_3$)$_4$]$_2$[IO$_2$F$_3$] and excess [N(CH$_3$)$_4$][F] in CH$_3$CN solvent. The [N(CH$_3$)$_4$]$_2$[IO$_2$F$_3$] salt was characterized by Raman, infrared, and $^{19}$F solid-state MAS NMR spectroscopy. Geometry optimization and calculation of the vibrational frequencies at the DFT level of theory corroborated the experimental finding that the IO$_2$F$_3^{2-}$ anion exists as a single isomer with a cis-dioxo and mer-trifluoro arrangement. The fluorine atom in IO$_2$F$_3^{2-}$ that is trans to one of the oxygen atoms is weakly bound with a calculated bond length of 228.1 pm. The IO$_2$F$_3^{2-}$ anion is only the second example of an AEO$_2$F$_3$ species after XeO$_2$F$_3^-$. 

Introduction

Iodine fluorides and oxide fluorides have been extensively investigated to study the relative repulsive effects of single-bonds to fluorines, double-bonds to oxygens, and lone pairs, in order to verify geometry predictions using the VSEPR model.$^1$ Three octahedral iodine(VII) fluorides and oxide fluorides have been prepared, IF$_6^{2-}$, IOF$_5^{2-}$ and IOF$_3^{2-}$$^4$ being AX$_6$, AYX$_5$, and AY$_2$X$_4$ molecules, respectively. Interestingly, the IOF$_5^{2-}$ anion was found to exist as a mixture of the cis- and trans-isomer, with the cis-isomer being an exception to the VSEPR rules. Prior to this study only two pseudo-octahedral iodine(V) fluorides and oxide fluorides were known, i.e., IF$_5^{2-}$ and IOF$_4^{2-}$$^5$ being AEX$_5$ and AEYX$_4$ VSEPR molecules, respectively. In addition, a few other pseudo-octahedral iodine(V) fluoride compounds have been reported, such as the organo-iodine(V) fluorides CF$_3$I$^7$ and C$_6$F$_3$IF$_4$.$^8$ Iodine(V) oxide fluorides make possible the comparison between the repulsive effects of lone pairs and bonding pairs. The repulsion caused by a lone pair can be very similar to that of a double bond.

The availability of anhydrous [N(CH$_3$)$_4$][F]$^9$ has resulted in the preparation of a number of iodine fluoride and oxide fluoride dianions, such as the IO$_2$F$_5^{2-}$, IOF$_5^{2-}$, and IF$_5^{2-}$$^{10}$ anions. The lack of any report of an iodine AEO$_2$X$_3$ species sparked interest in the synthesis of the IO$_2$F$_3^{2-}$ anion and investigation of its geometry and possible isomerism. Prior to this study, XeO$_2$F$_3^-\text{anion}$ was the only AEO$_2$F$_3$ species that has been synthesized,$^{13,14}$ which was shown to have a cis-dioxo arrangement based on the vibrational spectroscopy of its Cs$^+$ salt.$^{14}$

Results and Discussion

Synthesis of [N(CH$_3$)$_4$]$_2$[IO$_2$F$_3$]. The N(CH$_3$)$_4^+$ salt of the IO$_2$F$_3^{2-}$ anion reacts with a 4-fold molar excess of

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In the absence of a sufficient excess of [N(CH₃)₄][F], the IO₂F₃²⁻ anion in admixture with the colorless [N(CH₃)₄][IO₂F₃] salt in CH₃CN at temperatures higher than 100 °C is well-documented, however, the formation of bifluoride at temperatures below 30 °C is unprecedented. Extraction of [N(CH₃)₄][F] from the [N(CH₃)₄][IO₂F₃]-[N(CH₃)₄][F] mixture at low temperature also led to formation of [N(CH₃)₄][HF₂][IO₂F₃]. In the absence of a sufficient excess of [N(CH₄)₄][F], the IO₂F₃²⁻ anion apparently promotes proton abstraction from CH₃CN, even at −30 °C. The generated HF acts as a better fluoride-ion acceptor than the IO₂F₃²⁻ anion (eq 2), preventing the isolation of IO₂F₃²⁻ salts under stoichiometric conditions.

\[
\text{IO}_2\text{F}_3^{2-} + \text{HF} \rightarrow \text{IO}_2\text{F}_2^{-} + \text{HF}^- 
\] (2)

**Vibrational Spectroscopy.** The Raman and infrared spectra of [N(CH₃)₄][IO₂F₃] containing about 3-fold molar excess of [N(CH₃)₄][F] are shown in Figure 1. The observed vibrational frequencies for IO₂F₃²⁻ and their assignments based on the theoretical calculations are summarized in Table 1. In addition to the vibrational bands attributable to unreacted [N(CH₃)₄][F] and to the N(CH₃)₄⁺ cation of the [N(CH₃)₄][IO₂F₃] salt, nine and four anion bands were observed in the Raman and infrared spectra, respectively.

Three structures are conceivable for the IO₂F₃²⁻ anion; a trans-IO₂F₃²⁻ (I) isomer of C₂ᵥ symmetry and two cis-IO₂F₃²⁻ isomers (II) and (III), both having C₁ symmetry. The lone pair in a trans-dioxio arrangement would result in a slight deviation from linearity of the O–I–O moiety.

Nevertheless, close to mutual exclusive behavior of the Raman and infrared bands is expected, as is a large separation of the two I–O stretching modes due to maximum coupling of these modes. Strict mutual exclusion has been observed in vibrational spectra of trans-IO₂F₃²⁻ and trans-IO₂F₄⁻ anions, in which both anions contain linear IO₂ moieties. In the Raman and infrared spectra of [N(CH₃)₄][IO₂F₃], two intense I–O stretching bands were observed at 832 (Raman)/834(infrared) and 798(Raman)/802(infrared) cm⁻¹, consistent with a cis-dioxio arrangement in the IO₂F₃²⁻ anion. Furthermore, it was found by computational means that the trans-IO₂F₃²⁻ (I) isomer is not a local minimum on the ground-state potential energy surface (see Computational Results). The presence of a mixture of isomers was excluded based on the number of observed I–O stretching bands and on the solid-state NMR spectroscopic results (see Solid-State NMR Spectroscopy).

A total of 12 vibrational modes are expected for isomers II and III of the cis-IO₂F₃²⁻ anion, which span the irreducible representations Γ = 7A’ + 5A” and Γ = 8A’ + 4A”, respectively, in the C₃ point group, with all modes being Raman and infrared active. Isomer II is predicted to be less stable than isomer III by 46 kJ/mol. Furthermore, the predicted infrared and Raman vibrational spectra of (III) are in better agreement with experiment than those of (II), which suggests that the former is the experimentally observed isomer. Examination of the potential energy distribution (PED, not shown) of isomer III reveals that the two I–O stretching bands at 832 and 798 cm⁻¹ are only weakly coupled with each other and are characteristic of the stretching of the I–O bonds cis, ν(IOcis), and trans, ν(IOtrans), to the I–F bond, respectively. The lower frequency of ν(1–Otrans) compared to that of ν(1–Ocis) is a consequence of the trans-effect of the I–F bond, rendering the I–Otrans bond more ionic than I–Ocis. Three I–F stretching bands were observed at 432, 405, and 358 cm⁻¹. The latter band primarily involves the stretching of the weak I–F bond, combined in an out-of-phase fashion with the symmetric IF₂ stretch. Compared with the I–O stretching (849 and 818 cm⁻¹) and I–F stretching (468 and 445 cm⁻¹) frequencies of the IO₂F₃²⁻ anion, the lower stretching frequencies for the cis-IO₂F₃²⁻ anion are consistent with an increase of ionic character of the bonds in the dianion. As observed for iodine trans-dioxio species, the increased bond polarization upon increasing the ionic charge is more pronounced for the I–O bonds than for the I–F bonds. This is a direct consequence of the higher electronegativity of fluorine versus oxygen. The comparison of the stretching frequencies of cis-IO₂F₃²⁻ with cis-IO₂F₄⁻, which are related by formal replacement of a fluorine atom by a lone pair, reveals an even larger increase in polarization of the I–O and I–F bonds when decreasing the oxidation state on iodine from +VII to +V. Such an
Fluorides has previously been developed for xenon fluorides,\textsuperscript{17,18} the choice of FEP is based on its chemically inertness and the ease of heat-sealing FEP inserts. In addition to the FEP background signals, three resonances were observed with isotropic chemical shifts of 16.1, \(-4.7\) ppm (approximately 2:1 ratio) and \(-91.9\) ppm. The resonance at \(-91.9\) ppm is attributable to \([\text{N(CH}_3\text{)}_4]^{+}\). The chemical shifts at 16.1 and \(-4.7\) ppm can be assigned to the \text{IF}_2 and \text{IF}' groups of the \text{IO}_2\text{F}_3^- anion. The shift of the more covalently bonded \text{IF}_2 moiety is close to \(\delta^{(19}\text{F})\) of \([\text{N(CH}_3\text{)}_4]^{+}\text{IO}_2\text{F}_2\) in \text{CH}_3\text{CN solvent} (13.7 ppm).\textsuperscript{15} A lower chemical shift of the \text{IF}' is consistent with a more polar, weaker \text{IF}' bond shifting \(\delta^{(19}\text{F})\) to the direction of \text{IF}'. Proton-decoupling resulted in line widths of \(\Delta \nu^{1/2} \approx 150\) Hz (16.1 ppm) and \(\Delta \nu^{1/2} \approx 245\) Hz (\(-4.7\) ppm) which did not allow for the observation of a resolved \(2J^{(19}\text{F}^{19}\text{F})\) coupling pattern. The difference in line widths is in agreement with an unresolved doublet and triplet pattern, suggesting a maximum value of 80 Hz for the \(2J^{(19}\text{F}^{19}\text{F})\) coupling constant. Such a value for the \(2J^{(19}\text{F}^{19}\text{F})\) coupling constant in an iodine(V) oxide fluoride is in line with the reported coupling value for \text{IF}_5 of 85 Hz.\textsuperscript{19}

The observation of relatively narrow resonances in the solid-state \textsuperscript{19}\text{F} NMR spectrum of \textit{cis}-\text{IO}_2\text{F}_3^- anion is in stark contrast to the broad resonances observed for the \textit{trans}-isomer. The choice of FEP is based on its chemically inertness and the ease of heat-sealing FEP inserts.
contrast to the broad lines observed in the solid-state NMR spectrum of the [N(CH₃)₄][IO₂F₂]. While ¹²⁷I relaxes slowly in the [N(CH₃)₄][IO₂F₂] salt, fast quadrupolar relaxation is observed for the cis-IO₂F₂⁻ anion, resulting in self-decoupling of the ¹⁹F nucleus.

Theoretical Calculations

(a) Geometry. The geometries of the three isomers of the IO₂F₂⁻ anion were calculated using density functional theory at the SVWN5/DZVP level of theory. The C₂ᵥ-symmetry trans-isomer was found to have a single imaginary vibrational frequency, and therefore is not a local minimum. The C₃ᵥ-symmetry isomers II and III were found to be local minima, with the former isomer less stable than the latter by 46 kJ/mol. The predicted gas-phase geometries of isomers II and III are summarized in Table 2, as are the calculated and experimental gas-phase geometries of the IO₂F₂⁻ precursor. The lower energy of isomer III is in line with larger ligand repulsion caused by the lone pair compared to that of the I–O bonds. Having one I–O bond trans and one cis to the lone pair in isomer III is favored versus both I–O bonds being cis to the lone pair as in isomer II. Comparison with calculated gas-phase and experimental geometry of the parent compound, IO₂F₂⁺, showed that the I–F and I–O bonds elongate upon addition of F⁻ to form IO₂F₂⁻, which is consistent with increased polarization of the IO and IF bonds. The I–F bond in isomer III is weak, with a calculated bond length of 228.1 pm. The weakness of this IF⁻ bond reflects the difficulty in forming the IO₂F₂⁻ anion and is in agreement with vibrational frequencies (see Vibrational Spectroscopy). As expected, the O–I–O and F–I–F angles in IO₂F₂⁻ contract upon addition of F⁻. The F–I–F angle in IO₂F₂⁻ isomer III significantly deviates from 180°.

(b) Atomic Charges. SVWN5/DZVP Löwdin atomic charges of IO₂F, IO₂F₂⁺, IO₂F₂⁻, and IO₃F⁻ have been computed for the series IO₂F, IO₂F₂⁺, IO₂F₂⁻, and IO₃F⁻ and are summarized in Table 3. In general, the magnitudes of the negative charges on oxygen and fluorine increase with the number of fluorine atoms n in IO₂Fₙ⁻. This is consistent with the notion of increasing ionic character of the I–O and I–F bonds as the number of fluorine ligands n increases. In isomer III of cis-IO₂F₂⁻, the weakly bonded F⁻ has a significantly larger negative charge (−0.66e) than the two other fluorine atoms (−0.59e), agreeing with the prediction of a rather ionic I–F⁻ bond based on the vibrational and NMR spectroscopic data. Furthermore, in isomer III of cis-IO₂F₂⁻, the oxygen atom trans to the F⁻ ligand carries a larger negative charge (−0.81e) than the cis oxygen atoms (−0.76e), confirming the greater ionic character of the I–O trans bond relative to I–O cis.

(c) Vibrational Frequencies. The calculated vibrational frequencies of the two cis-isomers (II) and (III) of the IO₂F₃⁻ anion are listed in Table 1. The agreement between the unscaled calculated frequencies of isomer III and the experimental vibrational frequencies is reasonably good. However, the sequence of calculated νₛ(IF₃) and νₚ(IF₃) is opposite that of the experimental values. This reversed frequency sequence can be attributed to an overemphasis of I–F⁻ involvement in νₛ(IF₃) stretch, which results in lowering the calculation frequency. Calculations showed that the IO stretching modes are only weakly coupled, while coupling between the IF stretching modes is more pronounced.

The fluoride-ion acceptor properties of IO₂F₂⁻ have been studied. The [N(CH₃)₄][IO₂F₃] salt has been prepared and characterized by solid-state ¹⁹F MAS NMR and vibrational spectroscopy in conjunction with theoretical calculations. Of the three possible isomers of the IO₂F₃⁻ anion, only the cis-IO₂F₃⁻ anion with a mer-trifluoro arrangement was observed as the exclusive product, which is a result of the repulsion caused by the lone pair. The resulting cis-IO₂F₃⁻ anion is presently only the second known AO₂F₃⁻ species, beside the isoelectronic XeO₂F₃⁻.

Materials and Apparatus. All volatile materials were handled on a Pyrex vacuum line equipped with glass/Teflon J. Young valves. Nonvolatile materials were handled in the dry nitrogen atmosphere of a dry box (Omni Lab, Vacuum Atmospheres).

Acetonitrile solvent (Baker, HPLC grade) was purified according to the standard literature method. The syntheses of [N(CH₃)₄][IO₂F₃] and [N(CH₃)₄][IO₂F₂⁺] have been described previously.

Preparation of [N(CH₃)₄][IO₂F₃]. Inside a drybox, [N(CH₃)₄][IO₂F₂] (0.189 mmol) and [N(CH₃)₄][F] (0.754 mmol) were loaded into a 34 in. o.d. FEP reactor equipped with a Swagelok ORM2 stainless-steel valve and a Teflon-coated stirring bar. Approximately 4.7 mL of anhydrous CH₂CN was condensed at −196 °C onto the solid mixture and allowed to warm to −30 °C. The reaction mixture was stirred while maintained between −35 and 30 °C using an ethanol bath cooled by a Thermo NESLAB CC-100 immersion cooler for 100 h. The CH₂CN solvent was pumped off while slowly warming from −30 to 0 °C, yielding a fine, white powder consisting of [N(CH₃)₄][IO₂F₃] and [N(CH₃)₄][F].


**Vibrational Spectroscopy.** The Raman spectrum of [N(CH₃)₄]₂-[IO₂F₃] was recorded on a Bruker RFS 100 FT Raman spectrometer with a quartz beam splitter, a liquid-nitrogen-cooled Ge detector, and a low-temperature accessory. The backscattered (180°) radiation was sampled. The actual usable Stokes range was 50 to 3500 cm⁻¹ with a spectral resolution of 2 cm⁻¹. The 1064-nm line of an Nd:YAG laser was used for excitation of the sample. The low-temperature spectrum of [N(CH₃)₄]₂[IO₂F₃] was recorded on a powdered sample in a melting point capillary using a laser power of 200 mW. The FT-infrared spectrum of [N(CH₃)₄]₂[IO₂F₃] was recorded on a Nicolet Avatar 360 FTIR spectrometer at ambient temperature. An AgCl pellet was formed in a Wilks minipress inside the dry box by sandwiching the sample between two layers of AgCl disks. The spectra were acquired in 64 scans at a resolution of 2 cm⁻¹.

**Solid-state NMR Spectroscopy.** Inserts were fabricated from FEP (a copolymer of perfluorinated polypropylene and polyethylene) as previously described. Solid-state NMR spectra were recorded unlocked on a Varian INOVA 500 (11.744 T) spectrometer equipped with a Sun workstation. The ¹⁹F NMR spectra were obtained using a Varian 4-mm HFXY MAS T3 probe tuned to 469.756 MHz. Free induction decays for the ¹⁹F spectra were accumulated with spectral width settings of 400 kHz. The number of transients accumulated for ¹⁹F spectra were 128 using pulse widths of 1 µs; relaxation delay of 2 s were applied. Proton-decoupled ¹⁹F NMR spectra were recorded using the TPPM decoupling mode. The ¹⁹F spectra were referenced to external neat CFCI₃ at room temperature.

**Theoretical Calculations.** Löwdin atomic charges, molecular geometries, harmonic vibrational frequencies, and infrared and Raman vibrational intensities of the isomers of the IO₂F₃²⁻ anion were calculated using density functional theory methods. Löwdin atomic charges are obtained using a Mulliken population analysis based upon symmetrically orthogonalized orbitals. The SVWN5 functional (Slater exchange plus Vosko-Wilk-Nusair formula 5 correlation) was used in conjunction with the double-ζ valence polarized (DZVP) basis set. All calculations were performed using the GAMESS quantum chemistry program.

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