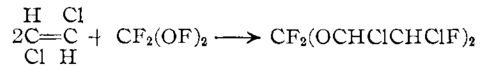
The reaction



$$2\overset{H}{\underset{Cl}{C}}=\overset{Cl}{\underset{H}{C}} + CF_2(OF)_2 \longrightarrow CF_2(OCHClCHClF)_2$$

apparently occurred in about 9% yield. The more volatile products were not identified.

Bis(1,2-dichloro-2-fluoroethoxy)difluoromethane is a liquid at 25° with a density of 1.63 g/ml at 24°. The infrared spectrum is given in Table II. The peak at 2941 cm^{-1} is the result of CH stretch. Those near 1100 and 1200 cm^{-1} are probably CF stretch or CH bend. The two at about 800 cm^{-1} are the result of CCl stretch.

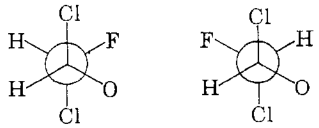
Anal. Calcd for $C_5H_4Cl_4F_4O_2$: C, 19.13; H, 1.28; Cl, 45.18; F, 24.21. Found: C, 19.15; H, 1.02; Cl, 44.42; F, 24.81.

The ^{19}F nmr spectrum shows absorptions at +60.7 ppm, assigned to CF_2, and at +142.4, 143.7, 145.4, and 146.7 ppm, assigned to CF. These have relative areas of 4:1:1:1:1, respectively. The separation between the first and second and between the third and fourth CF peaks is about 52 cps. This is the magnitude of the coupling expected for hydrogen and fluorine attached to the same carbon atom.

The proton nmr spectrum has peaks at 5.91, 6.18, and 6.72 ppm which are in the ratio of 1.00:2.05:1.01, respectively. The separation of the first and third peaks is 49 cps. This suggests that two types of hydrogens are present, one of which is coupling with a fluorine attached to the same carbon.

The peaks in both the proton and ^{19}F nmr spectra which have been described above show further splitting of 5–10 cps under high resolution. This has made complete analysis of the spectrum impossible. Part of the difficulty may arise from a spin–spin coupling constant between the two nonequivalent protons and the chemical shift between them of about the same value (about 8 cps).

These nmr data suggest that more than one isomer of the CHClCHClF group is present—one corresponding to the *cis*-addition product and one to the *trans*-addition product as shown by the two conformations



Even with free rotation about all bonds, the atoms in the two configurations are not equivalent.

Heating the sample to +60° and cooling it to −40° did not change the spectrum.

Acknowledgments.—This work was supported in part by the National Science Foundation. Nmr data were obtained with the assistance of Dr. M. Lustig of Rohm & Haas, Mr. B. J. Nist of the University of Washington, and Mr. D. Balls of the University of Idaho.

Contribution from the Western Research Center,
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Infrared and Raman Spectra of the Hexafluoroiodine(V) Anion, IF_6^-

By Karl O. Christe,[1] Jacques P. Guertin,
and Wolfgang Sawodny

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In the course of a systematic investigation of the halogen fluoride ions, the structure of and the type of bonding in ClF_2^-,[2-4] ClF_2^+,[5,6] ClF_4^-,[7,8] and IF_6^+ [9] have recently been established. In particular, ClF_2^- [4] and ClF_4^- [8] appear to be, as far as structure and bonding are concerned, closely related to isoelectronic (considering only valence electrons) XeF_2 and XeF_4, respectively. The existence of representatives of the hexafluorohalogenate(V) anions, IF_6^- [10-15] and BrF_6^-,[16] is well known; however, no data on their structure and bonding have been reported. These compounds are of special interest since they are isoelectronic and probably also isostructural with XeF_6. The latter seems to have a unique structure and for the past 3 years numerous efforts to establish its structure have been unsuccessful. Furthermore, a hexafluorohalogenate(V) salt with respect to structural investigation offers several advantages over XeF_6. For example, its preparation is easier, its reactivity is lower, and the anions are probably separated by relatively large cations, thus rendering polymeric structures rather unlikely. However, the lattice interactions can be expected to be greater for ionic structures. This paper is concerned with data obtained for $CsIF_6$.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a standard Pyrex-glass high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Iodine pentafluoride (Allied Chemical) was purified by distillation. Cesium fluoride (99.9% from K & K Laboratories, Inc.) was dried for 48 hr at 500°. Outside of the vacuum system the materials (owing to their hygroscopic nature) were handled in the dry nitrogen atmosphere of a glove box.

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(1) Synthetic & Propellant Chemistry Group, Rocketdyne, A Division of North American Rockwell Corp., Canoga Park, Calif. 91304.

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Preparation of $Cs^+IF_6^-$.—In a typical experiment, CsF (49 mmoles) and IF_5 (237 mmoles) were introduced into a passivated 50-ml Monel reactor connected to a Monel pressure gauge and a Monel control valve (Whitey, M6TS6). The mixture was vigorously shaken for 4 hr at 100°. Unreacted IF_5 was removed by pumping on the cylinder for 48 hr at 25°. The nonvolatile, white, crystalline product was shown to have the composition $CsIF_6$ by the increase in weight of the starting material (CsF) and by elemental analysis. *Anal.* Calcd for $CsIF_6$: Cs, 35.6; I, 34.0; F, 30.5. Found: Cs, 35.3; I, 34.5; F, 30.1.

Vibrational Spectra.—The infrared spectrum of solid $Cs^+IF_6^-$ was recorded on Beckman Models IR-9, IR-12, and IR-11 prism-grating spectrophotometers in the range 4000–33 cm^{-1}. Samples were dry powders between AgCl plates or polyethylene disks. The Raman spectrum of solid $Cs^+IF_6^-$ was recorded on a Cary Model 81 spectrophotometer, using the blue mercury line. (4358 Å) as exciting line and a saturated KNO_2 solution as filter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses were used.

Results and Discussion

Figure 1 shows the infrared spectrum of solid $Cs^+IF_6^-$. Identical spectra were obtained for samples from different preparations. Figure 2 shows the Raman spectrum of solid $Cs^+IF_6^-$. The observed frequencies of the infrared and Raman spectra are listed in Table I.

TABLE I

VIBRATIONAL SPECTRA OF $Cs^+IF_6^-$(s) AND THEIR ASSIGNMENT

Obsd freq, cm^{-1}	
Infrared	Raman
2450 w, b	
1900 w, b	
1304 vw	
1100 w, b	
888 m	
853 vw	
828 w	
754 vw	
653 m	673 (10)
592 m	591 (7)
534 m	546 (5)
485 vs	
463 w, sh	
322 w	
285 mw	

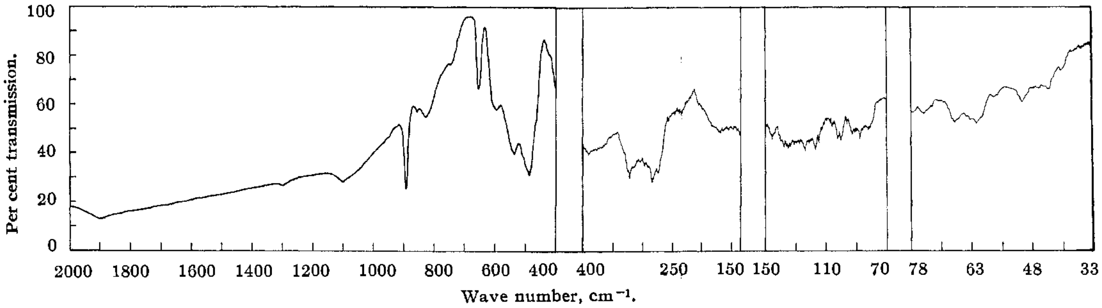

Figure 1.—Infrared spectrum of solid $Cs^+IF_6^-$.

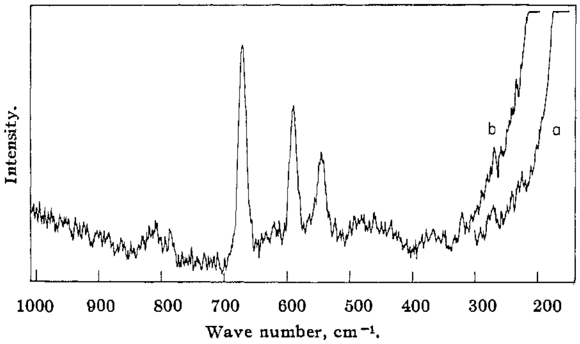

Figure 2.—Raman spectrum of solid $Cs^+IF_6^-$: (a) single slit; (b) double slit.

Most hexafluoride molecules and ions are octahedral (symmetry O_h). Their six normal modes of vibration are classified as $A_{1g} + E_g + 2\ F_{1u} + F_{2g} + F_{2u}$. Of these only the two F_{1u} modes (one stretching and one deformation vibration) will be infrared active, while only the A_{1g}, E_g, and F_{2g} modes (two stretching and one deformation vibration) will be Raman active. In the region of the stretching vibrations only one infrared and two Raman bands (following the rule of mutual exclusion) would be expected for IF_6^- in the case of symmetry O_h. The data of Table I (three Raman[17] and at least six infrared bands, apparently not followng the rule of mutual exclusion) indicate that IF_6^- does not have symmetry O_h in the solid state. This could arise because the IF_6^- anion does not have O_h coordination or because of lattice interactions.

Comparison of these data with those obtained for XeF_6[18-20] (the only other hexafluoride reported to have a symmetry lower than O_h) indicates a remarkable similarity between IF_6^- and XeF_6. This similarity is not surprising since IF_6^- and XeF_6 are "isolectronic" and belong to the same period of the periodic system. Gasner and Claassen[20] have recently reported the Raman spectrum of solid, liquid, and gaseous XeF_6. The Raman spectrum of IF_6^- mostly resembles that obtained for solid XeF_6[20] and that of XeF_6 in HF solution.[19]

In $Cs^+IF_6^-$ the occurrence of tetra or polymeric structures is considerably less likely than in XeF_6[21]

[17] The Raman spectrum indicates the presence of at least two additional bands of very low intensity at 322 and 274 cm^{-1} corresponding possibly to the two infrared bands at 322 and 258 cm^{-1}, respectively. This would further support the absence of a symmetry center.

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owing to the presence of the relatively large cesium cations separating the IF_6^- anions. Therefore, the vibrational spectra observed for IF_6^- are most likely due not to polymeric structures but either to a symmetry lower than O_h or to very unusual electronic properties.[22,23]

Acknowledgment.—We thank Dr. A. C. Jones of Shell Development Co., Emeryville, Calif., for the use of the Cary 81 spectrophotometer.

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Correspondence

The Absence of Steric Effects on the Proton Contact Shifts for $Co(C_5H_5N)_2X_2$ Complexes

Sir:

In a recent article,[1] the interpretation by Wayland and Drago[2] of the proton nmr contact shifts in the complexes $Co(C_5H_5N)_2X_2$ (where X = Cl, Br, or I) was criticized. Our interpretation suggested that the halide ion with the largest *Dq* would raise the energy of the d_{z^2} orbital most in the CoX_2 fragment so that energy matching of the metal orbitals and pyridine (L) orbitals would be less effective in forming CoL_2X_2 when X is chloride. This effect would lead to the smallest spin delocalization due to covalency in the metal–pyridine (py) bond when X is chloride and would account for the observed decrease in the contact shifts for the series $Co(py)_2I_2 > Co(py)_2Br_2 > Co(py)_2Cl_2$.

This will be referred to subsequently as the mo model.[2] The claim is made[1] that there is a steric effect present in these complexes that has been neglected in our analysis. Such a steric effect would cause the metal ion and ligand orbitals to mix differently in the chloro and iodo complexes and negate our conclusion. The fact that the angles in $[(C_6H_5)_3P]_2NiCl_2$ indicate a D_{2h} distortion was used to support this contention. The magnitude of the shift for a series of substituted pyridines was found to increase in the order: ~4-CH_2=CH-py ~ C_5H_5N ~ 4-CH_3-py < 3-CH_3-py ~ 3,4-$(CH_3)_2$-py ~ 3-C_2H_5-py < 3-5-$(CH_3)_2$-py. This order was proposed to result from increasing substituent steric effects. Since the size of the halides increases in the order $Cl^- < Br^- < I^-$, it was further proposed that the increase in ligand proton contact shift in the iodo complex compared to that in the chloro also results from a steric effect. Admittedly, our mo model is a qualitative rationalization of observed shifts and suffers from lack of a detailed theoretical analysis. In such instances it may be possible to say the same thing in different ways. Fortunately, this is not the case here. It is the purpose of this article to show that there is no real evidence for a steric effect dominating the trends in contact shifts for the complexes reported by either author.[1,2]

The first point that must be considered is whether the observed data support the contention that a steric effect is causing the trend in contact shifts for the series of substituted pyridine ligands. The argument presented[1] is that, as the steric requirements of the substituents increase, the spin delocalization to the ligand increases. The presence of an electronic substituent effect is dismissed because the electronic spectra for all of the complexes are very similar. This conclusion is clearly not justified, for electronic spectra are rather insensitive to small changes in the ligand electronic structure while contact shifts are sensitive to this property. An electronic substituent effect thus could cause large changes in contact shifts without having large effects on the electronic spectra. Figure 1 illustrates the near-linear relationship between the 2-H contact shift for the substituted pyridine ligands in the complexes CoL_2X_2 and the sum of the Taft σ^* values for the 3,5 positions.[3,4] The 2-H contact shifts for the pyridine ligands which differ only in the 4 position substituent are also consistent with an electronic substituent effect. The presence of correlations with substituent constants is generally taken as evidence for the absence of significant steric effects.[3,4]

The precise character of the observed electronic substituent effects must be very complex and is not yet completely understood. The substituents not only modify the ligand donor properties, but also the electron distribution in each of the ligand molecular orbitals. The order of increasing ligand contact shifts is consistent with the substituent effect on the ligand donor properties, and this could well be the dominant effect for this series of closely related pyridine-type ligands. It must be stated, however, that it is virtually impossible to compare the contact shift in two different proton-containing ligands without a complete knowledge of the wave functions for the ligand orbitals. Simple replacement of an H by a methyl group may change the ligand wave functions involved in bonding in such a way that very different contact shifts are observed for essentially the same metal–ligand interaction (*vide infra*). If ligand substitution prevented free rotation of the ligand in the complex,

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