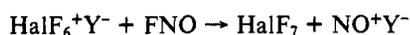


Communications

Steric Activity of the Central Atom Free Valence Electron Pairs in Free BrF_6^- and IF_6^- Ions

The BrF_6^- and IF_6^- anions belong to the interesting AX_6E class of compounds that contain six X ligands and one free valence electron pair E. The valence-shell electron-pair repulsion (VSEPR) rules^{1,2} predict for these compounds a distorted octahedral structure in which E becomes sterically active. While distorted structures have indeed been found for gaseous XeF_6 , solid IF_6^- and BiBr_6^{3-} salts, and solutions of SbCl_6^{3-} , SbBr_6^{3-} , and SbI_6^{3-} , the SeX_6^{2-} and TeX_6^{2-} ions normally have regular octahedral structures.² Recent work³ on TeX_6^{2-} and SeX_6^{2-} ions has shown, however, that these ions may undergo distortion under the influence of a nonsymmetric crystal field. It thus appears that these AX_6E compounds possess rather low energy barriers toward distortion and thereby exhibit varying degrees of fluxionality. Depending on the steric and bonding conditions and the symmetry of the environment, one might, therefore, expect for these AX_6E compounds a gamut of geometries ranging from relatively rigid distorted species through highly fluxional structures to relatively rigid octahedra. The purpose of this study was to investigate the influence of steric conditions, such as the maximum coordination numbers (CN), on the structure of such AX_6E species. It was, therefore, desirable to study ions or molecules that are closely related, but differ in the maximum coordination numbers of their central atoms.

From the known reaction chemistry of iodine and bromine fluorides, one can conclude that the maximum CN of iodine toward fluorine is 8, whereas that of bromine is only 6. Thus, displacement reactions of the type



provide IF_7 from the IF_6^+ cation, but BrF_5 and F_2 from BrF_6^{+4} . Furthermore, CsF or FNO form with IF_7 1:1 adducts containing the IF_8^- anion.^{5,6} Since in a rigid molecule the space requirement of a sterically active free valence electron pair slightly exceeds that of a fluorine ligand,⁷ one would predict that in IF_6^- there is enough space available for the free valence electron pair to be sterically active,⁸ while in BrF_6^- there is little or no room left for a seventh ligand and, therefore, the free valence electron pair should be sterically inactive.

When the steric activity of the free valence electron pairs in AX_6E species is studied, two considerations should be kept in mind.

First, the physical state of the AX_6E species is important. In the solid state, crystal field effects can, depending on the symmetry of this field, induce either symmetry or distortion in a fluxional AX_6E species.³ Therefore, these species should ideally be studied in the absence of crystal field effects, i.e. either as monomeric gaseous molecules or as dissolved ions. Second, for a fluxional compound the observed structure can appear to be different depending on the time scale of the technique used for the structure determination. For example, the time scale for an X-ray crystal structure determination is very long. Although the time scale of the X-rays themselves is short, the signals are time averaged, and therefore, only a time-averaged atom position can be seen, with the magnitude of the atomic thermal parameters serving as an indicator for the fluxionality of the species. The time scale of NMR spectroscopy is much shorter and approaches those of many fluxional rearrangements, thus frequently allowing their observation and the measurement of their energy barriers. Vibrational spectroscopy and electron diffraction provide the shortest time scale and are faster than the fluxional processes. They, therefore, result essentially in a picture of the fluxional species frozen in time.

Although Mössbauer spectra of solid CsIF_6 ⁸ and vibrational spectra of solid CsIF_6 and CsBrF_6 had previously been reported and were indicative of a distorted structure for the former^{8,9} and a centrosymmetric D_{3d} structure for the latter,¹⁰ no structural data were available on the free IF_6^- and BrF_6^- ions. During a recent study of $[\text{N}(\text{CH}_3)_4]^+$ salts of halogen fluorides,¹¹ it was found that CsBrF_6 and CsIF_6 have significant solubilities in CH_3CN . It, therefore, became possible to study the structures of the free BrF_6^- and IF_6^- ions in the absence of interfering crystal field effects.

The preparations of CsBrF_6 ¹⁰ and CsIF_6 ⁹ have previously been described. The compounds were handled in the dry N_2 atmosphere of a glovebox. The CH_3CN (Baker, Bioanalyzed, having a water content of 40 ppm) was stored over P_2O_5 , freshly distilled prior to its use, and handled either on a vacuum line or in the drybox. The final CH_3CN solvent that was used had a water content of less than 4 ppm.

Raman spectra of the CH_3CN solutions in flamed out glass NMR tubes were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm line of a Kr ion laser, respectively. The ¹⁹F NMR spectra were recorded on the same samples with a Varian Model EM 390 spectrometer equipped with a variable-temperature probe.

The BrF_6^- Anion. The Raman spectrum of a saturated CH_3CN solution of CsBrF_6 is shown in Figure 1. Three Raman active bands are observed at 565, 450, and 240 cm^{-1} , in excellent

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- (10) Bougon, R.; Charpin, P.; Soriano, J. C. R. *Hebd. Seances Acad. Sci., Ser. C* **1971**, *272*, 565. Note added in proof: On the basis of a private communication by K. Seppelt, solid CsBrF_6 crystallizes in space group $R\bar{3}$ with the octahedral BrF_6^- anions having an F-Br angle of 90.8° and an F-Br bond length of 1.854 (1) Å.
- (11) Wilson, W. W.; Christe, K. O. *Inorg. Chem.*, in press.

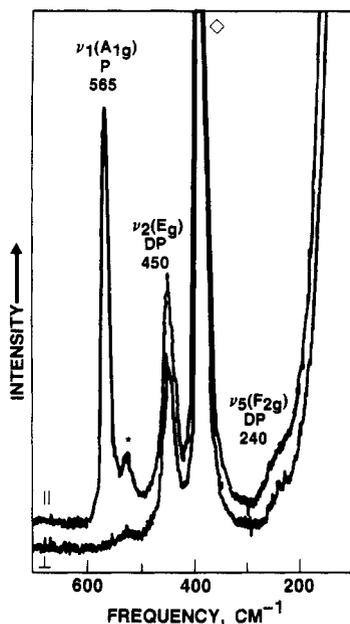


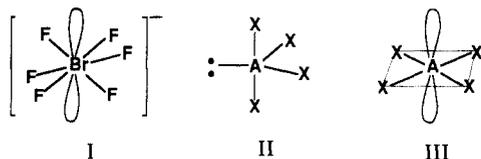
Figure 1. Raman polarization spectra of CsBrF_6 in CH_3CN solution. The weak band marked by an asterisk is due to BrF_4^- , and the band marked by a diamond belongs to CH_3CN .

agreement with the values of 562, 451, and 243 cm^{-1} previously reported¹⁰ for the solid. Of these, the 565- cm^{-1} band is highly polarized, whereas the 450- and the weak 240- cm^{-1} lines are depolarized. The observed number of bands, their relative intensities, and their polarization ratios are in excellent agreement with expectations for the octahedral point group O_h .

In the solid state, the space group of CsBrF_6 had been reported to be either $R3m$ (D_{3d}^5) or $R3$ (C_{3i}), thus resulting for BrF_6^- in D_{3d} symmetry.¹⁰ Although the Raman spectrum of BrF_6^- should not differ by much on going from O_h to D_{3d} symmetry, we consider this alternative less likely than O_h for the following reasons:

(i) The relative intensities of the 560- and 450- cm^{-1} Raman bands are reversed in the solid phase compared to those in CH_3CN solution. This suggests the possibility of different point groups for BrF_6^- in the solid state and in solution.

(ii) A D_{3d} structure for the free BrF_6^- anion would require equal occupation of two opposite ligand sites by a single free valence electron pair. This could be accomplished by placing the free valence electron pair of BrF_6^- , for example, into a p orbital (structure I). From a large body of experimental data it is known,



however, that a free valence electron pair occupies only one coordination site at a time. Thus, in SF_4 the free valence electron pair occupies only one equatorial site (structure II) and not two axial sites (structure III) despite the fact that pseudooctahedral structures tend to be energetically more stable than pseudo-trigonal-bipyramidal ones. The possible assignment of D_{3d} symmetry to BrF_6^- in solid CsBrF_6 ¹⁰ does not conflict with this conclusion. The D_{3d} symmetry could either reflect the site symmetry of BrF_6^- in the crystal or be the result of a slight compression of the BrF_6^- octahedra due to crystal-packing effects.

Since the above Raman spectrum suggests that on the time scale of vibrational spectroscopy the BrF_6^- anion is octahedral, the question remained whether the octahedron is rigid or fluxional. ^{19}F NMR spectroscopy was used to answer this question. For a nonfluxional BrF_6^- octahedron, Br-F spin-spin coupling should be observable as, for example, in BrF_6^+ , which exhibits a Br-F coupling constant of about 1580 Hz,⁴ because the bromine central atom would be located in an electrically symmetric field and

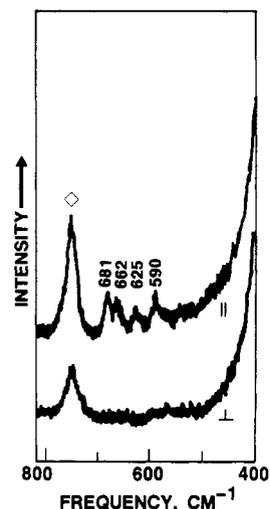


Figure 2. Raman polarization spectra of CsIF_6 in CH_3CN solution. The band marked by a diamond is due to CH_3CN .

quadrupole relaxation would be minimal. The ^{19}F NMR spectrum of BrF_6^- in CH_3CN , however, consisted over the temperature range -60 to $+40$ °C of a single resonance at $\phi = 94$ with an almost temperature independent line width of about 80 Hz with no detectable spin-spin coupling. This rules out the possibility of a rigid octahedral structure for BrF_6^- . The possibility of explaining the absence of Br-F spin-spin coupling in BrF_6^- by the presence of maybe a trace of free BrF_5 and an ensuing rapid exchange was also ruled out. It was shown that the addition of 20% of CsF , which would complex any free BrF_5 as BrF_6^- , to the sample did not alter the BrF_6^- signal.¹² It can, therefore, be concluded that the free BrF_6^- anion is octahedral on a vibrational spectroscopy time scale, but fluxional on the slower NMR time scale.

The question might be raised whether a small distortion of BrF_6^- from O_h should be observable in the Raman spectrum. Although we did not calculate theoretical Raman spectra for BrF_6^- as a function of varying degrees of distortion from O_h , the Raman spectra of gaseous XeF_6 ¹³ and the free IF_6^- anion (this work) strongly deviate from the predictions for O_h . It, therefore, appears safe to conclude that in free BrF_6^- the distortion from O_h , if any at all, must be rather small.

The IF_6^- Anion. The Raman spectrum of a saturated solution of CsIF_6 in CH_3CN is shown in Figure 2. Due to the lower solubility of CsIF_6 in CH_3CN , the spectrum is of lower intensity and quality than that of CsBrF_6 . However, on the basis of the complexity of the observed spectrum, i.e. at least three polarized Raman bands with a possible splitting of the highest frequency vibration due to Fermi resonance, it appears safe to conclude that free IF_6^- is not octahedral and does not have the same structure as BrF_6^- .

The ^{19}F NMR spectrum of IF_6^- in CH_3CN consisted of a singlet at $\phi = 13$ with a line width of about 40 Hz at -40 °C which broadened slightly with increasing temperature, possibly due to a quadrupolar effect. The absence of observable I-F spin-spin coupling¹⁴ rules out the possibility of a rigid octahedron, and the observation of a single sharp signal augurs also against a rigid distorted structure containing several nonequivalent fluorine atoms. Hence, it can be concluded that free IF_6^- is distorted on the time scale of vibrational spectroscopy and fluxional on the slower NMR time scale.

In conclusion, the Raman data suggest that on the fast time scale of vibrational spectroscopy the free BrF_6^- anion is octahedral while on the slower NMR time scale it is fluxional. Contrary to BrF_6^- , the free IF_6^- anion is strongly distorted on the vibrational

(12) A separate signal due to the free fluoride anion of the CsF was not observable with our spectrometer due to the low solubility of CsF in CH_3CN .

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spectroscopy time scale and is again fluxional on the slower NMR time scale. These results demonstrate that in BrF_6^- the bromine free valence electron pair is sterically inactive, while in IF_6^- the iodine free valence electron pair is sterically active. This difference is attributed to the smaller size of the bromine central atom, which with its maximum coordination number of 6 toward fluorine cannot accommodate a seventh ligand. The observation of fluxionality for both BrF_6^- and IF_6^- is not surprising in view of the fact that the ease of delocalization of the free valence electron pair can provide a low energy path for the deformation of these ions.

The failures to prepare a stable ClF_6^- anion¹⁵ are not attributed to steric effects since the maximum coordination number of chlorine toward fluorine is the same as for bromine, i.e. 6, as shown by the existence of the ClF_6^+ cation^{16,17} and the fact that ClF_5 undergoes rapid exchange with either CsF^{18} or FNO^{19} in ^{18}F radiotracer experiments. This conclusion is obviously based on the assumption that by analogy with BrF_6^- the chlorine free valence electron pair in ClF_6^- can be accommodated in a sterically inactive, centrosymmetric orbital. In our opinion, the instability of ClF_6^- is most likely due to the expected decrease in Lewis acidity in the series $\text{IF}_5 > \text{BrF}_5 > \text{ClF}_5$. By analogy to BrF_6^- , the free ClF_6^- anion should also be octahedral, contrary to previous predictions of C_{3v} symmetry made on the basis of the VSEPR rules^{1,2} and the Laplacian of the calculated electronic charge distribution.²⁰

Finally, we would like to emphasize the need for fast time scale methods when searching for the actual structures of fluxional molecules, while the slower methods can yield valuable information on the dynamics of the intramolecular motions. For ions it is desirable to study, whenever possible, the free ions and not the solids in order to avoid crystal field effects, which can impose either order or disorder on fluxional ions.³

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Registry No. BrF_6^- , 56713-48-5; IF_6^- , 27931-77-7; CsBrF_6 , 26222-92-4; CsIF_6 , 20115-52-0.

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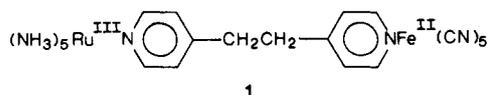
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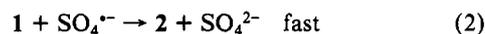
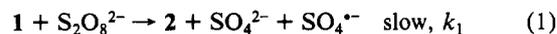
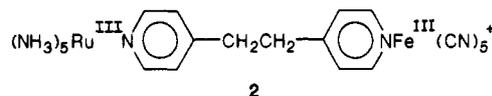
An Example of Intramolecular Electron-Transfer Assistance in a Bimolecular Redox Reaction: Peroxydisulfate Oxidation of (μ -1,2-Bis(4-pyridyl)ethane)pentaammineruthenium(III) Pentacyanoferrate(II) via Its Electronic Isomer

We report herein the first example of intramolecular electron-transfer assistance in a bimolecular redox reaction, namely, the oxidation of **1**, the title compound (1,2-bis(4-pyridyl)ethane

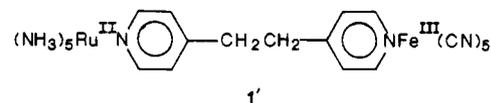


= BPA), by peroxydisulfate. Reactivity patterns for the peroxydisulfate oxidations of mono- and binuclear BPA complexes

of pentacyanoferrate(II) and pentaammineruthenium(II) provide strong evidence that the oxidation of **1** to **2** (eq 1,2) does not



proceed by direct oxidation of the Fe(II) center in **1**. Instead, the electronic isomer of **1**, **1'**, postulated to be present in small concentrations and in rapid equilibrium with **1**, is the reactive species.

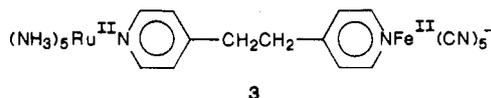


Aqueous solutions¹ containing substantial concentrations of **1** ($(2-5) \times 10^{-5}$ M, 25 °C, $I = 0.10$ M (NaCl), pH = 5.5 with $\text{H}_2\text{EDTA}^{2-}/\text{CH}_3\text{CO}_2^-$) were prepared by one of two procedures. In the first, equimolar solutions of $\text{Fe}^{\text{II}}(\text{CN})_5\text{OH}_2^{3-2}$ and $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{BPA}^{3+3}$ were mixed anaerobically and allowed to equilibrate⁴ according to eq 3. The resulting solutions display a MLCT



band at 368 nm ($\epsilon = 4.3 \times 10^3$ M⁻¹ cm⁻¹, corrected for incomplete reaction). By comparing this band with those of related Ru and Fe complexes (Table I), we infer that the oxidation states of the metal centers are as indicated in **1**. Additional supporting evidence comes from IR studies of the solid: the CN⁻ stretch at 2036 cm⁻¹ and the NH₃ deformation at 1327 cm⁻¹ are diagnostic⁵ of Fe(II) and Ru(III), respectively. It is noteworthy that electron-withdrawing effects (on spectroscopic and electrochemical properties) associated with substitution on the remote N are not transmitted through BPA.^{6,7} On the basis of this information and by comparison with similar unsymmetrical mixed-valence complexes,⁷ it is apparent that **1** is a valence-trapped species.⁸ Because of the competing outer-sphere electron-transfer reaction⁴ between the reactants in eq 3, k_3 was measured by utilizing equal concentrations of Ru(III) and Fe(II) complexes. From absorbance increases at 367 nm, $k_3 = (4.0 \pm 0.2) \times 10^3$ M⁻¹ s⁻¹. Values of $k_{-3} = (3.1 \pm 0.1) \times 10^{-3}$ s⁻¹ were obtained by adding 0.20 M 4-acetylpyridine to solutions of **1** and following the subsequent absorption increase at 490 nm.^{2,9} Solutions of **1** treated with excess $\text{S}_2\text{O}_8^{2-}$ ($(5.0-50) \times 10^{-4}$ M) exhibit first-order absorbance decreases at 380 nm, which yield $k_1 = (3.9 \pm 0.2) \times 10^2$ M⁻¹ s⁻¹.

In the second procedure, **1** was generated as a transient by oxidation of **3** with $\text{S}_2\text{O}_8^{2-}$. First, solutions containing **3** at $(2-5)$



- (1) Solutions of **1** are metastable. Even at low concentrations (2×10^{-5}), slight turbidities (undetectable to the eye but observed by shining the beam of a HeNe laser through the solution) develop after several minutes.
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 (4) These solutions also contain ~1% of $\text{Fe}^{\text{III}}(\text{CN})_5\text{OH}_2^{2-}$ and $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{BPA}^{2+}$ formed by outer-sphere electron transfer. When Ru(III) is in excess, then detectable amounts of Ru(II) are produced.
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