Inorg. Chem. **1983**, *22*, 2509–2513

same in both the ground and excited states,[15] it would appear that $Cr(phen)_3^{3+}$ is a better candidate for use as a photosensitizer than $Cr(bpy)_3^{3+}$ as long as the phenomenon of ground-state quenching of $^2T_1/^2E$ is recognized.

Acknowledgment. Financial support from the European Community, the National Research Council of Italy, the North Atlantic Treaty Organization (Grant No. 046.81), the Natural Sciences and Engineering Research Council of Canada (Grant No. A-5443), and the National Science Foundation (Grant No. CHE79-18013) is gratefully appreciated.

Registry No. $Cr(phen)_2(OH)_2^+$, 86409-84-9; $Cr(phen)_3^{2+}$, 15276-16-1; O_2, 7782-44-7; I^-, 20461-54-5.

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Infrared Matrix Isolation Study of the SO_2F^-, SOF_3^-, and $SO_2F_3^-$ Anions Ion Paired with Cs^+

KEVIN GARBER and BRUCE S. AULT*

Received January 19, 1983

The salt/molecule reaction technique has been coupled with the matrix isolation technique for the synthesis of several novel sulfur oxyfluoride anions. Reaction of CsF with SO_2 in argon matrices gave rise to a series of absorptions assigned to the SO_2F^- anion, in agreement with literature spectra. ^{18}O isotopic data confirmed the equivalence of the two oxygen atoms in this product anion. Reaction of CsF with thionyl fluoride, SOF_2, gave rise to absorptions at 623, 667, 695, and 1264 cm^{-1}, which have been assigned to the four stretching vibrations of the novel SOF_3^- anion, in a C_s geometry. The reaction of CsF with sulfuryl fluoride, SO_2F_2, gave rise to five product bands, which have been assigned to the $SO_2F_3^-$ anion, with a structure analogous to the known ClO_2F_3 species. Identification of this anion supports the claim that pentacoordinate sulfur anions play a role in the solution chemistry of SO_2F_2.

Introduction

Little is known about the complex oxyfluoride anions of sulfur, despite their likely intermediacy in solution reactions.[1] Of the several possible anions of this type, the fluorosulfinate anion, SO_2F^-, is one of the best characterized,[2-4] as it forms a stable solid at room temperatures with a variety of alkali metal cations. Thionyl fluoride, SOF_2, is known to exhibit some Lewis acid character through involvement of the sulfur d orbitals,[1] but there is no mention in the literature of the anion formed through fluoride ion addition, namely SOF_3^-. However, the isoelectronic chlorine analogue, $ClOF_3$, is well-known[5] and lends credence to the idea that the SOF_3^- anion should be stable. Sulfuryl fluoride, SO_2F_2, is known to be attacked by nucleophiles in solution, and a pentacoordinated intermediate anion has been postulated.[1] The fluoride ion addition to SO_2F_2 to form the $SO_2F_3^-$ anion has been studied in the gas phase by ion cyclotron resonance spectroscopy,[6,7] and the fluoride ion affinity of SO_2F_2 has been bracketed between 36 and 46 kcal/mol. However, this anion has never been isolated at room temperature and spectroscopically characterized, although again the isoelectronic species ClO_2F_3 is well-known.[8]

It is likely that the anions SOF_3^- and $SO_2F_3^-$ can be formed under appropriate experimental conditions, in a manner similar to that of the better known SO_2F^- anion. Matrix isolation provides a means for the study of such reactive species,[9] and in particular fluoride-containing anions, through the salt/molecule reaction technique.[10-12] In this approach, CsF is vaporized from a high-temperature oven and codeposited with a suitable fluoride ion acceptor diluted in a large excess of argon. Fluoride ion transfer has been shown to occur, leading to anion formation in an ion pair with the Cs^+ cation. The technique, then, provides a direct means for the formation and characterization of the oxyfluoride anions of sulfur. Consequently, such an investigation was undertaken to spectroscopically characterize these unusual anions and determine their structure to the degree possible.

Experimental Section

The experiments conducted in the course of this investigation were all carried out on a conventional matrix isolation system, which has been described previously.[13] The gas-phase reactants, SO_2 (Matheson), SOF_2 (PCR Research Chemicals), and SO_2F_2 and $S^{18}O_2$ (95% ^{18}O, Cambridge Isotope), were purified by repeated freeze/thaw cycles under vacuum prior to sample preparation. The SOF_2 was found to contain a considerable fraction of SO_2, and while the sample was distilled on the vacuum line, complete separation could not be achieved, due to similarities in boiling point. However, since separate experiments were conducted with SO_2 alone, product bands due to the reaction of SOF_2 could readily be identified. $S^{18}O_2F_2$ was prepared through the direct reaction of $S^{18}O_2$ with F_2 in a stainless-steel vacuum line. Complete separation of the product $S^{18}O_2F_2$ from the reactant $S^{18}O_2$ was not possible; the residual $S^{18}O_2$ did provide some complications to the resulting experiment and obscured a few regions of the spectrum. CsF was loaded into a stainless-steel Knudsen cell and outgassed under a vacuum prior to the start of an experiment. An oven temperature of 500 °C was sufficient to provide a vapor pressure of 1 μm of CsF. TlF was handled in a similar fashion; water absorption and outgassing were not as severe a problem as with CsF. Argon was used as the matrix gas in all experiments and was used without further purification.

Matrix samples were codeposited at roughly 2 mmol/h for 20–24 h before final scans were recorded on a Beckman IR-12 infrared

---

(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; pp 537-9.

(2) Robinson, E. A.; Lavery, D. S.; Weller, S. *Spectrochim. Acta, Part A* **1969**, *25A*, 151.

(3) Seel, F.; Jonas, H.; Riehl, L.; Langer, J. *Angew, Chem.* **1955**, *67*, 32.

(4) Burow, D. F. *Inorg. Chem.* **1972**, *11*, 573.

(5) Christie, K. O.; Curtis, E. C. *Inorg. Chem.* **1972**, *11*, 2196.

(6) Galembeck, S. E.; Faigle, J. F. G.; Riveros, J. M. *An. Acad. Bras. Cienc.* **1978**, *50*, 67.

(7) Sullivan, S. A.; Beauchamp, J. L. *Int. J. Mass. Spectrom. Ion Phys.* **1978**, *28*, 69.

(8) Christie, K. O.; Curtis, E. C. *Inorg. Chem.* **1973**, *12*, 2245.

(9) Craddock, S.; Hinchcliffe, A. J. "Matrix Isolation"; Cambridge University Press: New York, 1975.

(10) Ault, B. S.; Andrews, L. *J. Am. Chem. Soc.* **1975**, *97*, 3824.

(11) Ault, B. S. "Matrix Isolation Studies of Alkali Halide Salt Molecule Reactions with Lewis Acids and Bases"; Gole, J. L., Stwalley, W. C., Eds.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 197.

(12) Ault, B. S. *J. Phys. Chem.* **1979**, *83*, 837.

(13) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.

0020-1669/83/1322-2509$01.50/0

spectrometer. Survey scans and expanded-scale scans over the regions of interest were recorded at a resolution of approximately 1 cm^{-1}.

Results

Prior to the codeposition of CsF with SO_2, SOF_2, and SO_2F_2, blank experiments were conducted on each of the parent species. In each case, the spectrum was in good agreement with literature spectra;[14-16] comparisons were made to matrix spectra where available and to gas-phase spectra when matrix spectra were not available. A blank experiment of $Ar/S^{18}O_2$ showed a set of bands similar to that of the parent $S^{16}O_2$ but shifted 20–40 cm^{-1} to lower energy, as anticipated. In addition, the isotopic ratio appeared less than indicated by the manufacturer, based on the intensity of the mixed $S^{16}O^{18}O$ species, which was observed as well. On this basis, with comparable absorption coefficients assumed for all species, the isotopic ratio was estimated to be 65%. The argon matrix spectrum of $S^{18}O_2F_2$ was similar, showing a shift of all parent bands to lower energy, with the S–O stretches being affected most, and an apparent ^{18}O enrichment of 65%.

CsF + SO_2. These two reactants were codeposited into argon matrices in a number of experiments, with *M/R* ratios ranging from 250/1 to 1000/1. In each case, a set of four, and possibly five, product bands were observed between 200 and 1200 cm^{-1}. These bands were quite sharp, with a half-width of 1–2 cm^{-1}. The most intense band was located at 1178 cm^{-1}, with a slightly less intense band at 1100 cm^{-1}. In a number of experiments, this band at 1100 cm^{-1} appeared as a doublet, with a weak satellite band at 1108 cm^{-1}. This doublet structure is likely due to matrix site splitting, and further reference will be made only to the more intense component of the doublet. In the low-energy region, a medium-intensity band was located at 598 cm^{-1}, with a weak band at 471 cm^{-1}. Finally, a possible, very weak band was noted in the more concentrated experiments at roughly 360 cm^{-1}. The bands at 1178, 1100, and 598 cm^{-1} were particularly prominent in all of these experiments and grew as the concentration of SO_2 was increased. At the same time, all four bands grew at a constant rate relative to one another, indicating the formation of a single species.

TlF + SO_2. TlF was codeposited with samples of Ar/SO_2 in one experiment to determine the effect of the cation on product formation and band position. A comparable yield of product bands was observed, in addition to the fundamental of TlF at 441 cm^{-1}. These product bands were also sharp and fairly close to the bands observed with CsF and SO_2, being located at 1192, 1062, 589, and 488 cm^{-1}. In addition, the relative intensities of these four bands resembled those observed for the product bands in the CsF experiments.

CsF + $S^{18}O_2$. CsF was codeposited with a sample of $Ar/S^{18}O_2 = 500$ in one experiment, and as noted above, an isotopic enrichment of approximately 65% was observed. The spectrum showed triplet structure in each region where a single product band had previously been noted with $S^{16}O_2$. Relative intensities of the triplet components were 1/4/4, from the highest energy component to the lowest, which was identical with the ratio observed for the parent SO_2. These triplets were located at 1178, 1164, and 1140, at 1100, 1073, and 1056, at 598, 590, and 582, and at 471, 467, and 463 cm^{-1}, with the highest energy band of each triplet matching the product band observed in that spectral region when normal isotopic SO_2 was employed. Figure 1 shows the spectra obtained when CsF was reacted with SO_2 and ^{18}O-enriched SO_2 in argon matrices.

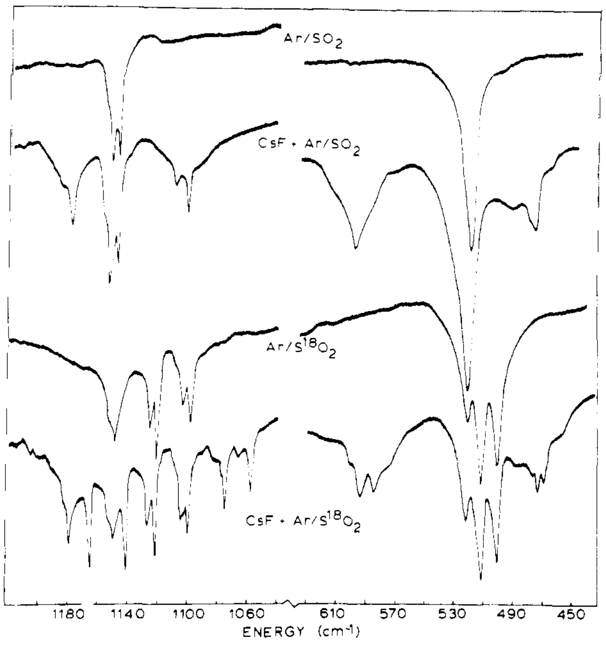

Figure 1. Infrared spectra, over selected spectral regions, of the products of the argon matrix reactions of CsF with SO_2 (second trace) and with isotopically labeled SO_2 (bottom trace), compared to spectra of SO_2 (top trace) and of the labeled SO_2 (third trace) in the absence of CsF.

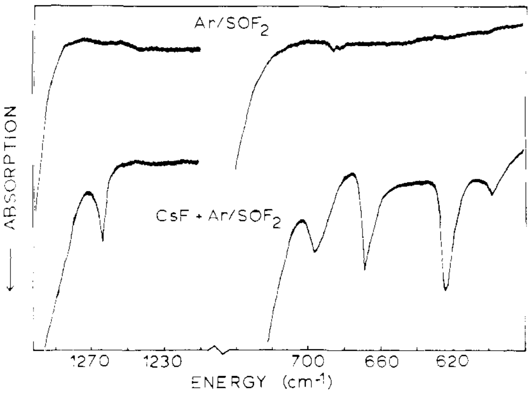

Figure 2. Argon matrix infrared spectrum of the product of the reaction of CsF with SOF_2, compared with the infrared spectrum of the parent SOF_2, at a dilution of $Ar/SOF_2 = 500$.

CsF + SOF_2. These two reactants were codeposited into an argon matrix in many experiments, over a concentration range from *M/R* = 1000 to *M/R* = 250. Since samples of SOF_2 invariably contained some SO_2 as well, the product bands described above for the reaction of CsF and SO_2 were observed, along with a new set of product bands, which can be ascribed to the reaction product of CsF with SOF_2. However, as estimated by yield of product bands, the reaction of CsF with SOF_2 has a relatively low cross section relative to SO_2. In any event, four product bands were observed, at 1264, 695, 667, and 623 cm^{-1}, as can be seen in Figure 2. All were somewhat broader than the product bands of CsF + SO_2, with half-widths of 6–8 cm^{-1}. In addition, these bands were not particularly intense, with optical densities of 0.10–0.20. Nonetheless, they were reproducible, grew in intensity as the concentration of the parent species was increased, and required the presence of both reactants for formation.

CsF + SO_2F_2. CsF was codeposited with sulfuryl fluoride in a number of experiments, again over the concentration range 1000/1 to 250/1. Several product bands were observed in all of these experiments and with a relatively high yield at even low concentrations. Under optimum conditions, five product bands were observed, at 1408, 1130, 925, 810, and 649 cm^{-1}. The last four were quite intense in all of the experiments, but as the concentration of SO_2F_2 was increased, parent absorption

---

(14) O'Loane, J. K.; Wilson, M. K. *J. Chem. Phys.* **1955**, *23*, 2313.
(15) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1971**, *55*, 1003.
(16) Sportouch, S.; Clark, R. J. H.; Gaufres, R. *J. Raman Spectrosc.* **1974**, *2*, 153.

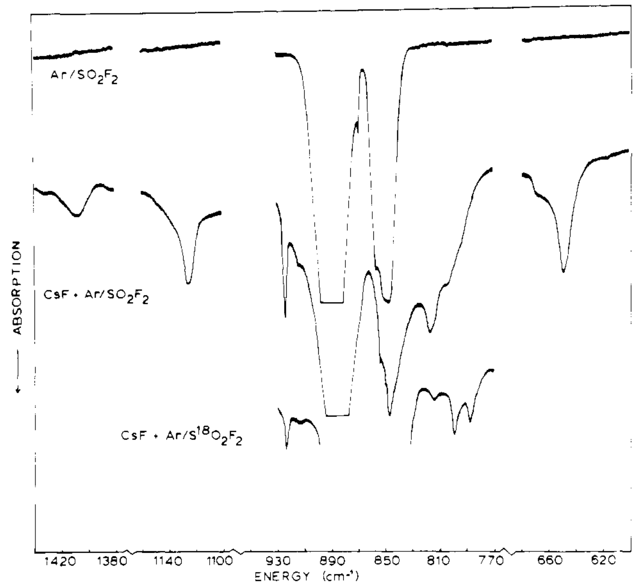

Figure 3. Infrared spectra, over selected spectral regions, of the products of the reactions of CsF with SO_2F_2 (middle trace) and with ^{18}O-enriched SO_2F_2 (lower trace) in argon matrices. The top trace shows a blank spectrum of a sample of $Ar/SO_2F_2 = 500$, over the same spectral region.

in the region 830–900 cm^{-1} made determination of the intensity of the 810-cm^{-1} band difficult. The 1408-cm^{-1} band was somewhat weaker than the other product bands, yet was reproducible, and followed the intensity ratios to the other product bands from one experiment to the next. Again, as parent concentration increased, parent absorption from 1430 to 1500 cm^{-1} made detection of this band somewhat difficult.

CsF + $S^{18}O_2F_2$. CsF was codeposited with a sample of $Ar/S^{18}O_2F_2 = 500$ in two experiments, with an enrichment of about 65% ^{18}O. Unfortunately, the sample was contaminated by some of the precursor $S^{18}O_2$, so that bands due to $S^{18}O_2$, $S^{16}O^{18}O$, and their reaction products with CsF were observed as well. Consequently, ^{18}O counterparts of the product bands of CsF with SO_2F_2 at 1408 and 1130 cm^{-1} were not observable. The product band at 925 cm^{-1} showed virtually no shift, while the product band at 810 cm^{-1} showed a pure ^{18}O counterpart at 788 cm^{-1} and a mixed $^{16}O^{18}O$ counterpart at 799 cm^{-1}. Finally, the product band at 649 cm^{-1} was present and showed only about a 1-cm^{-1} shift with ^{18}O. Spectra of the reaction products of CsF and SO_2F_2 are shown in Figure 3.

Discussion

The reaction of CsF or TlF with each of the parent sulfur oxyfluoride compounds gave rise to a series of infrared absorptions that could not be assigned to either parent species. Previous studies employing the salt/molecule reaction technique have shown that fluoride ion transfer to many acceptors occurs readily, to form a complex ion, in an ion pair with the cesium cation. As discussed below, similar results are apparent here; each of the three systems will be discussed separately, followed by conclusions for this class of anions.

CsF + SO_2. The argon matrix reaction between CsF and SO_2 is anticipated to form the SO_2F^- anion on the basis of the room-temperature crystalline studies of Seel and others.[2-4] The reaction gave rise to five product bands, at 1178, 1100, 598, 471, and 360 cm^{-1}, all of which were quite sharp and were of moderate intensity (other than the band at 360 cm^{-1}, which was quite weak). These bands grew as the concentration of SO_2 in the matrix was increased and at the same time maintained a constant intensity ratio to one another, marking them as arising from a single absorber. More importantly, these bands lie quite close to the bands due to the SO_2F^- anion in room-temperature crystals. Consequently, the product bands observed here are readily assignable to the SO_2F^- anion in isolated ion pairs with Cs$^+$. In addition, when TlF was substituted for CsF in one experiment, a similar set of product bands was observed, shifted 5–25 cm^{-1} from the band positions with Cs$^+$. These results suggest that the anion is not strongly perturbed or distorted by the presence of the metal cation.

Table I. Vibrational Frequencies[a] and Assignments for Isotopically Labeled SO_2F^- in Argon Matrices

species	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ref
$Cs^+S^{16}O_2F^-$	1100	598	471	360(?)	1178		*b*
$Cs^+S^{16}O^{18}OF^-$	1073	590	467		1164		*b*
$Cs^+S^{18}O_2F^-$	1056	582	463		1140		*b*
$Tl^+S^{16}O_2F^-$	1062	589	488		1192		*b*
$Cs^+S^{16}O_2F^-(s)$	1098	594	500	350	1175	275	2

[a] Frequencies in cm^{-1}. [b] This work.

Additional information was obtained in the current study that could not be obtained in the previous investigations. The most important is isotopic oxygen data; reactions of CsF with $S^{18}O_2$ led to product bands at 1140, 1056, 582, and 463 cm^{-1}, which can be assigned to the ^{18}O counterparts of the above product bands. These ^{18}O shifts are of a magnitude that suggests the initial band assignments for this anion are correct; these are the assignments made in Table I. In addition, since the parent $S^{18}O_2$ was roughly 65% enriched in ^{18}O, the intermediate species $S^{16}O^{18}OF^-$ was observed as well. In particular, the region around each product band appeared as a triplet, with the relative intensities identical with those of the parent SO_2 triplet. This demonstrates conclusively the presence of two equivalent oxygen atoms in the SO_2F^- anion, which could only be inferred from previous work.

Previous studies of anions containing both oxygen and fluorine have suggested that cation coordination occurs through the fluorine or fluorines rather than the oxygen.[17] A similar result is suggested here, in the S–F stretching vibration in the anion was broader than S–O stretches. It has been noted previously[18] that the stretching vibration of the coordinated fluorine is broadened by the metal cation. However, this is not particularly definitive and is not of great importance to the overall conclusions of the present study.

CsF + SOF_2. By analogy to previous reactions involving the salt/molecule technique, one might anticipate the formation of the SOF_3^- anion when these two reactants were codeposited. While product bands were observed in this system, complications were provided by the fact that the SOF_2 employed was invariably contaminated with SO_2, which could not be removed by fractional distillation due to the similarities in boiling points. Since the product bands of the SO_2F^- anion have been identified above, the remaining bands can be assigned to a product of the reaction of CsF with SOF_2. In particular, four product bands were observed, at 1264, 695, 667, and 623 cm^{-1}, and all four maintained a constant intensity ratio over a number of experiments. This indicates the presence of a single absorbing species, and with the high dilutions employed, up to 1000/1 in argon, this single species is very likely the 1/1 reaction product. In view of the above facts and the previous results of the salt/molecule reaction technique, the four product bands are assigned to the SOF_3^- anion, in an ion pair with Cs$^+$. This marks the first observation and spectral characterization of this anion, although several

---

(17) Ault, B. S. *J. Phys. Chem.* **1980**, *84*, 3448.
(18) Wermer, P.; Ault, B. S. *Inorg. Chem.* **1981**, *20*, 970.
(19) Alexander, L. E.; Beattie, I. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1745.
(20) Goggin, P. L.; Roberts, H. L.; Woodward, L. A. *Trans. Faraday Soc.* **1961**, *57*, 1877.
(21) Beattie, I. R.; Livingston, K. M. S.; Reynolds, D. J. *J. Chem. Phys.* **1969**, *51*, 4269.

Table II. Comparison of the Stretching Frequencies[a] of Selected 34-Electron Species

species	ν_1	ν_2	ν_7	ν_4	ref
SOF_3^-	1264	695	667	623	*b*
$ClOF_3$	1218	684	671	481	5
SF_4	892	867	730	668	19
PF_4^-	789	780	710	621	18

[a] Frequencies in cm^{-1}. Vibrational designations taken from ref 5. [b] This work.

Table III. Comparison of the Stretching Frequencies[a] of Selected 40-Electron Species

species	ν_{10}	ν_1	ν_7	ν_2	ν_4	ref
$SO_2F_3^-$	1408	1130	925	810	649	*b*
ClO_2F_3	1331	1093	695	683	487	8
SF_4O	1379	927	927	820	741	20
PF_5	1026	1026	944	817	640	21

[a] Frequencies in cm^{-1}. Vibrational designations taken from ref 8. [b] This work.

isoelectronic counterparts are known.

On the basis of location alone, band assignments are relatively straightforward. One anticipates a band due to the sulfur–oxygen stretch and three distinct bands due to sulfur–fluorine stretches, unless a symmetry of C_{3v} or higher is present. The observation of three bands between 600 and 700 cm^{-1} suggests three S–F stretches and hence a symmetry lower than C_{3v}. The band at 1264 cm^{-1} is assigned to the S–O stretching vibration, shifted down from the 1315-cm^{-1} position in parent SOF_2.

The SOF_3^- anion is a 34-valence-electron species, which may be compared readily with several other such species, as is done in Table II. Perhaps the most analogous compound is the neutral chlorine analogue $ClOF_3$, which has been the subject of a number of studies.[5] In this species, the Cl–O stretch was observed at 1218 cm^{-1}, down just slightly from the 1264-cm^{-1} position of the S–O stretch in SOF_3^-. Two of the three Cl–F stretches in $ClOF_3$ lie between 600 and 700 cm^{-1}, while the last was very weak and was located at 481 cm^{-1}. This is quite a bit lower than the lowest S–F stretch in SOF_3^- at 623 cm^{-1}. However, this may be due to an ion-pairing effect with the Cs^+ cation; on the basis of band shape and previous studies,[18] the 623-cm^{-1} band is most likely the stretching mode of the fluorine coordinated with the cesium cation. This coordination may have the effect of both shifting the band to higher energies and intensifying the band. Alternatively, one might argue that the original band assignments for $ClOF_3$ are incorrect, but no other likely candidates for this mode were observed, and the assignment is probably correct.

The structures of other known 34-electron species, such as $ClOF_3$, SF_4, and PF_4^-, are all based on a trigonal-bipyramidal structure, with a lone pair of electrons in one equatorial position. On the basis of the spectral similarities and number of observed vibrational bands, such a C_s structure is probably correct for the SOF_3^- anion as well. Certainly, a C_{3v} structure, such as for PF_3O (a 32-electron species), can be ruled out by the observation of three distinct S–F stretching modes. Finally, by analogy to PF_4^- in the $Cs^+PF_4^-$ ion pair, one might speculate that coordination of the Cs^+ cation is through one of the axial fluorines. This is anticipated also on the basis of the fact that axial fluorines in a trigonal-bipyramidal structure have more electron density and should attract the cation more effectively. In addition, the 481-cm^{-1} band of $ClOF_3$ was assigned to the symmetric axial stretching mode of the two axial fluorine. This mode appears shifted considerably in the SOF_3^- anion; coordination to the metal cation was suggested above as tne case of this shift. This would then support the conclusion that coordination is through one of the axial fluorines. In fact, designation of this mode as the symmetric axial stretch is no longer really appropriate; rather it is the stretch of the coordinated fluorine.

$CsF + SO_2F_2$. The reaction of CsF with SO_2F_2 in argon matrices gave rise to five product bands, two above 1100 cm^{-1} (at 1408 and 1130 cm^{-1}) and three in the S–F stretching region (at 925, 810, and 649 cm^{-1}). Intensity ratio data indicate that all five are due to a single absorber, and in view of the apparent stability of $SO_2F_3^-$ as determined by ICR spectrometry, these bands are assigned to the $SO_2F_3^-$ anion paired with Cs^+. ICR data indicate that the fluoride ion affinity of SO_2F_2 is roughly 40 kcal/mol, making it somewhat surprising that this anion has not been previously isolated under laboratory bench conditions. The synthesis of this anion is also in agreement with postulates of a pentacoordinate sulur anion in the base-catalyzed hydrolysis of SO_2F_2. This is thought to lead to the formation of the $SO_2F_2(OH)^-$ anion, analogous to the $SO_2F_3^-$ anion reported here, which would then undergo F^- displacement.

$S^{18}O_2F_2$ was synthesized to help assign the symmetric and antisymmetric S–O stretching modes. However, impurities $S^{18}O_2$ and $S^{16}O^{18}O$ and their reaction products with CsF obliterated a sufficient spectral region that counterparts of the 1408- and 1130-cm^{-1} product bands could not be observed. These two modes are assigned to the two S–O stretching modes and by analogy[8] to the isoelectronic ClO_2F_3; the upper mode is assigned as the antisymmetric stretch, and the lower band as the symmetric stretch. Of the three lower energy bands, only one showed distinctive behavior upon isotopic labeling with ^{18}O. This was the band at 810 cm^{-1}, which shifted to 788 cm^{-1} and showed a mixed $^{16}O^{18}O$ counterpart at 799 cm^{-1}. This suggests that the 810-cm^{-1} band corresponds to the stretching of the fluorine in the equatorial plane with the two oxygens. This S–F stretch would necessarily be vibrationally coupled to the two S–O bonds and hence should show some mass dependence of the oxygen atom. The other S–F vibrations are the antisymmetric and symmetric axial stretching modes, and these should show virtually no ^{18}O shift, as they are at roughly 90° to the S–O bonds and coupled at best only weakly through anharmonic terms. On the basis of intensities, the 925-cm^{-1} band is assigned as the antisymmetric stretching mode, and the 649-cm^{-1} band as the symmetric stretch. Finally, the 649-cm^{-1} band likely represents the stretch of the coordinated axial fluorine, and hence the designation of "symmetric axial stretch" is not particularly accurate.

The above assignments have assumed a trigonal-bipyramidal structure for this anion, with the two oxygen atoms in the equatorial plane with one fluorine and the remaining two fluorines in axial positions. Not only does this structure satisfactorily explain all of the vibrational bands and their ^{18}O dependencies (where observed) but this structure is in agreement with a number of other known 40-electron species, as shown in Table III. The closest analogy is ClO_2F_3, which shows precisely this structure. In addition, SOF_4 and PF_5 also show a basic trigonal-bipyramidal structure. Hence, on the basis of the vibrational data obtained here, such a C_{2v} structure seems most likely for the $SO_2F_3^-$ anion.

Conclusions

The salt/molecule reaction techniue has allowed the formation and spectroscopic characterization of the SO_2F^-, and $SO_2F_3^-$ anions, each ion paired with the cesium cation. The spectra of the SO_2F^- anion were in good agreement with literature spectra, and ^{18}O isotopic data obtained here confirmed the equivalence of the two oxygen atoms. The synthesis of the SOF_3^- anion represents the first identification of this anion under any conditions, although yields were relatively low throughout. The spectra and analogy to the known $ClOF_3$ species suggest an overall trigonal-bipyramidal structure, with a lone electron pair in one equatorial position, giving rise to a C_s geometry (neglecting the presence of the cation). Spectra of the $SO_2F_3^-$ anion were similar to those of known 40-electron species, including the chlorine counterpart, ClO_2F_3, and suggested a trigonal-bipyramidal structure with the two oxygen atoms in equatorial positions.

It is interesting also to note trends in reactivity in the current study. Samples of SOF_2 contained some impurity SO_2 in all experiments, and the yield (based on band intensities) of the SO_2 reaction product with CsF was greater than the yield of reaction product of CsF with SOF_2. One might infer a considerably greater cross section for the reaction of CsF with SO_2 relative to SOF_2. Likewise, while normal samples of SO_2F_2 did not contain any SO_2, samples of $S^{18}O_2F_2$ did contain some labeled SO_2 as well. Here, too, the yield of SO_2F^- was relatively greater than the yield of $SO_2F_3^-$, again indicating a greater reaction cross section with SO_2 than with SO_2F_2. While no attempt was made to compare relative reactivities of SOF_2 and SO_2F_2, product yields seem to indicate that SO_2F_2 is more reactive toward CsF than is SOF_2.

Acknowledgment. The authors gratefully acknowledge support of this research by the National Science Foundation, through grant CHE8100119, and B.S.A. thanks the Dreyfus Foundation for a Teacher-Scholar Grant. Dr. F. T. Prochaska is also gratefully acknowledged for his gift of a cylinder of SO_2F_2.

Registry No. SO_2F^-, 22539-11-3; SOF_3^-, 86527-07-3; $SO_2F_3^-$, 67269-52-7; CsF, 13400-13-0; SO_2, 7446-09-5; SOF_2, 7783-42-8.

Contribution from the DGR-SEP-SCPR, Centre d'Etudes Nucléaires de Fontenay-aux-Roses, Fontenay-aux-Roses 92260, France,
and DPC-SCM, Centre d'Etudes Nucléaires de Saclay, Gif/Yvette Cedex 91191, France

Azide Interaction with 4f and 5f Ions in Aqueous Solutions. 1. Trivalent Ions

C. MUSIKAS,[*,†] C. CUILLERDIER,[†] J. LIVET,[†] A. FORCHIONI,[‡] and C. CHACHATY[‡]

Received November 16, 1982

Solvent extraction and UV, Raman, and NMR spectroscopic studies were carried out on trivalent actinide and lanthanide aqueous azido complexes. Unlike trivalent d transition ions ($\beta_{11} \simeq 10^5$) 5f and 4f aqueous azido complexes are weak ($\beta_{11} \simeq 2.5$ for $Nd(N_3)^{2+}$), but the trivalent actinides exhibit formation constants 1 order of magnitude higher than the lanthanides. All the spectroscopic methods indicate that we are dealing with inner-sphere complexes and actinide–lanthanide differences must be attributed to higher covalent contributions in the 5f azides. ^{15}N NMR combined with ^1H NMR served to investigate the azide binding properties. With the trivalent 5f and 4f ions the binding occurs by one of the terminal nitrogen atoms. The M–N bond distance is close to 2.75 Å. The lanthanide(III)–(linear azide) moieties are bent with a bond angle close to 135°, unlike the homologous linear thiocyanate complexes.

Introduction

The 5f- and 4f-block ions form complexes with pure nitrogen donors that are difficult to observe in aqueous solutions due to unfavorable competition with the water molecules. However, investigations dealing with 4f and 5f trivalent ion–nitrogen donor complexes are of great interest because they offer an insight into the similarities and differences in the chemical behavior of the two f series.

Moreover actinide–lanthanide group separations[1,2] have been performed from media in which the trivalent ions are engaged in complexes with ligands possessing donor atoms less electronegative than oxygen. Consequently, investigations like the one reported here could lead to new actinide–lanthanide group separation processes. In a previous paper,[3] we showed that ^{14}N, ^{15}N, and ^{13}C nuclear magnetic resonance, Raman, and UV spectroscopic measurements indicate that lanthanide thiocyanato complexes are mostly inner sphere, and consequently 4f–5f group separations from thiocyanate media stem from differences in complex stability and not from differences in complex type[4] (inner sphere for 5 f ions vs. outer sphere for 4f). The greater stabilities of the actinide complexes could be attributed to higher covalent interactions, since the ionic radii of the 4f and 5f trivalent ions are closely comparable (1.1 to 0.9 Å). This paper deals with the binding properties of azide ions with f-series trivalent ions. The d-block ions form stable complexes in aqueous solutions.[5] Raman and infrared spectroscopic results indicate[6] that in $Co(N_3)_4^{2-}$, $Zn(N_3)_4^{2-}$, and $Sn(N_3)_6^{2-}$ the M—N═N═N moieties are bent.

The crystal structures of NaN_3[7] and $Co(NH_3)_5N_3(N_3)_2$[8] have been determined, and two kinds of N_3^- ions have been identified. Ionically bonded N_3^- ions in NaN_3 and the outer-sphere N_3^- ions in $Co(NH_3)_5N_3(N_3)_2$ are linear and symmetrical with N-N distances close to 1.15 Å. In covalently bonded azide, two N═N distances are observed, the longer between central nitrogen (N_2) and bonded nitrogen (N_1). In HN_3[9] and CH_3N_3,[10] for instance, the N_1–N_2 and N_2–N_3 distances differ by 0.11 Å (1.24 against 1.13 Å, slightly more than the distances observed for the inner-sphere N_3^- of $Co(NH_3)_5\ N_3(N_3)_2$, i.e. 1.2 and 1.15 Å. Covalently linked moieties M—N═N═N are bent with M-N_3 bond angles as follows: 112° in HN_3, 120° in CH_3N_3, and 125° in $Co(NH_3)_5N_3(N_3)_2$.

Few reports concerning the f-block azide complexes are to be found in the literature. It has been claimed that UO_2^{2+} ions form the aqueous species $UO_2(N_3)^+ \cdot xH_2O$, $UO_2(N_3)_2 \cdot yH_2O$, and $UO_2(N_3)_3^- \cdot zH_2O$.[11] Complexes with trivalent

---

[†] Centre d'Etudes Nucléaires de Fontenay-aux-Roses.

[‡] Centre d'Etudes Nucléaires de Saclay.

(1) R. E. Leuze and M. H. Lloyd, *Process Chem.*, **4**, 197 (1970).

(2) P. T. Gerontopoulos, L. Rigali, and P. G. Barbano, *Radiochim. Acta*, **4**, 75 (1965). W. W. Schulz, "The Chemistry of Americium", 1976, TID 26271-236.

(3) C. Musikas, C. Cuillerdier, and C. Chachaty, *Inorg. Chem.* **17**, 3610 (1978).

(4) P. K. Khopkar and J. N. Mathur, *J. Inorg. Nucl. Chem.*, **36**, 3819 (1974).

(5) L. G. Sillên and A. E. Martell, "Stability Constants of Metal Ion Complexes", Chemical Society, London, 1964; supplement, 1971.

(6) D. Forster and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1510 (1966).

(7) G. J. King, B. S. Miller, F. F. Carlson, and R. C. MacMillan, *J. Chem. Phys.*, **35**, 1442 (1961).

(8) G. J. Palenik, *Acta Crystallogr.*, **17**, 360 (1964).

(9) E. Amble and B. P. Dailey, *J. Chem. Phys.*, **18**, 1422 (1950).

(10) R. L. Livingston and C. N. R. Rao, *J. Phys. Chem.*, **64**, 756 (1960).

0020-1669/83/1322-2513$01.50/0