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DISCLAIMER

To Jane, without whose love this work could not have been completed.

PERFLUOROAROMATIC CATIONS AND RELATED STUDIES

Contents

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ABSTRACT

The radical cations $C_6F_6^+$ and $C_{10}F_8^+$ were synthesized in bulk solids for the first time through the reactions of hexafluorobenzene with dioxygenyl salts and of $C_6F_6^+$ with octafluoronapthalene. The novel compounds thus prepared were characterized by a number of physical and spectroscopic techniques, and the crystal structure of $C_6F_6^+AsF_6^-$ was determined from X-ray powder diffraction data.

Adducts formed by the interaction of chlorine with dioxygenyl salts were investigated and preliminary results are presented. Formation of these adducts is partly reversible, and does not appear to involve substantial oxidation of chlorine. These are tentatively formulated as salts of the previously unreported cation, $Cl_2O_2^+$.

Studies of the oxidizing power of dioxygenyl salts and the oxidizing and fluorinating properties of iridium hexafluoride were carried out with the aim of oxidizing inorganic anions to their corresponding neutral radicals. These experiments were unsuccessful, but give insight into the problems involved, and hold out some hope for future success.

The xenon (II) salts $Xe_2F_3^+RuF_6^-$ and $Xe_2F_3^+IrF_6^-$ were hydrolysed to produce RuO_4 and an as yet unidentified volatile iridium compound, possibly IrO_4.

In addition, the presence of $ClO_2^+IrF_6^-$ in preparations of $ClF_2^+IrF_6^-$ has been explained and a crystal structure thought to be that of the ClF_2^+ salt has been re-interpreted in the light of these findings.

I. INTRODUCTION

This thesis consists of several interrelated studies (Chapters III through VI), and two separate, short investigations (Chapters VII and VIII). The greater part of the work deals with the preparation and characterization of several radical cations, most notably $C_6F_6^+$ and $C_{10}F_8^+$, along with attempts to prepare a number of inorganic free radicals by one-electron oxidation of the corresponding anions.

Chapter VII describes the controlled hydrolysis of xenon (II) salts of pentavalent ruthenium and iridium. Chapter VIII is a reinvestigation and clarification of the composition of adducts formed in the reaction of chlorine triflouride with iridium pentafluoride.

The apparatus and techniques of inorganic fluorine chemistry, utilized in all parts of this work, are detailed in Chapter II. Some specialized procedures were developed for use in individual experiments, and these are laid out in the appropriate chapters. A brief history and discussion of theoretical considerations is presented at the beginning of each chapter.

II. METHODS AND MATERIALS

General Methods

Since a great number of the compounds dealt with in this work are air-sensitive (often dangerously so), they must be handled in vacuum systems or in the relatively inert atmosphere of a dry box. The corrosive nature of many inorganic fluorine compounds required the construction and use of a metal vacuum system, to which vessels of metal, fluorinated polymers, and fused silica or pyrex glass may be attached.

Involatile air-sensitive solids were handled in a Vacuum Atmospheres Dri-Lab, with two continuous-flow drying trains which kept both oxygen and water concentrations at a minimum. These were regenerated in alternation on a regular schedule.

Apparatus was tested for leaks using a Consolidated Vacuum quadrupole mass spectrometer helium leak detector when first assembled, and re-tested each time a connection was broken. Teflon FEP tubing was found to be somewhat porous to helium, so that leak-testing of such apparatus had to be performed rapidly.

The vacuum line and drybox have been described in detail by Schriver,[1] and by several others.[2-4] The vacuum system used in this work was constructed of 1/4 in. monel and copper tubing, monel Swagelok fittings, and monel and brass Whitey 1KS4 valves, with both stainless steel- and Kel-F plastic-tipped valve stems (see Fig. II-1).

Vacuum was provided by small recirculating oil-seal pumps and by a high vacuum manifold with a 2-inch diameter silicone oil diffusion pump. Pressures as low as 5×10^{-3} mm, measured by a Hastings thermocouple

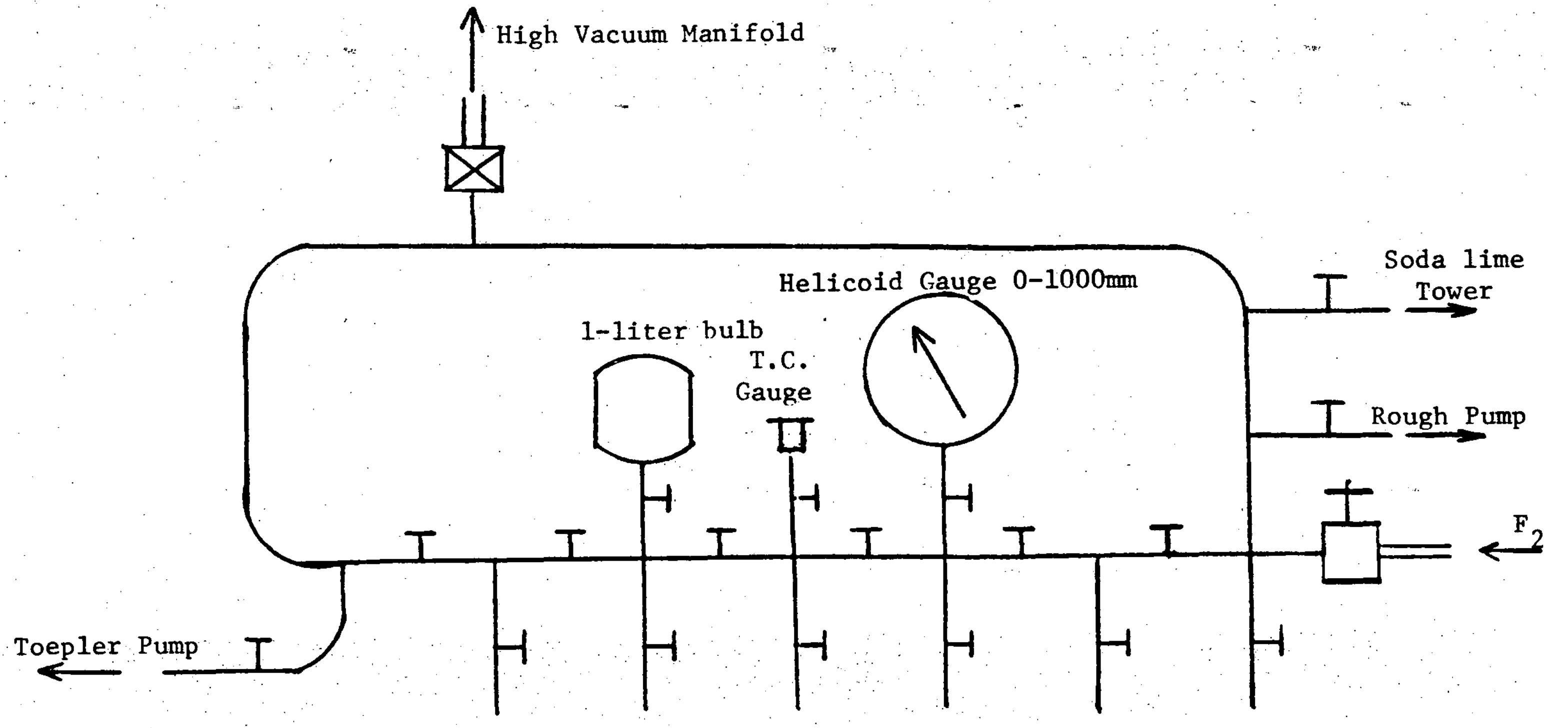

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Fig. II-1. Schematic diagram of the metal vacuum line.

gauge, were commonly obtained. Pressures in the range 0 to 1500 mm were routinely measured by a Bourdon-type Helicoid gauge manufactured of monel for use with fluorine or oxygen.

High-pressure and high-temperature reactions were carried out in specially-fabricated monel/stainless steel autoclave bombs capable of withstanding pressures of 500 atmospheres at temperatures up to 600°. Under such extreme conditions attack on the walls of the bombs often occurred, with resultant contamination of the product by hexafluoronickelate (IV) salts. This was minimized by insertion of a tight-fitting nickel sleeve which was better able to resist attack and allowed easier recovery of the product. When an operation called for a larger volume, medium-pressure (2-12 atm) container, a 150 ml monel can with removable lid was employed. The bottom of the can was made from 2 in. o.d. monel tubing, with a wall thickness of 1/16 in. To this was welded a disc of 1/16 in. monel sheet, The top of the can was welded monel sheet, recessed for a Teflon O-ring which provided a leak-tight seal, and with a jacket through which water or compressed air could be run to cool the lid. Cooling was necessary to protect the soft Teflon O-ring when the temperature of the can bottom exceeded 150°, and to present a cold surface (inside lid) for sublimation of volatile materials.

In early experiments, Kel-F reaction vessels were used to allow visual observation of reaction mixtures. It was found, however, that dioxygenyl salts and, to a lesser extent, iridium hexafluoride caused Kel-F to crack and leak even after short exposures to these strong oxidizers. Subsequently, reaction vessels were constructed of

Teflon FEP tubing, a fluorinated ethylene-propylene copolymer not so susceptible to attack, and, when possible, of fused silica. Teflon FEP proved to be more transparent and resistant to extremes of temperature than Kel-F, but was slightly more porous, and such vessels were stored in the drybox whenever possible to prevent the entry of oxygen or moisture.

Both the Teflon FEP and fused silica vessels were connected to brass Whitey valves by means of Swagelok 3/8 in. to 1/4 in. reducing unions, with Teflon ferrules in the 3/8 in. connection. Lengths of FEP tubing were heated at one end until soft, then crimped with a flat-nosed pliers to form a leak-tight seal. Fused silica vessels with an outside diameter at the open end of 10 mm were inserted into 3/8 in. unions which had been bored out to 10 mm for the purpose. The Teflon ferrules were stretched over the 10 mm necks with the aid of gentle heating.

Instrumentation

Infrared spectra were obtained on a Perkin-Elmer 337 Infrared Spectrometer over the range 400-4000 cm^{-1}. Gases generally were examined in a silver-plated monel cell with AgCl windows and a 10 cm path length. Where contact of the gases with metal surfaces was to be avoided, as in the hydrolysis of $Xe_2F_3^+MF_6^-$ salts, a cell of similar size, machined from a solid block of Kel-F, was employed. Solids and liquids were pressed between AgCl windows in a Kel-F cell.

Raman spectra were routinely run on a Cary 83 Raman Spectrometer using Ar^+ laser excitation at 488 nm. For more precise data, and for compounds sensitive to the blue exciting line of the Cary 83, samples were taken to the USDA Western Regional Research Laboratories in Albany, California, where Kr^+ and Ar^+ lasers provided a wide range of excitation wavelengths. Back-scattered light at 180° was analyzed by a Spex 1401 double monochromator and photon counter. A low-temperature cell utilizing a liquid nitrogen cooled copper block was available for thermally unstable or light-sensitive materials, as was a cold nitrogen gas stream for temperatures down to -75°. Samples of solids and liquids were loaded into 1.0-1.5 mm O.D. quartz or pyrex capillaries, which were dried at 190° for several days prior to introduction into the dry box. Once filled, the capillaries were temporarily sealed by a plug of Kel-F grease for removal from the drybox, then sealed in a micro-flame.

Electron paramagentic resonance spectra were obtained using a Varian V4500 EPR spectrometer with a 9-inch magnet, operating in X-band (9.5 GHz), with a variable temperature probe capable of maintaining the samples at temperatures as low as -110°. The spectra were run by Richard Wilson of this department. Samples were held in 4 mm O.D. pyrex, quartz, or Kel-F tubes.

Bulk magnetic susceptibilities were determined using a Princeton Applied Research vibrating-sample magnetometer, operating at liquid helium temperatures and above. Samples were contained in specially fabricated Kel-F tubes with a threaded piston to insure tight packing of the solid, and a Viton O-ring seal.

X-ray powder diffraction patterns for solid samples were photographed on a General Electric Precision Powder Camera, using CuKα radiation and a graphite monochromator. Solid materials were finely powdered and shaken, tapped, or vibrated into 0.3-0.5 mm O.D. quartz capillaries which were dried and sealed in the same manner as those used for Raman spectra. X-ray films were measured on a Norelco illuminated film measuring device and, where possible, indexed.

Suppliers of Chemicals and Materials

Matheson Gas Products, East Rutherford, New Jersey, supplied:

- Anhydrous hydrogen fluoride
- Bromine pentafluoride
- Bromine trifluoride
- Chlorine
- Chlorine trifluoride
- Fluorine
- Iodine pentafluoride
- Phosphorous pentafluoride
- Tungsten Hexafluoride
- Xenon

PCR Inc., Gainesville, Florida:

- Hexafluorobenzene
- Octafluoronapthalene
- Potassium hexafluorophosphate

Pacific Oxygen Co., Oakland, California:

Argon

Oxygen

Ozark-Mahoning Co., Tulsa, Oklahoma:

Arsenic pentafluoride

Potassium difluorophosphate

Mallinkrodt Chemical Works, St. Louis, Missouri:

Potassium fluoride

Silver Nitrate

Alfa Inorganics, Beverly Massachusetts:

Cesium nitrate

Cationics Inc., Cleveland, Ohio:

Antimony pentafluoride

Research Organic/Inorganic Chemical Corp., Sun Valley, California:

Cesium fluoride

Fluorocarbon Corp., Anaheim, California:

Teflon FEP and Kel-F tubing

Traco, Inc., Somerville, New Jersey:

Quartz capillaries for X-ray and Raman spectroscopy

Halocarbon Products Corp., Hackensack, New Jersey:

Kel-F grease

Units

An attempt has been made to standardize units throughout this thesis. Temperatures are given in degrees centigrade unless otherwise noted. Pressures are in mm of mercury or atmospheres as indicated. Weights are in grams, energy units are k-cal mol^{-1} or electron volts. Vibrational frequencies are stated in reciprocal centimeters, unit cell dimensions in angstroms. Magnetic susceptibilities are in cgs units, magnetic moments in Bohr magnetons.

III. OXIDIZING AND FLUORINATING PROPERTIES OF IRIDIUM HEXAFLUORIDE

The remarkable oxidizing capabilities of the third transition series hexafluorides have been described by Bartlett,[5] who showed that the electron affinities of these molecules increase regularly in the sequence $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$. A study by Jha[6] of the reactions of PtF_6 with O_2, Xe, NO, CO and NF_3 established upper and lower limits for its electron affinity. That PtF_6 is a more powerful oxidizer than IrF_6 has been demonstrated by the oxidation of O_2:[2,4]

$$O_{2(g)} + PtF_{6(g)} \rightarrow O_2^+ PtF^-_{6(s)}$$

$$O_{2(g)} + IrF_{6(g)} \rightarrow \text{no reaction} \quad .$$

On the other hand, although both PtF_6 and IrF_6 convert nitrosyl fluoride to nitrogen oxide trifluoride, the yield of ONF_3 is much greater in the case of IrF_6, proceeding according to the equation:

$$3IrF_{6(g)} + 4ONF_{(g)} \rightarrow 3NO^+IrF^-_{6(s)} + \frac{1}{2} F_{2(g)} + ONF_{3(g)} \quad ,$$

whereas the PtF_6 reaction gives only a trace. It would appear, then, that the fluorine ligands in IrF_6 are more labile.

Because of its relative ease of preparation,[7] iridium hexafluoride is a more convenient reagent than platinum hexafluoride. An investigation into the feasibility of generating neutral inorganic radicals by one-electron oxidation of NO_3^-, PF_6^-, $PO_2F_2^-$, WOF_5^- and ReO_4^- by IrF_6 was undertaken. The ease with which IrF_6 gives up fluoride ion, however, thwarted these preparations, and the product in each case was a known high-valent fluoride or oxyfluoride.

Historical Background

NO_3. The nitrate radical, NO_3, was first proposed by Ogg[8] as an intermediate in the decomposition of N_2O_5. Johnston[9] later extended the chemistry of NO_3 to other nitrogen-oxygen kinetic systems. It has been prepared and identified by its characteristic optical absorption spectrum[10] in flash-photolyzed ceric ammonium nitrate solutions. NO_3 has been prepared directly from NO_2 and atomic oxygen on molecular sieves, and characterized by epr spectroscopy.[11] These spectra indicate an axially symmetric, planar D_{3h} molecule, a finding substantiated by other workers[12-14] who observed the radical in irradiated crystals and glasses. Calculations by Olsen and Burnelle,[15] however, suggest a weak Jahn-Teller distortion in the plane, lowering the symmetry from D_{3h} to C_{2v} in the gas-phase molecule. The electron affinity of NO_3 was estimated from a molecular beam study to lie between 2.77 and 3.2 eV.[16] This puts the oxidation of NO_3^- well within the range of IrF_6. Since the decomposition of NO_3 via the mechanism

$$2NO_3 \rightarrow 2NO_2 + O_2$$

appears[9] to have a fairly low activation energy, the radical would probably have to be trapped at low temperatures and identified by an epr spectrum.

PF_6. The hexafluorophosphate radical has not been prepared or suggested in chemical reactions. It is electron affinity, however, may be estimated by comparison with the ionization potential of SF_6, which is isoelectronic with PF_6^-. This value, 15.29 eV,[17] is probably somewhat high, due to the slightly larger nuclear change in SF_6. Christe[18] has claimed evidence for the similar species AsF_6, from AsF_5 and fluorine atoms, as the high energy oxidizer in the photochemical oxidations of NF_3, O_2 and Xe. These reactions, however, proceed equally well in the absence of AsF_5, and no other evidence for AsF_6 was obtained.

PO_2F_2. The difluorophosphate radical, PO_2F_2, was first observed by Symons and co-workers[19] in γ-irradiated POF_3 containing HPO_2F_2 impurity. Evidence for the existence of PO_2F_2 as a moderately stable free radical has been presented by Des Marteau and Eisenberg,[20] who obtained intensely colored yellow-orange solutions from the decomposition of xenon (II) difluorophosphates in $CFCl_3$ and Cl_4. The uv and epr spectra of these solutions strongly resemble those of the isoelectronic species SO_3F. The dimer of PO_2F_2, however, was not observed, as the decompositions followed the route:

$$FXeOPOF_2 \rightarrow Xe + \frac{1}{2}O_2 + POF_3$$

and

$$Xe(OPOF_2)_2 \rightarrow Xe + \frac{1}{2}O_2 + P_2O_3F_4 \quad ,$$

the peroxy-bridged dimer $P_2O_4F_4$ being apparently much less stable than $F_2OP{-}O{-}POF_2$, the anhydride of difluorophosphoric acid. This is also the only product of the photolysis of POF_2Br in the presence of excess oxygen.[21] It is worth noting that the reaction of XeF_2 with $HOPOF_2$ gives not the difluorophosphates of xenon, but fluorination products, POF_3 and PF_5, along with Xe, O_2 and HF.[20]

WOF_5. The oxopentafluorotungstate (VI) ion, WOF_5^-, was first prepared by Bartlett and Robinson[22] in the fluorination of WO_3 by SeF_4 in the presence of KF. The nitrosyl salt, $NO^+WOF_5^-$, is produced along with WF_6, in the reaction of NF_3 with WO_3.[23] Thus, a strong fluorinating agent can completely eliminate the oxide ligands around tungsten, provided the oxo-complex is not stabilized by salt formation. Upon one-electron oxidation of the anion, the resulting "tungsten (VII)" oxyfluoride might be expected to form a peroxy-bridged dimer, or possibly to eliminate oxygen:

$$2WOF_5 \rightarrow \frac{1}{2} O_2 + F_5W\text{-}O\text{-}WF_5 \quad .$$

ReO_4. The highest known oxide of rhenium is Re_2O_7,[24] a stable, high-boiling solid. Early reports[24,25] of volatile "rhenium octoxide", Re_2O_8, have not been substantiated, and the material in question was most likely perrhenic acid, $HReO_4$. Being a radical molecule, ReO_4 would also be expected to dimerize, with the resulting peroxy-bridged molecule unstable at elevated temperatures to oxygen and Re_2O_7. In an oxidizing medium, however, ReO_4 might persist long enough to allow it to be trapped at low temperature and characterized by epr (naturally occurring rhenium has two isotopes of spin 5/2, Re^{185} and Re^{187}). Additionally, the dimeric species, Re_2O_8 would probably be sufficiently volatile for vapor-phase infrared spectra, if sufficiently stable to persist at room temperature.

The Reaction of IrF_6 with $AgNO_3$

Silver nitrate (0.16 g, 0.94 mmol) was dissolved in iodine pentafluoride (2 ml) (m.p. 9.4°, b.p. 102°) in a Kel-F reaction vessel. Not all of the silver nitrate dissolved. No reaction occurred between $AgNO_3$ and IF_5 at room temperature. Iridium hexafluoride was prepared by heating Ir powder in an excess of F_2 to 300° for several hours. IrF_6 (vapor pressure 226 mm at 25°), in excess of the amount required for:

$$AgNO_3 + IrF_6 \quad NO_3 + AgIrF_6$$

was condensed into the reaction vessel at -196°, and the contents allowed to warm up. As the IF_5 solvent melted, IrF_6 dissolved in it to produce a bright yellow solution. A brown solid, later identified as silver difluoride (AgF_2) was formed and floated in the IF_5, while the pressure above the liquid rose to 250 mm at 25°. An infrared spectrum of the gaseous products showed absorptions due to IrF_6, IF_5 and nitryl fluoride, NO_2F. On removing the volatile material by pumping into a liquid nitrogen trap, a brown residue was left behind. X-ray powder diffraction photographs indicated the presence of silver difluoride and one or more other phases, probably lower fluorides of iridium. Thus, the reaction may be written:

$$IrF_6 + AgNO_3 \xrightarrow{IF_5} AgF_2 + NO_2F + IrF_x \qquad (x < 6)$$

Since the X-ray powder pattern did not contain lines due to $NO_2^+IrF_6^-$, which would surely have been formed from IrF_5 and NO_2F, it is likely that $x < 5$ in the above equation.

The Reaction of IrF_6 with $CsNO_3$

Cesium nitrate was dissolved in iodine pentafluoride and IrF_6 was added until the solution became yellow. Some non-condensible gas was evolved during the reaction. The infrared spectrum of gaseous products showed only IrF_6 and IF_5. No NO_2F was seen in the gases. An X-ray powder diffraction photograph indicated the presence of approximately equal quantities of $CsIrF_6$ and nitrosyl hexafluororidate, $NO_2^+IrF_6^-$. The net reaction is:

$$CsNO_3 + IrF_6 \xrightarrow{IF_5} CsIrF_6 + NO_2IrF_6 + \frac{1}{2} O_2$$

Here nitrate is oxidized to molecular oxygen, perhaps via a nitrate radical, NO_3 :

$$NO_3^- + IrF_6 \rightarrow NO_3 + IrF_6^-$$

$$NO_3 \rightarrow NO_2 + \frac{1}{2} O_2$$

$$NO_2 + IrF_6 \rightarrow NO_2^+IrF_6^- \quad .$$

The Reaction of IrF_6 with $CsPF_6$

Cesium hexafluorophosphate was prepared by the reaction of cesium fluoride and phosphorus pentafluoride in anhydrous hydrogen fluoride solution. 0.38 g (2.5 mmol) cesium fluoride was dissolved in about 4 ml of anhydrous hydrogen fluoride. Phosphorus pentafluoride was admitted at a pressure of about 1100 mm Hg. White $CsPF_6$ precipitated rapidly. When uptake of the gas ceased, the PF_5 and HF solvent were removed slowly under vacuum. The product, 0.66 g (2.4 mmol), was identified as pure $CsPF_6$ by its characteristic X-ray powder pattern, and by a Raman spectrum[45] (ν_1 PF_6^- 705 cm^{-1}).

$CsPF_6$ was dissolved in several ml of IF_5, and a small quantity of IrF_6 was condensed onto the solution at -78° (dry ice-isopropanol slush bath). On warming to room temperature, the IrF_6 dissolved in the IF_5, imparting a bright yellow color to the liquid. A slow evolution of gas was accompanied by gradual decoloration of the solution. The solvent was removed under vacuum, leaving a white solid residue.

An infrared spectrum of the evolved gases showed bands due to PF_5, IF_5, CF_4 and COF_2, the latter two the result of attack on the Kel-F reaction vessel. An X-ray powder pattern of the white solid indicated the presence of cesium hexafluoroiridate, $CsIrF_6$, as well as the starting material, $CSPF_6$.

The net reaction, then may be written:

$$CsPF_6 + IrF_6 \xrightarrow{IF_5} CsIrF_6 + PF_5 + \frac{1}{2} F_2$$

It is possible that the reaction proceeds through an intermediate, $[PF_6]$:

$$CsPF_6 + IrF_6 \rightarrow CsIrF_6 + PF_6$$

$$PF_6 \rightarrow PF_5 + \frac{1}{2} F_2$$

but no evidence was seen for this species.

When IrF_6 was added to a saturated solution of PF_5 in anhydrous HF, no decoloration of the solution was observed. However, a small amount of OPF_3, present as an impurity in the commercial PF_5, was removed apparently by conversion to PF_5.

The reaction of IrF_6 with KPF_6 was also run in bromine pentafluoride solution. Again, the only volatile product was PF_5.

The Reaction of IrF_6 with KPO_2F_2

Iridium hexafluoride was reacted with potassium difluorophosphate in a static system, both neat and in iodine pentafluoride solution, and in a flow system diluted with argon.

In the static system, IrF_6 was condensed onto finely divided KPO_2F_2 contained in a Kel-F tube, and allowed to warm up. After 2 hr, an infrared spectrum of the gases showed only IrF_6, while a Raman spectrum and X-ray powder pattern of the solid showed no change from the original KPO_2F_2 starting material.

When IF_5 was added to the reactants, a vigorous reaction took place, with evolution of a non-condensible gas. The yellow color of IrF_6 faded. An infrared spectrum now showed the presence of PF_5, as well as CF_4 from attack on the container walls. The solid residue which remained after removal of volatiles contained potassium hexafluoriridate as shown by its X-ray powder pattern.

In the flow system, potassium difluorophosphate, held in a Kel-F trap, was exposed to iridium hexafluoride carried by a stream of argon gas through the reaction vessel and then through a trap held at -78°. The IrF_6 effused slowly from a can whose temperature was varried from 0° to ambient, depending upon the desired concentration of IrF_6. The cold trap captured nearly all the IrF_6 and a small amount of a white solid which was not volatile after deposition, and was not characterized due to insufficient quantity. No other compound appeared in infrared spectra of the contents of the trap.

As in the case of the OPF_3 impurity in PF_5, $PO_2F_2^-$ was completely fluorinated to PF_5, with evolution of molecular oxygen:

$$IrF_6 + KPO_2F_2 \quad KIrF_6 + PF_5 + O_2 + IrF_x \qquad (x < 6)$$

The Reaction of IrF_6 with $KWOF_5$

Potassium oxopentafluorotungstate (VI), $KWOF_5$, was prepared by the reaction of potassium fluoride, water and tungsten hexafluoride in anhydrous hydrogen fluoride solution. A 1:1 mixture of KF and H_2O was prepared by reaction of KOH pellets with excess HF. An excess of tungsten hexafluoride was then combined with this solution to produce the desired oxopentafluoride:

$$WF_6 + KF + H_2O \rightarrow KWOF_5 + 2HF$$

The remaining WF_6 and HF were easily removed under vacuum, leaving the pure white $KWOF_5$ behind. It was identified by its Raman spectrum,[46] which consists of bands at:

1041 cm^{-1}	W-O stretching
698	W-F stretching
321	F-W-F bending
312	F-W-F bending

The spectrum is quite similar to that of the parent oxyfluoride, WOF_4, which has the same point symmetry, C_{4v}.

When IrF_6 was exposed to the dry solid $KWOF_5$, no reaction was apparent. In the gas-phase infrared spectrum, a small amount of WF_6 was observed. Addition of a few ml of anhydrous HF caused the reaction of proceed rapidly, as indicated by decoloration of the solution. Some non-condensible gas was produced. The gases above this solution included a quantity (>5%) of WF_6, some SiF_4, CF_4 and COF_2, a preponderance of HF, and an unidentified material absorbing at around 950 cm^{-1} (PWR band) and 1160 cm^{-1}, which faded with time. Attempts to isolate this substance from HF and WF_4 by trap to trap distillation were unsuccessful.

A similar reaction was carried out using bromine pentrafluoride as solvent. The amount of WF_6 produced in this reaction was greater than that in the HF case.

The Reaction of IrF_6 with $KReO_4$

Potassium perrhenate (0.05 g, 0.17 mmol) was ground to a fine powder and placed in a teflon FEP reaction tube. Iridium hexafluoride (0.05 g, 0.17 m-mol) was condensed onto the powder at -196° and the tube was warmed slowly to room temperature. No immediate reaction was apparent. An infrared spectrum of the gases present showed only IrF_6 and tetrafluoromethane (from attack on the reaction tube and/or IR cell).

Gentle heating of the gas-solid mixture caused the white solid to become gray, but no change was observed in the composition of the gases. An x-ray powder pattern of the solid showed only lines due to $KReO_4$.

When bromine pentafluoride was condensed onto solid $KReO_4$ with the intention of reacting the resulting solution with IrF_6, oxygen was evolved, the liquid became orange, and a black involatile residue was formed (possibly ReO_2).

IV. OXIDIZING PROPERTIES OF DIOXYGENYL SALTS

The dioxygenyl ion, O_2^+, was first prepared by Bartlett and Lohmann[26] as the compound $O_2^+PtF_6^-$, from the fluorination of platinum in the presence of silica. Since then, many dioxygenyl salts have been made by a number of different routes. Young and co-workers[27] prepared O_2PF_6, O_2AsF_6 and O_2SbF_6 by the reaction of O_2F_2 with the corresponding pentafluorides. O_2BF_4 also was prepared from O_2F_2 and BF_3 by Solomon et al.[28] O_2AsF_6 and O_2SbF_6 are more easily prepared by heating[29] or photolyzing[30] mixtures of oxygen, fluorine and AsF_5 or SbF_5. A recent paper[31] by McKee and Bartlett clarifies the fluoroantimonate system, and describes convenient syntheses for O_2SbF_6 and $O_2Sb_2F_{11}$. O_2AuF_6 has been prepared by Leary and Bartlett.[32] Edwards et al.[33] have reported the new salts: O_2RuF_6, O_2RhF_6, O_2BiF_6, $O_2Bi_2F_{11}$, O_2NbF_6, $O_2Nb_2F_{11}$ and $O_2Ta_2F_{11}$. The same investigators have also prepared O_2PdF_6.[34]

With an electron affinity for the free ion of 12.2 eV,[35] the O_2^+ salts are powerful oxidixing agents. Gibler[36] showed that O_2PtF_6 will convert IF_5 to IF_6^+. The reaction of IF_5 with O_2AsF_6 was carried out in this work to determine whether O_2^+ alone can accomplish this oxidation, or if Pt(V) were involved. $O_2^+BF_4^-$ has been shown[28] to oxidize N_2O_4, producing $NO_2^+BF_4^-$. Stein[37] has further demonstrated the oxidizing capability of O_2^+ by fixing xenon as the xenon (II) salt, $XeF^+Sb_2F_{11}^-$:

$$Xe_{(g)} + 2O_2^+SbF_6^-{}_{(s)} \rightarrow XeF^+Sb_2F_{11}^-{}_{(s)} + 2O_{2(g)} \quad .$$

O_2AsF_6 was chosen because of its ease of preparation and handling, and because of the volatility of its decomposition and reaction by-products, as an oxidative reagent in reactions with IF_5, $XeOF_4$, BrF_5, $KReO_4$, KPF_6, SO_2, KSO_2F and KPO_2F_2. In the attempted oxidation of ClF_5 by O_2^+, a 1:1 mixture of O_2AsF_6 and O_2AuF_6 was employed, in the belief that ClF_6^+ might form a more stable salt with AuF_6^- (Ref. 32) than with AsF_6^-. When this combination failed, and noting the recent photochemical preparation of $ClF_6^+PtF_6^-$ by Christe,[38] a mixture of O_2AsF_6 and PtF_6, and also IrF_6^-, was reacted with ClF_5.

The Reaction of O_2AsF_6 with IF_5

Dioxygenyl hexafluoroarsenate was prepared by both the static thermal method of heating a 2:1:1 mix of oxygen, fluorine, and arsenic pentafluoride to 300°,[29] and by photolysis of a similar mixture of gases using a high-intensity mercury-vapor uv light.[30] Yields in each case were essentially 100%.

The product is a very finely divided powder, with the texture and appearance of talc. It gives a cubic X-ray powder pattern ($a_0 = 8.00$Å), and an intense Raman spectrum:[39] $O_2^+ \nu_{0-0}$ 1858 cm^{-1}, $AsF_6^- \nu_1$ 687, ν_2 574, ν_5 375 cm^{-1}.

Excess iodine pentrafluoride, carefully distilled to eliminate IF_7 and IOF_5, was condensed onto O_2AsF_6 held at -196° in a fused quartz reaction vessel. The IF_5 melted quickly and became red-orange as gas evolved at the solid-liquid interface. Cooling to 0° was sufficient to freeze the IF_5 and quench the reaction, as evidenced by the disappearance of color and cessation of gas evolution. The reaction was allowed to proceed until all the O_2AsF_6 had dissolved and the color had faded. The excess IF_5, along with oxygen and arsenic pentafluoride produced in the reaction, was removed under vacuum, leaving a white, crystalline residue. This material was shown by X-ray powder diffraction (body-centered cubic, $a_0 = 9.44\text{Å}$) and Raman spectroscopy[40] to be $IF_6^+ AsF_6^-$. The reaction may be described:

$$2O_2^+AsF_6^-{}_{(s)} + IF_5{}_{(\ell)} \rightarrow IF_6^+AsF_6^-{}_{(s)} + 2O_2{}_{(g)} + AsF_5{}_{(g)} \quad .$$

Gravimeric data indicate the reaction to be approximately 50% efficient based on O_2AsF_6.

The Reaction of O_2AsF_6 with $XeOF_4$

Xenon oxide tetrafluoride was prepared by D. E. McKee by reaction of xenon hexafluoride with quartz.[41] Its purity was demonstrated by a gas-phase infrared spectrum.

0.1 gm O_2AsF_6 was placed in a fused quartz reaction tube fitted with a brass Whitey valve. 1.5 ml $XeOF_4$ (m.p. -28°, vapor pressure at 23°, 29 mm Hg) was condensed into the solid at -196°. On warming to room temperature, the solid dissolved completely to give a deep red solution. A gas evolved from the solution, but much more slowly than in the case of IF_5. Heating the solution caused the $XeOF_4$ to reflux, but did not significantly increase the rate of increase in the pressure of the gases above it. Cooling the solution to -196° caused the deep red color to vanish. A non-condensible gas was present. The reaction mixture was then irradiated with high intensity uv light from a 500-watt mercury-vapor lamp for 1 hr. The pressure approximately doubled, from 500 mm to 1050 mm, but there was still no vigorous reaction. The volatiles were removed under vacuum. An infrared spectrum showed the presence of $XeOF_4$ and AsF_5. The white solid which remained was examined by Raman spectroscopy and found to be pure O_2AsF_6.

The Reaction of O_2AsF_6 with BrF_5

Bromine pentrafluoride was fluorinated at 1000 mm Hg and 150° for several days to convert a small but significant bromine trifluoride impurity to the pentafluoride. The now colorless BrF_5 was condensed onto about 0.1 g (0.4 mmol) O_2AsF_6 contained in a quartz tube at -196°. As the mixture warmed and the BrF_5 melted, gas was rapidly evolved at the liquid-solid interface. The solid appeared to dissolve somewhat, although no color change was evident. When the last of the solid had disappeared, the volatiles were removed under vacuum. Nothing remained in the reaction vessel. An infrared spectrum of the volatile products of the reaction showed the presence of BrF_5 and AsF_5. O_2AsF_6 decomposes rapidly in the presence of BrF_5. Contrary to the situation in the IF_5 and $XeOF_4$ systems, no deeply-colored intermediate was observed.

The Reaction of O_2AsF_6 and O_2AuF_6 with ClF_5

Chlorine pentafluoride was prepared by the action of high-pressure fluorine on cesium tetrafluorochlorate (III), $CsClF_4$, at elevated temperatures. Since ClF_5 does not form a stable adduct with cesium fluoride at room temperature, ti may be prepared free of chlorine trifluoride in this manner. A high pressure monel bomb containing about 50 g of $CsClF_4$, prepared from CsF and chlorine trifluoride, was filled with fluorine gas to a pressure of 100 atmospheres at room temperature. The bomb contained several stainless steel ball bearings to aid in breaking up the solid as the entire bomb was shaken by a mechanical agitator and heated to 300° for 3 days. The yield was a small (<1 ml) but pure sample of ClF_5, shown by its infrared spectrum[101] to be free of ClF_3, ClO_2F and any other volatile impurity.

A 1:1 mixture of O_2AsF_6 and $O2AuF_6$ (prepared by Kevin Leary) was prepared and loaded into a fused silica reaction tube in the dry box. The DlF_5 described above was condensed onto the intimately mixed solids at -196°. On warming, some of the solid dissolved, coloring the solution deep blue. Some non-condensible gas evolved slowly.

After 15 min, the color faded. A yellow solid lay undissolved beneath the now colorless liquid. An infrared spectrum of the gases above the solution showed the presence of ClF_5 and AsF_5, plus some SiF_4, CF_4 and COF_2 from attack on the reaction vessel and teflon o-rings of the infrared cell. An X-ray powder pattern of the yellow solid which remained after pumping away the excess ClF_5 showed it to be isostructural with $ClO_2^+IrF_6^-$ (see Chapter VIII), and a Raman spectrum confirmed its identification as $ClO_2^+AuF_6^-$.[38]

The Reaction of O_2AsF_6 and IrF_6 with ClF_5

When chlorine pentafluoride (~0.5 ml) was condensed onto 0.17 g (0.77 mmol) O_2AsF_6 held in a Teflon FEP tube at -78°, the solid took on the intense purple coloration previously observed in interactions between Cl_2 (and other chlorine-containing compounds) and O_2^+ salts. No lower chlorine fluorides, and no chlorine oxyfluorides were observed in the infrared spectrum of the ClF_5, however, and the liquid appeared colorless before use, so that the strong color is not believed due to Cl_2 impurity. As in the previous experiments, removal of the liquid under vacuum gave back pure white O_2AsF_6.

Next, iridium hexafluoride (0.75 mmol) and ClF_5 (0.5 ml) were co-condensed onto the solid O_2AsF_6 at -196°C and allowed to warm to -78°. The resulting solution was a deep greenish blue, due to the combination of bright yellow IrF_6 with the purple color described above. If the solution was warmed to 0°C, oxygen began to evolve. The purple color faded somewhat after a few minutes, but the yellow IrF_6 persisted. The reaction appeared to have involved only O_2AsF_6 and ClF_5. On removal of the volatile gases (O_2, ClF_5, AsF_5, IrF_6) at room temperature, a pale yellow solid remained. (IrF_6 is appreciably soluble in FEP, and colors it yellow. Most of the color of the solid was due to the walls of the vessel.) A raman spectrum of the solid contains bands due to O_2AsF_6, plus a strong band at 1050 cm^{-1}, likely due to $ClO_2^+AsF_6^-$. The solid hydrolyzed rapidly in water, giving off chlorine gas. No blue iridium-containing material was formed in the hydrolysis.

The Reaction of O_2AsF_6 and PtF_6 with ClF_5

0.17 g (0.77 m-mol) dioxygenyl hexafluoroarsenate was placed in a Teflon FEP reaction tube. 0.79 m-mol platinum hexafluoride (prepared by Kevin Leary) was condensed onto the solid at -196° along with an excess (∿ 0.5 ml) of chlorine pentafluoride (shown by infrared spectroscopy to be free of ClF_3 and ClO_2F). The contents of the tube were warmed to -78°. PtF_6 dissolved in the liquid ClF_5 (m.p. -103°, b.p. -14°), to give a deep blue green solution at -78°, turning to pale yellow on warming to 0°. A small amount of noncondensible gas evolved. The solid at the botton of the tube was red orange, and of a smaller volume than the O_2AsF_6 starting material. The tube was agitated, and the temperature cycled several times from -78° to room temperature.

An infrared spectrum of the gases showed only ClF_5, AsF_5, and CF_4 (from attack on the vessel). The volatile gases were removed, leaving a hard, sticky orange solid, with a sufficient vapor pressure to allow it to sublime under vacuum at room temperature. The consistency of the solid made it impossible to load into 0.5 mm x-ray powder capillaries. A larger (1.5 mm) capillary was loaded for the purpose of obtaining a raman spectrum, but no spectrum was obtained using the Cary 83 spectrometer with its 488 nm exciting line. The appearance and physical properties of the orange solid are consistent with those described by Roberto and Mamantov[42] for $ClF_4{}^+PtF_6{}^-$.

The Reaction of O_2AsF_6 with $KReO_4$

Potassium perrhenate (0.200 g, 0.69 m-mol) and dioxygenyl hexafluoroarsenate (0.153 g, 0.69 m-mol) were mixed intimately in the dry box and transferred to a Teflon FEP reaction tube, which was then connected to the vacuum system. No reaction took place between the dry powders on long standing or when heated gently.

Sulfuryl fluoride, SO_2F_2 (m.p. - 135.8°, b.p. - 55.4°) was condensed onto the white solids in sufficient quantity to immerse them. The vessel was maintained at -78° and agitated to encourage dissolution of the solids in the liquid SO_2F_2. Little or none of the powder dissolved. The mixture was warmed slowly to room temperature. A small amount of noncondensible gas had formed. An infrared spectrum of the gases at room temperature and 300 mm Hg showed only a weak, sharp absorption at 775 cm^{-1} in addition to bands due to SO_2F_2.

When anhydrous hydrogen fluoride was condensed onto the $KReO_4/O_2AsF_6$ mixture, no vigorous reaction ensued, and little of the solid dissolved. Some noncondensible gas was evolved, however, and an x-ray powder pattern of the residue in the tube showed only potassium hexafluoroarsenate, indicating that reaction did indeed take place, and that the rhenium present must have been removed as a volatile species. No rhenium compound appeared in the infrared spectrum of the gases, however.

The Reaction of O_2AsF_6 with KPF_6

0.025 g each of potassium hexafluorophosphate (0.14 m-mol) and dioxygenyl hexafluoroarsenate (0.11 m-mol) were mixed in the dry box and placed in a Teflon FEP tube. The dry solids did not interact. Anhydrous hydrogen fluoride was condensed onto the mixture and warmed first to 0° and then to room temperature and above. None of the solid appeared to dissolve, no color change was observed, and no noncondensible gas evolved. An infrared spectrum of the vapor above the liquid HF gave no evidence for phosphorous-containing substances. A raman spectrum of the white solid residue after removal of the HF showed the presence of O_2AsF_6 and PF_6^-. It would seem that neither of the reactants is sufficiently soluble in HF to allow interaction. Since O_2PF_6 is unstable at room temperature,[27] the reaction:

$$O_2AsF_6 + KPF_6 \rightarrow O_2PF_6 + KAsF_6$$

should proceed, with decomposition of O_2PF_6 to oxygen, fluorine, and phosphorous pentafluoride, possible via the radical $PF_6^{\bullet}$.

The Reaction of O_2AsF_6 with SO_2

Sulfur dioxide (b.p.-10°) was obtained from a cylinder and used without purification after its purity was established by means of an infrared spectrum. 0.015 g (0.07 m-mol) O_2AsF_6 was placed in a Teflon FEP tube and exposed to SO_2 gas at room temperature. At a pressure of 200 mm Hg, the reaction is slow, but noticeable. When the SO_2 was condensed onto the solid O_2AsF_6 at -196P and allowed to melt, the interaction proceeded rapidly. The gaseous products are SO_2F_2 and AsF_5 (identified by infrared spectrometry), and O_2 (identified by its vapor pressure of 150 mm at -196°). The net reaction may be written:

$$SO_2 + 2O_2AsF_6 \rightarrow SO_2F_2 + 2O_2 + 2AsF_5$$

It may be that an intermediate in this reaction is the radical species $SO_2F^{\bullet}$. Disproportionation of $SO_2F^{\bullet}$ (see below) results in formation of SO_2F_2 and SO_2, the latter being re-oxidized by O_2AsF_6.

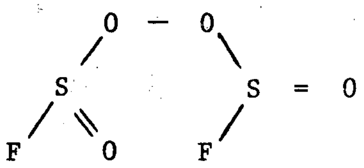
The Reaction of O_2AsF_6 with KSO_2F

0.050 g (0.41 m-mol) potassium fluorosulfinate and 0.080 g (0.36 m-mol) dioxygenyl hexafluoroarsenate were mixed in the dry box and loaded into a Teflon FEP reactor with no immediate reaction. Anhydrous hydrogen fluoride was condensed onto the solids, and the vessel was warmed to 0°. Reaction was rapid, with the evolution of O_2. An infrared spectrum of the gases showed, in addition to bands for HF, absorptions due to SO_2F_2 and SO_2, in approximately equal amounts. These molecules are the expected products from the disproportionation of the free radical $SO_2F^\cdot$. The reaction may be written:

$$O_2AsF_6 + KSO_2F \xrightarrow{HF} KAsF_6 + SO_2F^\cdot + O_2 \quad ,$$

$$2SO_2F \rightarrow SO_2F_2 + SO_2 \quad .$$

No color was observed, even fleetingly, in the reaction medium. It is possible that $SO_2F^\cdot$ dimerizes very rapidly to an O-bonded intermediate:



which is unstable toward SO_2F_2 and SO_2. Another possibility is a route involving free fluorine radicals:

$$SO_2F^\cdot \rightarrow SO_2 + F^\cdot$$

$$SO_2F^\cdot + F^\cdot \rightarrow SO_2F_2.$$

The Reaction of O_2AsF_6 with KPO_2F_2

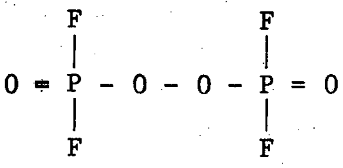
0.025 g (0.18 m-mol) potassium difluorophosphate and 0.030 g (0.14 m-mol) dioxygenyl hexafluoroarsenate were combined in a fused silica reaction vessel. No reaction occurred between the dry solids. Tungsten hexafluoride was condensed onto the solids and refluxed at slightly above room temperature. Again, there was no reaction, both constituents being insoluble in WF_6. The WF_6 was removed under vacuum, and iodine pentafluoride was added. The mixture took on a faint orange color, and gas slowly evolved. An infrared spectrum of the gases, however, showed only IF_5 and AsF_5 (no phosphorous-containing material was seen).

In another experiment, a 1:1 mole ratio of KPO_2F_2 and O_2AsF_6 were heated to 120° for two days in a monel autoclave bomb. The only gaseous product visible in the infrared was phosphoryl fluoride, OPF_3. The solid product was white and soft, giving no Raman spectrum and a weak and diffuse powder pattern in which lines due to $KAsF_6$ were detected. The solid did not react vigorously with water.

The remainder of the solid may be a polymeric oxyfluoride of composition $(PO_2F)_n$:

$$2O_2AsF_6 + 2KPO_2F_2 \rightarrow 2KAsF_6 + OPF_3 + (PO_2F)_n + \frac{5}{2}O_2$$

This reaction could proceed through an intermediate, $PO_2F_2^{\bullet}$, which might be expected to dimerize by means of an O-O linkage:



$$O=P(F)_2-O-O-P(F)_2=O$$

Breakage of the P - O bond would be facilitated by the formation of a new P - F bond, forming OPF_3 and O-O-P(O), which might lose the terminal oxygen atom, and polymerize.

Of course, it would be possible for further fluorine abstraction to occur, with formation of another OPF_3 molecule, and P_4O_{10}, but the slow reaction with water is not characteristic of such a product.

V. THE REACTION OF O_2^+ SALTS WITH Cl_2 AND CHLORINE-CONTAINING REAGENTS

The ionization potential of elemental chlorine is 11.48 eV (265 kcal mol^{-1}), compared to 12.06 eV (278 kcal mol^{-1}) for oxygen. This suggested the use of O_2^+ salts as one-electron oxidizers for fixing Cl_2:

$$Cl_{2(g)} + O_2^+A^-_{(s)} \rightarrow O_{2(g)} + Cl_2^+A^-_{(s)} \quad .$$

Since the lattice energy of the Cl_2^+ salt should be slightly smaller than that of the O_2^+ salt due to the larger volume of the cation, the reaction would depend on the 13 kcal mol^{-1} difference in ionization potentials for its driving force.

Such a reaction was carried out for each of the dioxygenyl salts: O_2AsF_6, O_2SbF_6 and $O_2Sb_2F_{11}$. The results are not clear cut. A thermally unstable adduct is formed in each case, with little or no initial O_2 evolution. The adducts are lavender colored solids at -78° and below, whose exact composition is not established, although the findings suggest a 1:1 stoichiometry.

Historical Background

Olah and Comisarow have reported[43] direct observation of the Cl_2^+ ion by epr in SbF_5, HSO_3F-SbF_5 and HF-SbF_5 solutions of chlorine monofluoride ClF. They proposed the disproportionation reaction.

$$5ClF + 3SbF_5 \rightarrow 2Cl_2^+ + ClF_2^+ + 3SbF_6^-$$

and suggested a temperature-dependent equilibrium between Cl_2^+ and another radical they later claimed to be ClF^+ (Ref. 44). The assignment of these spectra have been questioned by Eachus, Sleight and Symons,[47] and by Christe and Muirhead[48] on both spectroscopic and chemical grounds. Symons and co-workers agreed that the data support a radical containing two equivalent chlorine atoms, but maintain that the epr parameters can only be explained by the presence of at least one atom of oxygen in the radical. This is further supported by the work of Christe and Muirhead, who found that a solution prepared from reagents carefully purified so as to contain no oxygen or moisture failed to give the reported spectra. Only when the antimony pentrafluoride was distilled in glass apparatus before use did the signal appear.

Many other radical cations have been identified in antimony pentafluoride and "superacid" solutions, including Br_2^+, I_2^+ and $C_6F_6^+$ Refs. 49, 51-53). The diatomic species, however, do not give strong or well resolved epr spectra from room temperature down to -196°. Resonance Raman spectra, however, have been recorded for Br_2^+ and I_2^+, showing as many as four overtones for the dinuclearstretching made. The fundamental for I_2^+ is at 238 cm^{-1}, that of Br_2^+ at 360 cm^{-1} in superacid solution,[49,50] and at 368 cm^{-1} in the solid $Br_2^+Sb_3F_{16}$.[54] The reaction of Br_2 with O_2AsF_6 has been shown by Glemser and Smalc[21] to give the chocolate brown, diamagnetic solid, $Br_3^+AsF_6^-$.

The reactions of dioxygen difluoride with Cl_2, HCl, ClF and ClF_3 have been studied by Streng and Grosse.[56,57] They reported formation of a deep-violet compound, stable at -78 and below, which they claimed to be $(O_2ClF_3)_n$. This material was found to be soluble in anhydrous HF, forming a strongly-colored, unstable solution which evolved oxygen. Thermal decomposition of "$(O_2ClF_3)_n$" gave[57] O_2 and ClF_3. Subsequently, Gardiner reported[58] the preparation of such a compound by uv photolysis of an O_2/ClF_3 mixture at -78° (but see later p. 49). This violet compound was in equilibrium with oxygen gas and other, blue, compound, the color depending upon the O_2 pressure above the solids. He suggested the structures F_2ClO_2F and $F_2ClO_2ClF_2$ for the violet and blue compounds, respectively, but presented only visible spectra to substantiate these claims.

Experimental Observations

When chlorine gas was admitted to an evacuated quartz or FEP reaction vessel containing O_2AsF_6 at room temperature, the white solid turned yellow-green and began to decompose to gaseous constituents. An infrared spectrum of the gases produced in the reaction showed only arsenic pentafluoride, and no chlorine fluorides or oxides. The color change in the solid was reversible and dependent upon the Cl_2 pressure. If the gases were pumped away before the solid had completely decomposed, it regained its original appearance, and was show by Raman spectroscopy to be pure O_2AsF_6.

On admission of chlorine to a vessel containing O_2SbF_6 or $O_2Sb_2F_{11}$, the white solids became purple-gray at low pressure, slowly turning black and liquefying as the pressure rose. This reaction could not be reversed, and pumping on the resultant blue-black oil caused it to lose chlorine and oxygen slowly.

If the solids were maintained at -78° during exposure to gaseous or liquid chlorine, deep purple solids were formed,which were stable at -78° and lower. These granular, free flowing solids had no appreciable vapor pressure, and were quite soluble in anhydrous HF, forming deep blue solutions which were somewhat less stable than the solids, evolving O_2 and Cl_2 slowly at -78° but faster at higher temperatures.

A volumetric study of the oxygen evolution in the reaction of $O_2Sb_2F_{11}$ and Cl_2 at -78° was undertaken using the Toepler pump described earlier in the section dealing with the prepartion of $C_6F_6^+AsF_6^-$. The results are summarized in Table V-1. In the latter two experiments, the chlorine was distilled at -112°, prior to use, to remove possible impurites (although none was visible in an infrared spectrum run at 1500 mm pressure In addition, the chlorine was added more slowly to avoid warming of the solid. With these precautions, O_2 evolution was essentially nil.

The deep purple solids thus prepared decomposed on warming toward 0° to the same materials produced in the room-temperature reactions. This allowed a gravimetric study to be carried out on the Cl_2+ O_2 Sb_2F_{11} reaction. (Such a study was not feasible in the case of O_2AsF_6, as the gaseous decomposition products developed dangerously high pressures in the weighing vessels when brought to room temperature.) The experimental technique consisted of condensing liquid Cl_2 onto the weighed O_2^+ salt slowly at -78° to assure complete contact of the two reactants (Neither $O_2Sb_2F_{11}$ nor the reaction products is soluble in Cl_2), followed by evacuation of the vessel for 15 min or more to remove the uncombined chlorine. As the data in Table V-2 indicates, the results were not reproducible. The

Table V-1

O_2 Evolution in the reaction $Cl_2 + O_2S_bF_{11} \xrightarrow{-78°}$.

Expt. No.	$O_2Sb_2F_{11}$ (mmol)	O_2 Evolved (mmol)	$O_2/O_2Sb_2F_{11}$
1	0.726	0.205	28.3%
2	0.305	0.074	24.3%
3	0.572	0.105	18.4%
4	0.707	0.023	3.3%
5	0.630	0.023	3.7%

Table V-2

Gravimetric data for the reaction $Cl_2 + O_2Sb_2F_{11} \xrightarrow{-78°}$.

Expt. No.	$O_2Sb_2F_{11}$ (mg)	Product (mg)	Mole Ratio $Cl_2:O_2Sb_2F_{11}$
1	351.8	594.7	6.57
2	147.8	149.9	0.13
3	277.0	296.4	0.59
4	342.5	381.5	0.80
5.	305.4	501.	4.56
6	315.8	335.6	0.43*
7	292.9	338.6	1.06

* Not corrected for O_2 evolution.

mole ratios in experiments 1 through 5 have been corrected for O_2 evolution by reducing the number of moles of $O_2Sb_2F_{11}$ by the corresponding number of moles of O_2 evolved. It is likely that some chlorine uptake (in each experiment) is a consequence of chlorine fluoride formation (the extent of the latter being correlated with the quantity of evolved oxygen). The fate of the 1/2 mole of F_2 which must be produced in the decomposition of a mole of $O_2Sb_2F_{11}$ is not clear, but no flourine was detected in the evolved gas. The masses of the products in Table 2 may include Cl_2 dissolved in SbF_5 from the same source (decomposition of $O_2Sb_2F_{11}$), but this should be small at -78° where SbF_5 is quite solid. The wide scatter in the gravimetric data is understandable in view of the relatively large wieght of the weighing vessel, which, with its brass Whiley valve, a Monel reducing union, a quartz or FEP tube, and Swagelok connecting nuts weighed very nearly 200 g. In most of these experiments, the chemicals made up only about 0.15% of the total weight.

In a further effort to clarify the combining ratio of the reactants, $O_2Sb_2F_{11}$ was reacted with an equimolar quantity of Cl_2, measured volumetrically. Repeated cooling to -196° and warming to -78° was necessary to insure contact of the solid and gas/liquid. All but 7% of the chlorine was taken up. The product was the purple solid previously described but small lighter-hued spots remained where, presumably, complete reaction had not occurred. Addition of another 0.25 mole of Cl_2 per mole of $O_2Sb_2F_{11}$ failed to reduce the size of the light areas, and no more Cl_2 was taken up. In a similar experiment, a Cl_2:$O_2Sb_2F_{11}$ mole ratio of 0.5 was used, producing a pale blue product with only a few darker spots.

EPR Spectrum

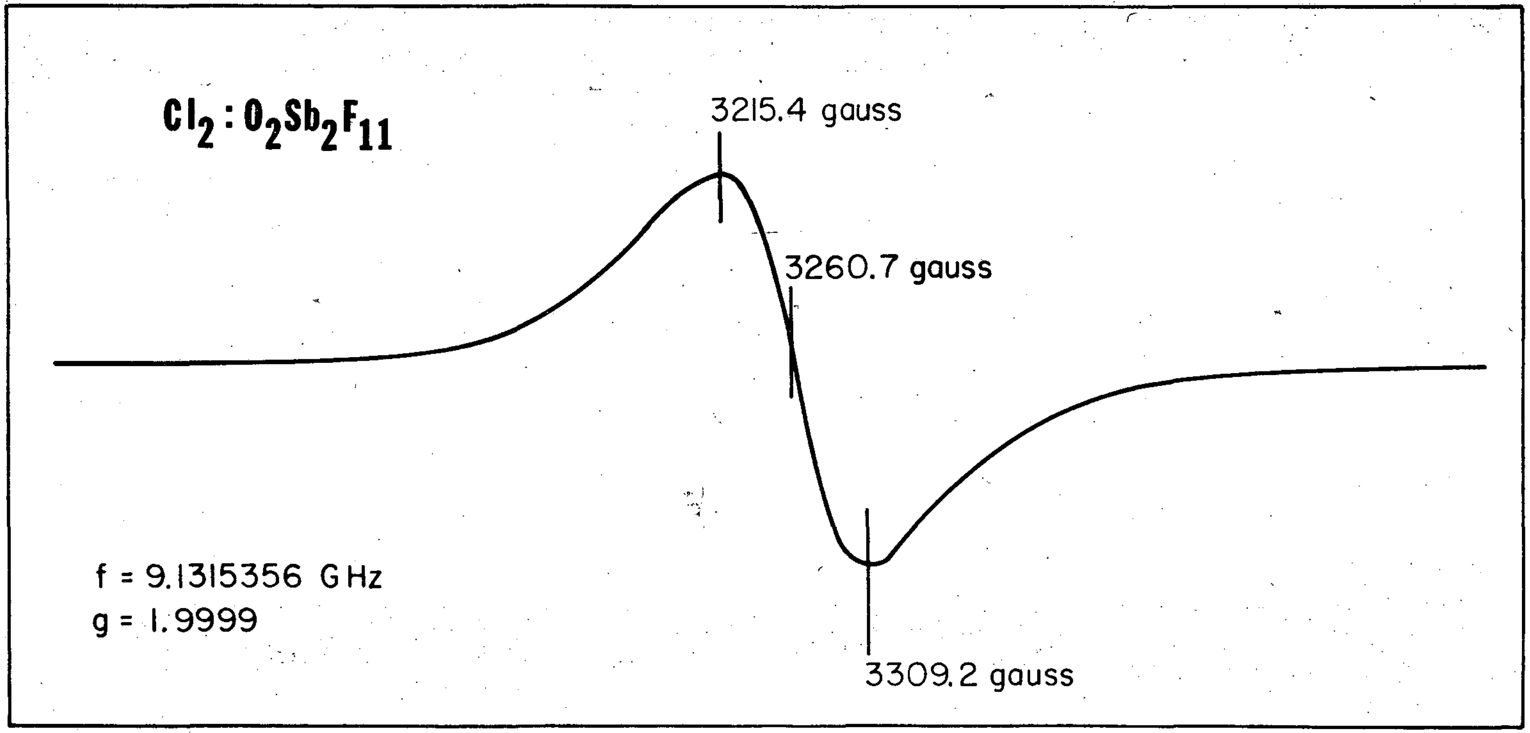
Since the purple solids prepared from chlorine and dioxygenyl salts could not be handled at room temperature, and consisted of granules 0.3 mm in diameter or larger, they proved difficult to load into capillary tubes for examination. It was necessary, therefore, to prepare the material in situ. $O_2Sb_2F_{11}$ was placed in a 3/16 in. O.D. pyrex tube which was connected to the vacuum system by means of a 3/16 in. to 1/4 in. swagelok reducing union with Teflon ferrules, and Cl_2 was condensed onto the solid at -78°.

An epr spectrum of the compound thus prepared exhibited a very strong, symmetric resonance at $g = 1.999$ (Fig. V-1), with a linewidth of 90 gauss, at a temperature of -110°. Olah and Comisarow reported g-values of 1.998 for "Cl_2^+"[43] and 2.006 for "ClF^+."[44] In contrast, a sample of $O_2Sb_2F_{11}$ gave a weak, asymmetric signal at around $g = 1.93$ at -110°. Di Salvo et al. report[59] signals from $O_2Sb_2F_{11}$ at 20°K with g-values of 1.96 ($g_\perp$) and 1.74($g_\parallel$).

Raman Spectra

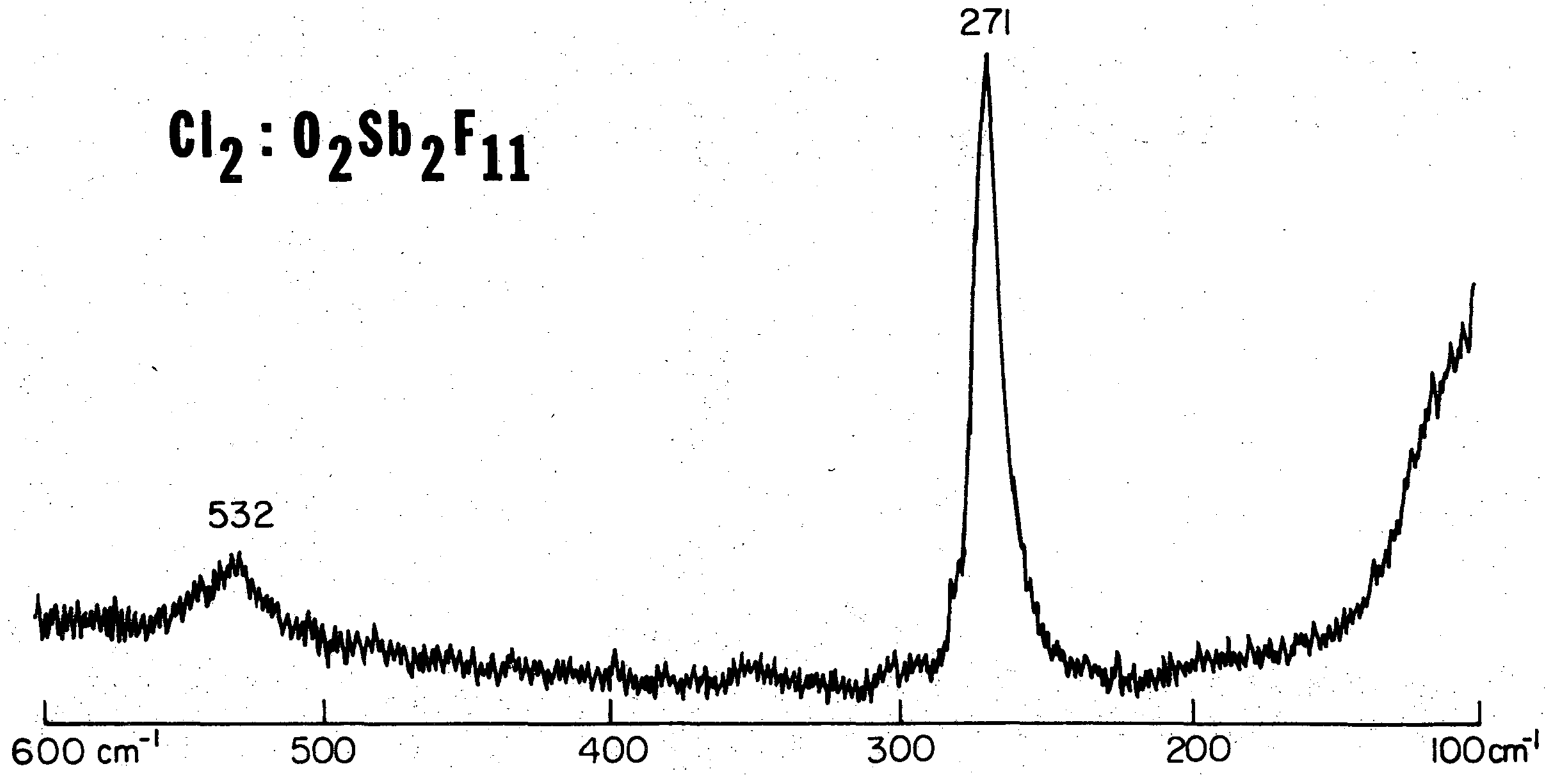
Samples of the purple products of the reactions of Cl_2 with O_2AsF_6 and $O_2Sb_2F_{11}$ were prepared in 1.0 mm pyrex capillaries which were scaled to 1/4 in. glass tubing. They were mounted in a liquid nitrogen-cooled low temperature Raman cell consisting of a cold copper block to which the samples were affixed, surrounded by a vacuum jacket with optical windows. The spectra were recorded by the technique of 180° back-scattering with laser excitation at 647.1 nm. The spectra (Fig. V-2)

0 0 0 0 4 2 0 1 8 6 2



XBL 749-7346

Fig. V-1. EPR spectrum of the $Cl_2:O_2Sb_2F_{11}$ adduct.

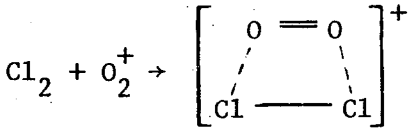


XBL 7410-7490

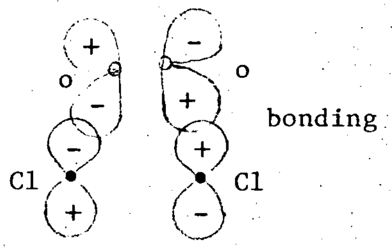
Fig. V-2. Raman spectrum of the $Cl_2:O_2Sb_2F_{11}$ adduct.

of the two compounds are essentially identical, and consist of a rather intense peak at 271 cm^{-1} and a much weaker one around 532 cm^{-1}. The vibrational frequencies of the anions in these compounds are nearly invisible due to the very high noise level in the spectra. The O_2^+ stretching frequencies at 1858 cm^{-1} $(O_2AsF_6)^{60}$ and 1865 cm^{-1} $(O_2Sb_2F_{11})^{61}$ are not observed, or is Cl_2^+ (645 cm^{-1}).[62]

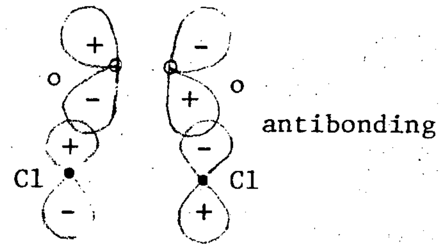
Visible spectra of these materials were not obtained due to experimental difficulties. Gardiner, however, reported[58] the visible spectrum of his "violet compound of chlorine, fluorine and oxygen" which seems to have a similar color, and may be the parent molecule of the cations in these salts. This spectrum shows strong absorption in the region 350 to 650 nm. Laser excitation at 647.1 nm could thus result in observation of a resonance Raman spectrum.[63] The peaks at 271 and 532 cm^{-1} could be the fundamental and first overtone of the Cl-Cl stretching mode in the radical cation $Cl_2O_2^+$. The drop in frequency from the solid chlorine value of 540 cm^{-1} (Ref. 70) may be explained by the formation of two weak chlorine-oxygen bonds:



A simple molecular orbital model for this interaction considers the π^* antibonding orbitals in O_2^+ and Cl_2 in a trapezoidal cation:



and



Since there are three electrons available, two from chlorine, one from O_2^+, two should fill the bonding orbital, and the other becomes antibonding. The net results, then, is a total bond order of 1/2, or two 1/4-bonds. Since chlorine is the more electronegative of the two elements, the electron density in the π* region of the Cl_2 entity would be increased by this type of bonding, and the strength of the Cl-Cl bond diminished.

Attempts to obtain spectra of the deep blue-black aoil which results from thermal decompositions of the compounds prepared from dioxygenyl fluoroantimonates were unsuccessful, due to their intense coloration.

Infrared Spectra

The $Cl_2/O_2Sb_2F_{11}$ adduct was prepared in a Teflon FEP reactor and removed to the drybox. The product was converted to the previously-described blue-black oil on warming to room temperature, and this material was spread onto AgCl discs which were then pressed together in a Kel-F solid sample infrared cell. The spectrum thus obtained is shown in Fig. V-3. The sharp band at 1530 cm^{-1} and its overtone at 3060 cm^{-1} are indicative of a gas phase molecule, and are most likely due to an O-O stretching mode (V_{O_2} = 1555 cm^{-1}).[45] The proximity of this frequency to that of free oxygen suggests a weakly bonded O_2-X species, such as OOF or OOCl. Indeed, infrared spectra of O_2F, frozen in a solid N_2 matrix, exhibit O-O stretching frequencies of 1500 cm^{-1} for the mononer, and 1510 cm^{-1} for the dimer, O_4F_2.[64,65] Similar measurements on O_2Cl in an argon matrix revealed an O-O stretch at 1441 cm^{-1}.[33] The corresponding O-F and O-Cl stretching frequencies in O_2F and O_2Cl are 586 cm^{-1} (Ref. 64) and 407 cm^{-1}.[66] The somewhat broad band around 590 cm^{-1} in Fig. 3 may be due to the O-F stretch in O_2F, but its assignment is less certain because it is in the range of the very intense Sb-F absorptions.

A possible explanation of the presence of O_2F in this spectrum follows. The deep purple compound formed from $O_2^+Sb_2F_{11}^-$ and Cl_2 may be the unstable salt $Cl_2O_2^+Sb_2F_{11}^-$. At temperatures above -78°, this material dissociates into the parent compounds:

$$Cl_2O_2^+Sb_2F_{11}^- \rightarrow Cl_2O_2F + 2SbF_5 \quad .$$

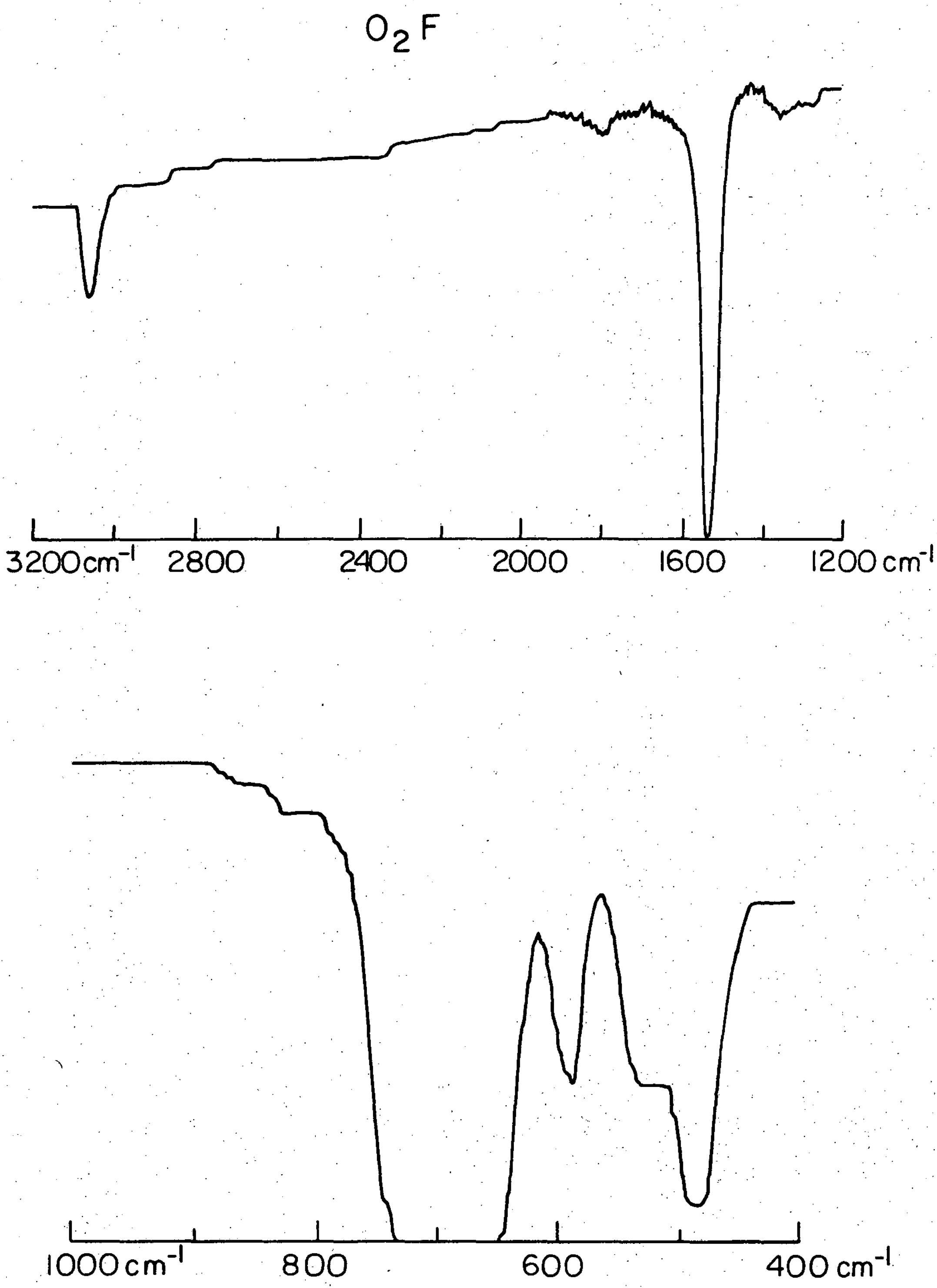


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Fig. V-3. Infrared spectrum of O_2F.

The remaining Cl-O bond is further destabilized by formation of the O-F bond and a second dissociation occurs:

$$Cl\text{-}Cl\text{-}O\text{-}O\text{-}F \rightarrow Cl\text{-}Cl + O\text{-}O\text{-}F$$

The resulting O_2F is not complexed immediately by the SbF_5 because the pentafluoride reacts with the AgCl windows of the infrared cell to form $Ag^+SbF_5Cl^-$.[67]

Reaction Chemistry of $Cl_2O_2^+Sb_2F_{11}^-$

The reactions of the purple solid formed from $O_2Sb_2F_{11}$ and Cl_2 at -78° with nitric oxide, nitrosyl fluoride, fluorine and hexafluorobenzene were investigated. The products are essentially those which would be expected from reactions of the above reagents with a mixture of Cl_2 and and O_2^+ salt. That is, they support the formulation of the purple solid as the salt $Cl_2O_2^+Sb_2F_{11}^-$, with a weak chlorine-oxygen bond in the cation.

Nitric Oxide

It was displacement of hexafluorobenzene by nitric oxide from the salt $C_6F_6^+AsF_6^-$ which confirmed the identity of the $C_6F_6^+$ ion. An attempt was therefore made to displace the cationic species present in the $Cl_2/O_2Sb_2F_{11}$ adduct with nitric oxide. NO (Technical grade), purfied by fractional distillation at -160° to remove traces of nitrogen dioxide, was admitted to a quartz tube containing the purple solid prepared as described previously. The temperature was maintained at -78° throughout the reaction. The color of the solid faded slowly to yellow-green, and the pressure fell slightly. An infrared spectrum of the gases above the cold solid contained bands for nitrosyl fluoride

(ONF) and nitric oxide. On warming to room temperature, the gases above the solid, which was now white, also included nitrosyl chloride (ONCl), nitrogen dioxide (NO_2), and some hypochlorous acid (HOCl). The white solid which remained was examined by Raman spectroscopy and X-ray powder photography and found to be $NO^+SbF_6^-$.[68]

The origin of HOCl in these spectra is somewhat mysterious. No hydrogen-containing molecules were seen in infrared spectra of the chlorine or nitric oxide gases, and the solid $O_2Sb_2F_{11}$ was stored in a pyrex tube in the dry atmosphere of the drybox prior to use, so that the presence of HF in it is unlikely. In subsequent experiments the chlorine was distilled before use, and the HOCl bands were nearly eliminated. The presence of NO_2, ONCl, and ONF are explained by the reactions:

$$Cl_2O_2^+ + 3NO \rightarrow 2ONCl + O_2 + NO^+$$
$$Cl_2O_2 + Sb_2F_{11}^- \rightarrow Cl_2O_2F + 2SbF_5$$
$$Cl_2O_2F + NO \rightarrow ONF + Cl_2 + O_2$$

and

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \quad .$$

Formation of the neutral radical Cl_2O_2F would probably involve cleavage of one of the Cl-O bonds, and because of formation of the O-F bond, weaken the remaining Cl-O bond further. The reaction chemistry of this species, then, is expected to be essentially that of O_2F and Cl_2.

Nitrosyl Fluoride

The purple solid was next reacted with ONF with the hope of displacing the parent Lewis base of the cation. The general reaction:

$$A^+Sb_2F_{11}^- + 2ONF \rightarrow AF + 2NO^+SbF_6^-$$

will proceed if ONF is a stronger base than AF, and if AF is sufficiently volatile to allow its removal. In view of the instability of the Cl_2/O_2^+ addust, the reaction was expected to produce Cl_2P_2F as a first product, which would likely dissociate rapidly into Cl_2 and O_2F. The experiment was carried out in essentially the same manner as in the nitric oxide reaction. The gas-solid reaction proceeded slowly at -78°, but the gas-phase reactions between the initial product and ONF were rapid, yielding ONCl, ON_2Cl, and NO_2. In this experiment, no fluorine-containing molecules were observed in the gases. This is most likely due to oxidation of chlorine to form ClF, which then forms a solid complex with SbF_5. Oxidation of chlorine in the nitric oxide case is prevented by the presence of the reducing agent, NO. Oxidation of ONF to NO_2 and NO_2Cl may be achieved either by the cation itself, by Cl_2O_2F, or by O_2F. The reaction sequence may be as follows:

$$ONF + Cl_2O_2^+Sb_2F_{11}^- \rightarrow NO^+SbF_6^- + SbF_5 + Cl_2O_2F$$

$$Cl_2O_2F + ONF \rightarrow NO_2 + 2ClF + \frac{1}{2}O_2$$

$$Cl_2O_2F + ONF \rightarrow NO_2F + ClF + \frac{1}{2}O_2 + \frac{1}{2}Cl_2$$

$$\frac{1}{2}Cl_2 + Cl_2O_2F + ONF \rightarrow ONCl + 2ClF + O_2$$

$$2\ ClF + SbF_5 \rightarrow Cl_2F^+SbF_6^-$$

$$NO_2F + SbF_5 \rightarrow NO_2^+SbF_6^- \quad .$$

The species represented by $[Cl_2O_2F]$ may be a molecule or simply a mixture of Cl_2 and O_2F.

Fluorine

Fluorine gas was admitted to a vessel containing the purple solid at -78°. The F_2 pressure was initially 200 mm. No change in the pressure or in the appearance of the solid occurred during 10 min of exposure. The F_2 pressure was increased to 750 mm and subsequently to 1500 mm, with still no apparent interaction between the solid and gas. An infrared spectrum of the gas after 30 min showed no new absorptions, and in particular showed no increase in absorptions due to HF. The solid was warmed to room temperature under 1500 mm of F_2 pressure and decomposed in its normal fashion. Again, there was no detectable change in the infrared spectrum.

Hexafluorobenzene

C_6F_6 was condensed into a vessel containing the purple solid at -78°. The solid C_6F_6 was slowly worked down the sides of the tube using a heat gun. When contact was made between the two solids, the familiar yellow color of $C_6F_6^+$ appeared (see Chapter VI), and chlorine (identified by its yellow-green color) was evolved. In the absence of a solvent, however, the reaction became uncontrolled, and no $C_6F_6^+$ salt was recovered. This result added further weight to the conjecture that the cation contained an O_2^+-like entity.

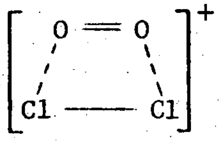
Alternate Syntheses

Attempts were made to prepare the deep purple compounds by alternate routes in order to confirm their composition. A mixture of chlorine monofluoride, fluorine, and oxygen was photolysed at -78° in the manner of Gardiner.[58] Similarly, a mixture of chlorine trifluoride and oxygen, as well as a 2:2:1 mixture of chlorine, fluorine, and oxygen was photolysed using a high-pressure mercury lamp with a pyrex filter. In each case, no colored products were formed, and infrared spectra showed that only chloryl fluoride (ClO_2F), along with SiF_4 from attack on the quartz vessel, was present. All attempts to duplicate Gardiner's photolytic syntheses met with failure, although it is almost certain that O_2F radicals should have been formed in his experiments.

Subsequently, a mixture of Cl_2, O_2, F_2 and AsF_5, prepared by decomposing the Cl_2/O_2AsF_6 adduct, was photolysed at -78°. After 2 hr of irradiation, no solid product has formed, and the only new materials visible in the infrared were SiF_4 and BF_3 from attack on the pyrex bulb in which the gases were held. Apparently, Cl_2 inhibits the gas-phase production of O_2F, or prevents its reaction with AsF_5 under conditions which have been routinely used to prepare O_2AsF_6 in the absence of clorine.

Conclusions

The reactions of O_2^+ salts with chlorine at -78° produce deep purple, paramagnetic solids whose reaction chemistry is that of an O_2^+:Cl_2 mixture. No oxygen evolves in the preparations when they are carefully carried out at -78°. Quantitative oxidation of chlorine is not observed in the preparations or in their decomposition products. Decomposition at ryom temperature in the presence of silver chloride appears to produce gaseous O_2F, a molecule not previously observed above -40°. O_2F is, however, most likely an intermediate in the photolytic preparation of O_2^+ salt from mixtures of O_2, F_2 and arsenic or antimony pentafluoride,[71] and must, therefore, have at least a short lifetime at 20°. Since there is no evidence of a strong oxygen-chlorine bond in these adducts, and, indeed the adduct formation appears to be only slightly, if at all, exothermic, it seems likely that neither the Cl-Cl nor O-O bond is broken when the adduct is formed. The structure of the cation in these salts is, therefore, probably:



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The Cl-O bond in $Cl_2O_2^+$ is probably similar to that in OOCl, which has been found[66] to have an extremely small stretching force constant, even lower than that in OOF.[72] Benson and Buss[73] have calculated the Cl-OO bond energy as about 8 kcal.

VI. SALTS OF THE HEXAFLUOROBENZENE CATION, $C_6F_6^+$, AND THE OCTAFLUORONAPTHALENE CATION, $C_{10}F_8^+$

A number of organic radical cations have been detected spectroscopically in antimony pentafluoride and "superacide" solutions, including $C_6F_6^+$ (Refs. 53,69) and $C_{10}F_8^+$ (Refs. 74-76). Their epr spectra are well-resolved at -196° and show the expected ^{19}F hyperfine splittings. It is not certain precisely how these species arise, i.e., what the oxidizing agent in these solutions might be. Because antimony pentafluoride is generally prepared from either the metal or Sb_2O_3 and fluorine (which generally contains some oxygen), under conditions known to produce O_2^+ salts,[61] it seems likely that a small quantity of O_2^+ impurity in the SbF_5 or "superacid" may be responsible. Charge-transfer interactions have been observed[77,78] in solutions of aromatic hydrocarbons and fluorocarbons in tungsten and molybdenum hexafluorides, as evidenced by their strong concentration-dependent colorations. Stable complexes are not formed, however, and the colors vanished when the solutions

Although the unusually high electron affinities of the heavier transition metal hexafluorides (PtF_6 and IrF_6 in particular) suggested[5] their utility in synthesising salts of the $C_6F_6^+$ ion (I = 9.97 eV),[35] attempts by Jha to prepare $C_6F_6^+PtF_6^-$ resulted in destruction of the aromatic ring and fluorination by PtF_6.[6] As described below, IrF_6 reacted with C_6F_6 initially to form a bright-orange solid, believed to be $C_6F_6^+IrF_6^-$ (Ref. 79). This material decomposed on warming to room temperature, however, due to the strongly oxidizing and labile nature of the hexafluoroiridate (V) anion.

Since the AsF_6^- ion has considerable kinetic stability, it appeared that $O_2^+AsF_6^-$, with its potent one-electron oxidizer, O_2^+ ($E = 12.2$ eV),[80] would be an ideal reagent for synthesis of a $C_6F_6^+$ salt. It was necessary to use tungsten hexafluoride in these reactions as a solvent for the hexafluorobenzene and as a moderator for the rapid, exothermic reaction. Other more common solvents such as carbon tetrachloride or perfluoropropane were found to have insufficient heats of fusion and heat capacities to control the raction, and very low yields were obtained using these materials.

A. Salts of the Hexafluorobenzene Cation, $C_6F_6^+$.

The Reaction of IrF_6 with C_6F_6

Liquid C_6F_6 (b.p. 80.2°) was placed in a Kel-F tube, and IrF_6 was condensed into the tube held at -196°. As the contents were permitted to warm, the condensed IrF_6 moved down the sides of the vessel toward the hexafluorobenzene, which was still solid. A bright orange solid was formed at the point of contact. Suddenly, the entire contents of the trap burst into flame. The pressure in the system jumped from 25 mm to over 500 mm Hg. The fire died out after a few seconds, leaving the inside of the trap coated with a fine dark green powder. The vessel was taken into the drybox and opened. All that could be obtained from the walls of the tube was a fine grey-black powder, too small a quantity to characterize. In light of subsequent experiments, this was probably metallic iridium. An infrared spectrum of the gases produced indicated the presence of hexafluorobenzene, carbon tetrafluoride, hexafluoroethylene, and other carbon fluorides.

The Reaction of IrF_6 with C_6F_6 in WF_6

It was previously been observed[78] that solutions of hexafluorobenzene in tungsten hexafluoride exhibit a strong yellow-green coloration. This feature has been attributed to a charge-transfer interation in which the planar aromatic ring is ionized by the spherically symmetric hexafluoride. No stable salt is isolable, however, and the constituents may be separated easily by fractional distillation.

From the heat reaction of hexafluorobenzene and iridium hexafluoride (above, it was apparent that a great deal of heat was generated, although a metastable orange solid was formed before the reaction became uncontrolled. In order to dissipate this thermal energy, and to insure a smooth reaction in a homogeneous reaction medium, tungsten hexafluoride (m.p. 2.0°, b.p. 17.1°) was employed as solvent for both reactants, and as a heat sink.

0.5 g (2.6 mmol) hexafluorobenzene was placed in a Kel-F trap, and tungsten hexafluoride (2 ml) was condensed onto it to form the green solution described earlier. This solution was then frozen and iridium hexafluoride was condensed onto the solid at -196°. The trap was warmed slowly to room temperature. As the solids melted, the reaction proceeded smoothly, producing an orange brown solid which floated on the surface of the WF_6 which retained its green coloration due to the presence of a molar excess of C_6F_6 over IrF_6, which was entirely consumed in the reaction. The solvent and excess C_6F_6 were removed under vacuum and the solid was examined in the drybox. During the 20 min required to transfer the reaction vessel into the drybox, the solid had lost its orange color, and was now a uniform light brown. This material was put into quartz Raman and X-ray powder capillaries which were sealed in the flame of a micro torch, a small plug of Kel-F grease serving to protect the samples from the air during this operation. A metallic mirror was formed at the point where the capillaries were sealed off. No Raman spectrum was obtained from this material. An X-ray powder photograph contained only lines due to metallic iridium.

The Reaction of IrF_6 with C_6F_6 in BrF_5

Bromine pentafluoride was purified by fluorination at 150° under an initial fluorine pressure (r.t.) of 1000 mm Hg until it was colorless and no impurities appeared in its infrared spectrum. Hexafluorobenzene (0.2 gm, 1.1 mmol) was placed in a Kel-F trap, and BrF_5 was condensed onto it. The result was a red-brown solution, indicating some reduction of the bromine pentafluoride. IrF_6 was then condensed onto the solution. A vigorous reaction ensued, with some gas evolution. The result was a red-brown solution. Removal of the solvent and volatile products left a brownish residue. An X-ray powder pattern of this solid contained reflections due to iridium pentafluoride,[81] along with a few low angle lines of undetermined origin. An attempt to obtain a Raman spectrum of this material using the Cary[83] spectrometer resulted in thermal decomposition of the sample by the blue (4880Å) laser exciting source.

On the Reactions of IrF_6 with C_6F_6

Although the initial product of the reaction between hexafluorobenzene and iridium hexafluoride produces a bright orange solid, especially at reduced temperatures, this compound is thermally unstable towards lower iridium fluorides and even iridium metal, with concurrent fluorination and destruction of the aromatic ring. The extent of reduction of the iridium hexafluoride depends on the relative quantity of hexafluorobenzene available, and upon the solvent, if any. In the presence of bromine pentafluoride (which also attacks the ring), the pentafluoride is the primary reduction product even when excess C_6F_6 is present. Iridium pentafluoride was also formed in the tungsten hexafluoride-mediated reaction when a deficiency of C_6F_6 was used. In the case of the neat reaction as well as in the WF_6/excess C_6F_6 case, the iridium hexafluoride was reduced all the way to the metal.

The bright orange metastable solid is believed, in part because of its appearance, to contain the hexafluorobenzene cation, most likely as the hexafluoroiridate(V) salt, $C_6F_6^+IrF_6^-$. Due to its thermal instability (most probably the result of the strongly oxidizing nature of Ir(V) and the relative lability of the fluoride ligands demonstrated in other reactions), it was not successfully characterized. It was for these reasons that a study of the oxidation of C_6F_6 by dioxygenyl salts was undertaken.

The Reaction of O_2AsF_6 with C_6F_6

A small quantity (~0.15 g, 0.67 mmol) of dioxygenyl hexafluoroarsenate was placed in a fused silica reaction tube connected to a brass Whitey vlave by means of a 3/8 in. Swagelok union which was drilled out to accommodate the 10 mm diameter of the top of the tube. A molar excess of hexafluoribenzene was condensed into the tube and allowed to react with the solid. A very small amount of the canary yellow solid, $C_6F_6^+AsF_6^-$, was produced by the initial gas-solid reaction. When contact was made between liquid and solid, however, the reaction became violent and the contents of the tube ignited.

The Reaction of O_2AsF_6 with C_6F_6 in WF_6:
The Preparation of $C_6F_6^+AsF_6^-$

As in the iridium hexafluoride/hexafluorobenzene reaction, a mediator was required to control the rate of reaction. No satisfactory solvent has been discovered for dioxygenyl salts. They react slowly enough with tungsten hexafluoride, however, to allow its use as solvent for the hexafluorobenzene, and as a heat sink for the liquid/solid reaction.

In a typical experiment, 1.5 mmoles O_2AsF_6 (0.33 g, 1.5 mmol) was placed in a 3/8 in. O.D. Teflon FEP tube equipped with a brass Whitey valve. Quartz tubes were also used, but the product usually contained a certain amount of WOF_4 impurity when prepared in glass. Approximately 0.5 ml of WF_6 was then condensed onto the solid at -196°, followed by a slight molar excess of C_6F_6 and another 0.5 ml of WF_6. As the tube was allowed to warm to 0° in an ice bath, the WF_6 melted first, dissolving the C_6F_6 as it moved slowly down the sides of the tube. The reaction begins immediately upon contact between liquid and solid, proceeding rapidly to completion, with evolution of all of the oxygen, as demonstrated by quantitative measurement using a Toepler pump (see below). The product, canary yellow $C_6F_6^+AsF_6^-$, was a fine, soft powder, which floated without dissolution on the surface of the WF_6. The WF_6 was removed under vacuum slowly at 0° to avoid bumping and to reduce thermal decomposition of the product. When the solid appeared dry, the tube was warmed to room temperature to insure removal of excess C_6F_6 and any volatile decomposition products. Yield of $C_6F_6^+AsF_6^-$ was generally 25 to 35% based on O_2AsF_6, occasionally as high as 46%. Continued pumping at room temperature resulted in rapid decomposition of the product.

Determination of Evolved Oxygen in the Reaction of O_2AsF_6 with C_6F_6 in WF_6

A manually operated, borosilicate glass Toepler pump was assembled and connected to the metal vacuum system via a glass U-trap and kovar-to-glass graded seal. A series of bulbs, whose volumes were determined by weighing the quantities of mercury required to fill them, formed the reservoir into which gases were pumped and in which their pressure was measured. These volumes were as follows:

Bulb	Volume (ml)	Total Volume of Reservoir (ml)
1	0.24_4	0.24_4
2	3.64	3.88
3	20.47	24.35
4	52.85	77.20

Using this pump, a large or small volume could be determined with similar accuracy.

$C_6F_6^+AsF_6^-$ was prepared as described above, except that before removal of the WF_6 and volatile products, the reaction vessel was cooled to -196°. A liquid nitrogen bath was placed around the glass U-trap leading to the Toepler pump to remove any residual WF_6 or arsenic pentafluoride from the gas. The residual gas was then pumped into the calibrated volume and its pressure was determined by measuring the difference in height between columns of mercury above which stood the gas sample on the one hand, and the system vacuum on the other. The temperature of the gas was read from a mercury thermometer in proximity to the calibrated bulbs. Once the PVT data for the sample had been collected, it could be expanded from the Toepler pump reservoir into an infrared cell, and a spectrum obtained to verify its composition The gas from the O_2AsF_6/C_6F_6 in WF_6 reaction did not attack the mercury in the Toepler pump even after extended periods of exposure, and was therefore presumed free of elemental fluorine. A small quantity of WF_6 was occasionally observed in the infrared spectrum, but never more than 1% of the total.

Results of several determinations of the oxygen evolved in this reaction are summarized below.

Expt.	O_2AsF_6 reacted (mmol)	O_2 evolved (mmol)	O_2:O_2AsF_6
1	1.68	1.80	1.07
2	1.47	1.44	0.98
3	1.76	1.63	0.93

The Reaction of O_2AsF_6 with C_6F_6 in HF

When it was discovered that $C_6F_6^+AsF_6^-$, prepared in WF_6, was exceedingly soluble in anhydrous hydrogen fluoride (see below), an attempt was made to utilize HF as solvent/mediator for the preparation as well. About 2 ml of HF was condensed onto 0.30 g (1.4 mmol) O_2AsF_6 in a Teflor FEP tube. A faint purple color was observed, possibly due to some chlorine containing impurity (see the section on the reaction of Cl_2 with O_2AsF_6). A small amount of the solid appeared to dissolve, and some (<10%) of the O_2AsF_6 decomposed over a period of 15 minutes at room temperature in contact with liquid HF. The solution was cooled to -196°, and C_6F_6 was distilled into the tube. When the mixture was allowed to warm to 0°, the melting HF quickly became bright yellow, but the reaction proceeded uncontrollably and the yield of $C_6F_6{}^+AsF_6{}^-$ was very low. Apparently HF has not sufficient latent heat of fusion to enable it to control this exothermic reaction. In addition, the product, being soluble in HF, is exposed to solid O_2AsF_6, perhaps resulting in some further oxidation. This was not a useful preparative method.

EPR Spectra of $C_6F_6^+$ Salts

EPR spectra were obtained from the neat powders prepared from hexafluorobenzene and O_2AsF_6 and $O_2Sb_2F_{11}$ in WF_6, as well as from solutions of these powders in iodine pentafluoride, antinomy pentafluoride, and anhydrous hydrogen fluoride. Except for the HF solution spectra, the samples were contained in 3/16 in. or 4 mm O.D. pyrex tubes. Samples were transferred in a drybox from the vessels in which they were prepared to the sample tubes. In the case of the neat powders, the open end of the tube was plugged with Halocarbon grease and sealed in a flame on removal from the drybox. For the solution spectra, the solid was placed in a 3/16 in. pyrex (Kel-F in the case of HF) tube which was inserted into a 3/16 in. swagelok union connected to a brass Whitey valve. The sample tubes could then be evacuated and an appropriate quantity of solvent distilled onto the solid.

$C_6F_6^+AsF_6^-$ powder exhibited a very strong, broad, symmetric resonance (Fig. VI-1) at g = 2.0063, with a line-width of about 20 gauss at room temperature. Spectra obtained at temperatures as low as -120° were essentially the same. A similar resonance was observed in the spectrum of material prepared from $O_2Sb_2F_{11}$. Spectra of $C_6F_6AsF_6$ solutions in IF_5 and SbF_5 at -110° were no better resolved.

According to Bazhin, et al.,[69] solutions of hexafluorobenzene in superacid gave resolved spectra of $C_6F_6^+$ with g = 2.0038. An unresolved signal at g = 2.004 was observed from a sample of C_6F_6 dissolved in antinomy pentafluoride. No signal was detected from a solution of C_6F_6 in WF_6.

When $C_6F_6AsF_6$ was dissolved in anhydrous HF and the resulting yellow solution quickly frozen to a glass in liquid nitrogen, the spectrum at -100° showed some signs of hyperfine structure, but no further information could be obtained from this spectrum.

The Magnetic Susceptibility of $C_6F_6^+AsF_6^-$

A Princeton Applied Research Vibrating Sample Magnetometer was utilized to determine the magnetic susceptibility of $C_6F_6^+AsF_6^-$ in the temperature range 3.8°K to 71.5°K. Samples were held in specially fabricated Kel-F tubes, which were loaded with the freshly prepared compound and kept at -196° until ready for use. Several properties of this material severely hampered an accurate determination of its magnetic moment. In order to insure removal of all tungsten(VI) fluoride and oxyflouride, as well as excess hexafluorobenzene from the

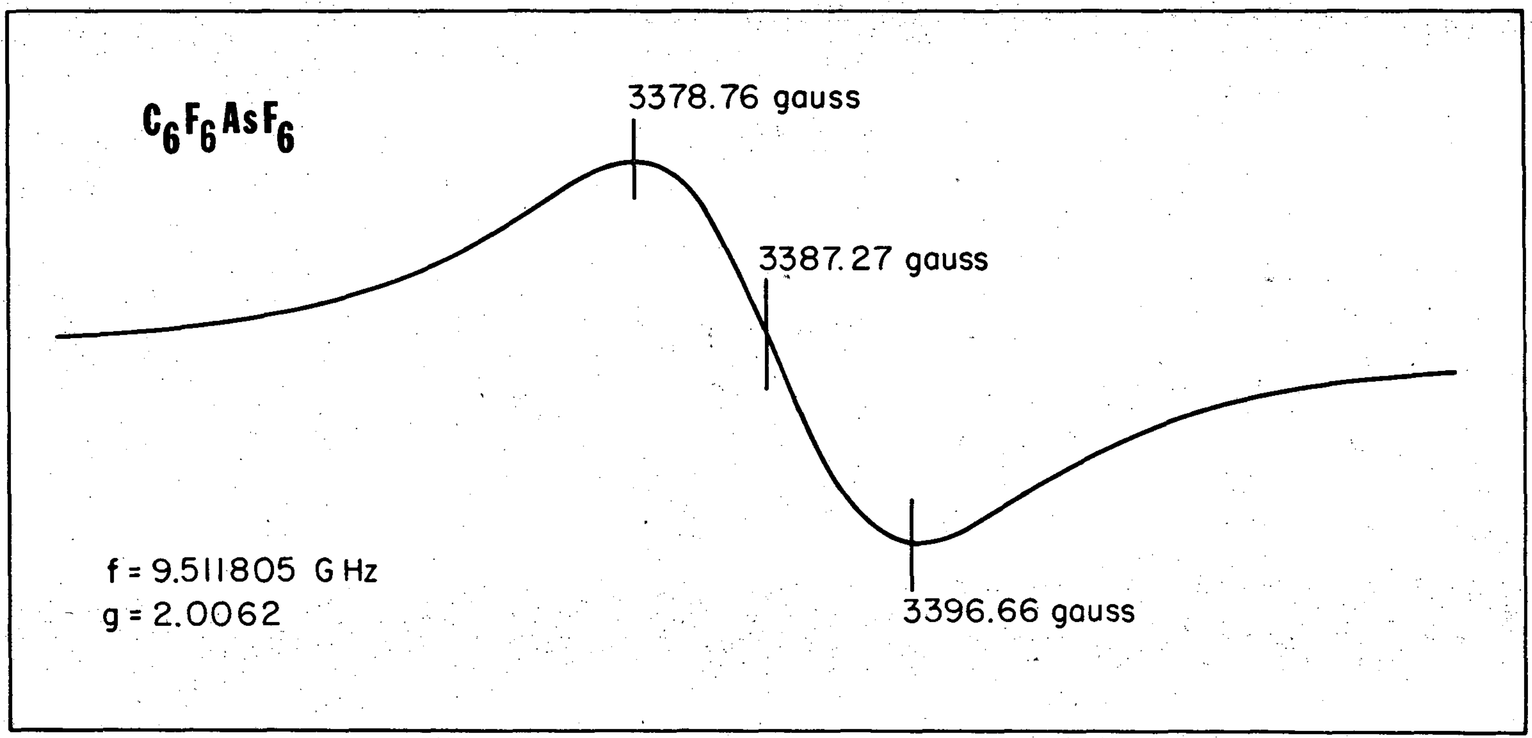

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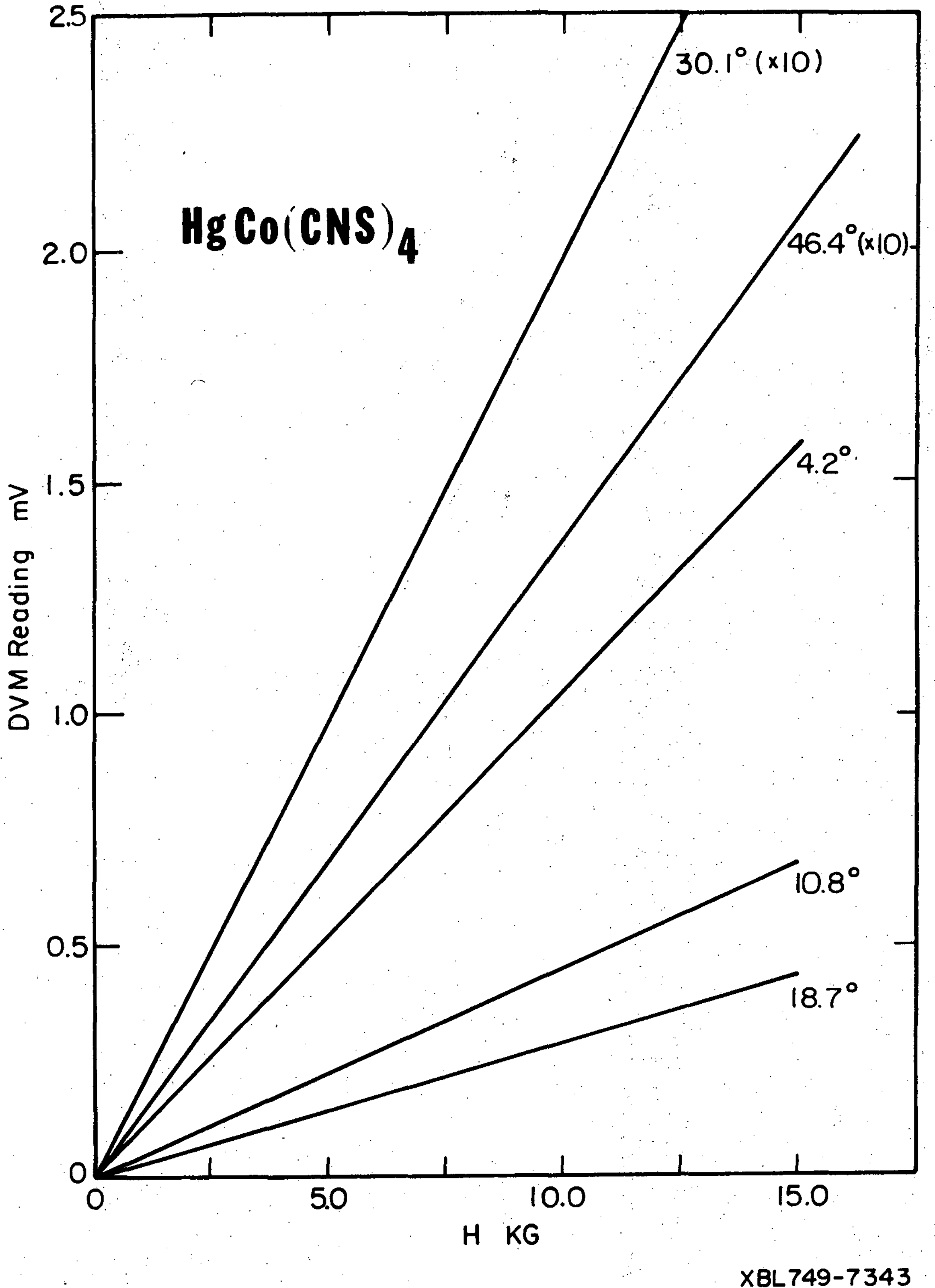
Fig. VI-1. EPR spectrum of solid $C_6F_6AsF_6$ at -110°.

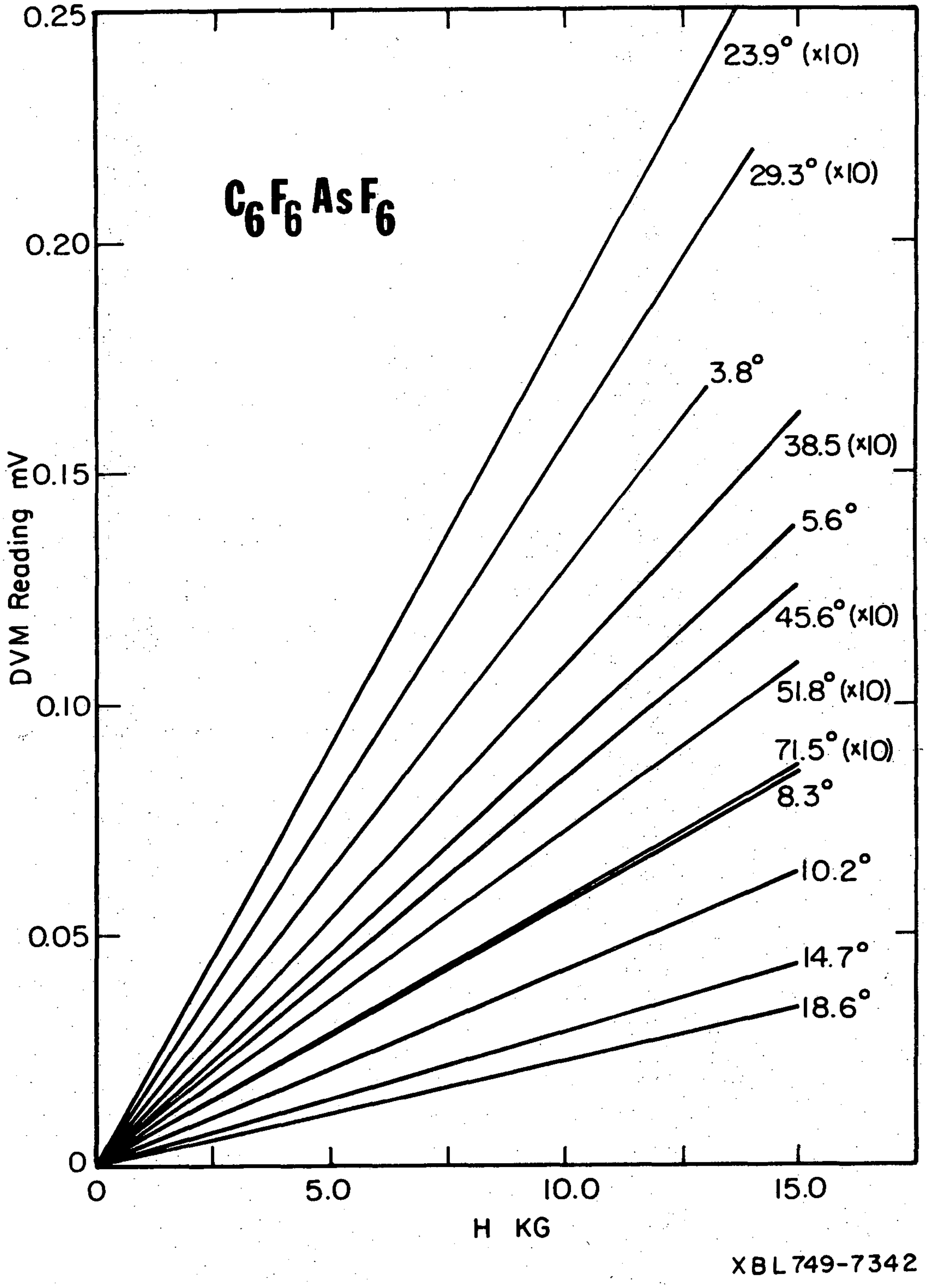
preparation, it was necessary to expose the thermally unstable powder to ambient temperatures while evacuating the reaction vessel. Further decomposition (to diamagnetic products) resulted from the manipulation in the inert atmosphere of a drybox required to load the sample tubes. In addition, the pressure-sensitive nature of the compound, which had to be packed and compressed into the sample tube, resulted in a less pure sample.

All of these difficulties have the effect of reducing the observed moment of the material. The determination was carried out twice, data from the second attempt being considered more accurate because the compound was prepared in Teflon FEP apparatus rather than in fusec silica (thus minimizing the WOF_4 impurity), and because the room-temperature manipulations were kept to a minimum. A wider temperature range was studied in the second experiment as well (3.8°K to 71.5°K as compared to 4.2°K to 52.2°K).

The technique followed was the same in each case. The magnetometer was first calibrated using a standard sample of mercury tetrathiocyanato cobaltate(II) (curie constant 2.28) over the temperature range 4.2°K to 46.4°K (Fig. VI-2). The $C_6F_6^+AsF_6^-$ sample was then put into the magnetometer and moments measured at twelve temperatures from 3.8°K to 71.5°K, and at field strengths of 2.5, 5.0, 7.5, 10.0, and 12.5 kilogauss. From a plot of the digital voltmeter reading vs applied magnetic field (Fig. VI-3), the gram magnetic susceptibility of the sample at each temperature is calculated (Table VI-1). It is also apparent from this plot that there is no residual paramagnetism (possibly arising from



VI-2. Standard calibration data for the vibrating sample magnetometer (temperatures in degrees Kelvin).



VI-3. Magnetic data for $C_6F_6AsF_6$ (temperatures in degrees Kelvin).

Table VI-1. Magnetic susceptibility vs temperature of $C_6F_6^+AsF_6^-$

T (°K)	χ_m (cgs)	$1/\chi_m$	μ_{eff} (B.M.)
3.8	0.0607	16.47	1.36
5.6	0.0437	22.88	1.41
8.3	0.0266	37.57	1.36
10.2	0.0198	50.51	1.28
14.7	0.0137	73.10	1.28
18.6	0.0109	91.92	1.28
23.9	0.00859	116.40	1.29
29.3	0.00733	136.42	1.32
38.5	0.00509	196.49	1.26
45.6	0.00392	254.97	1.20
51.8	0.00336	297.47	1.18
71.5	0.00266	375.74	1.24

metallic impurities or contamination of the sample tube). A plot (Fig. VI-4) of the reciprocal molar susceptabilities (gram susceptibilities divided by the sample weight) vs the absolute temperature shows that the compound obeys the Curie law, $\chi_m = C/T$, with $\mu_{eff} \approx 1.3$ B.M. For the reasons detailed above, the true moment is undoubtedly in excess of this value, as expected for a species such as $C_6F_6^+$, containing one unpaired electron.

Vibrational Spectra of $C_6F_6^+$ Salts

The infrared spectrum of $C_6F_6^+AsF_6^-$, pressed between the silver chloride windows of a Kel-F solid cell, is shown in Fig. VI-5, along with the spectrum of liquid hexafluorobenzene, similarly obtained. Considerable decomposition of the $C_6F_6^+$ salt occurs during handling at room temperature and from contact with the windows of the cell. Those bands which grow with time, as the decomposition proceeds, are marked by an X, and are primarily hexafluorobenzene and octafluorocyclohexa-1, 4 diene (see the section on thermal decomposition of $C_6F_6^+AsF_6^-$). The remaining absorptions are due to the undecomposed solid. ν_3 and ν_4 of the octahedral AsF_6^- ion appear at around 700 and 400 cm^{-1}, respectively. The carbon-fluorine stretching frequency at 1490 cm^{-1} is significantly lower than that in C_6F_6, 1530 cm^{-1}. The ring stretching frequency, however, is slightly higher, appearing at 1030 cm^{-1} as compared to 1019 and 1994 cm^{-1} in the liquid. The drop in the C-F stretching frequency is surprising, in that the positive charge on the ring might be expected to strengthen the C-F bonds. This could simply be due to crystal-packing effects, however. Removing an

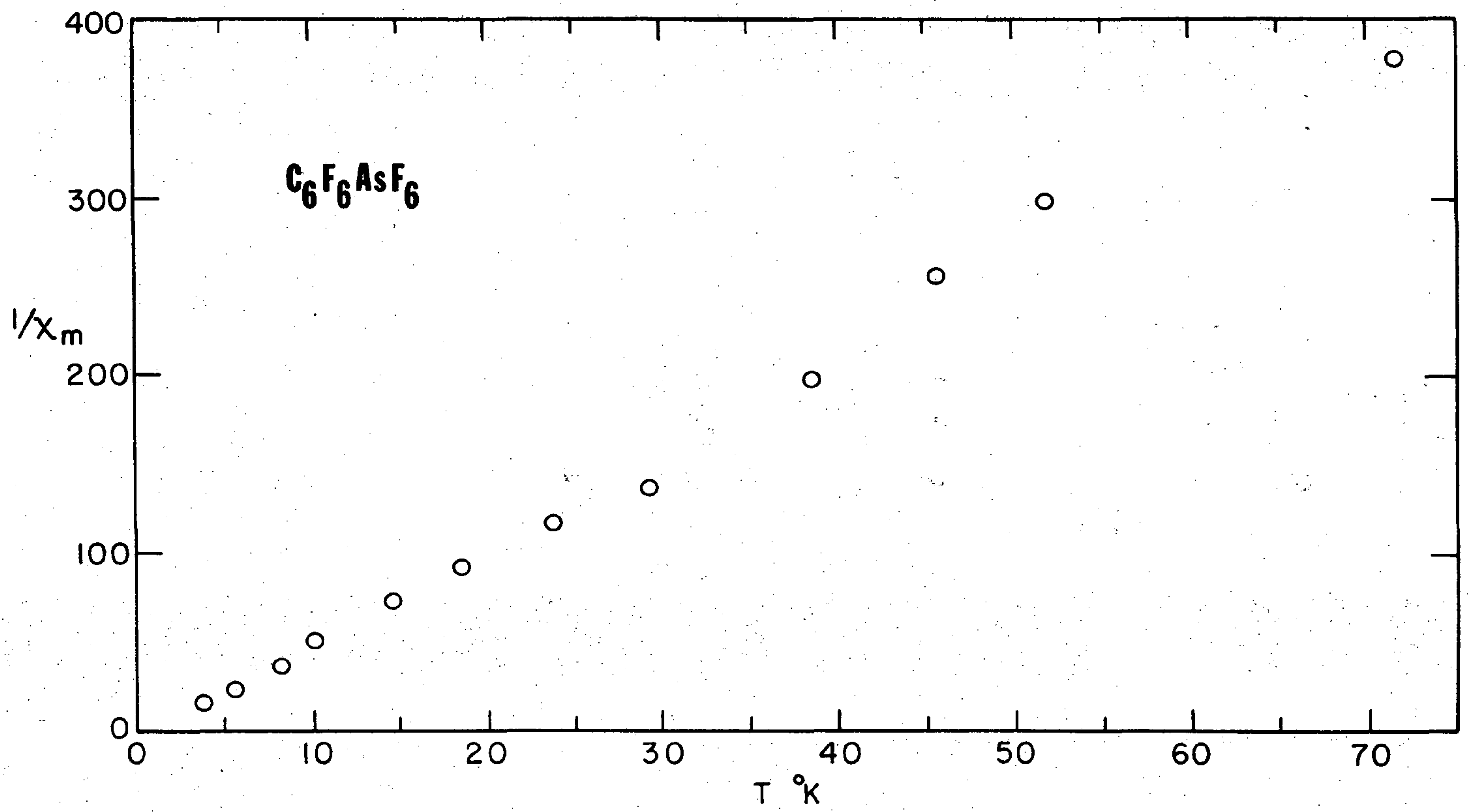


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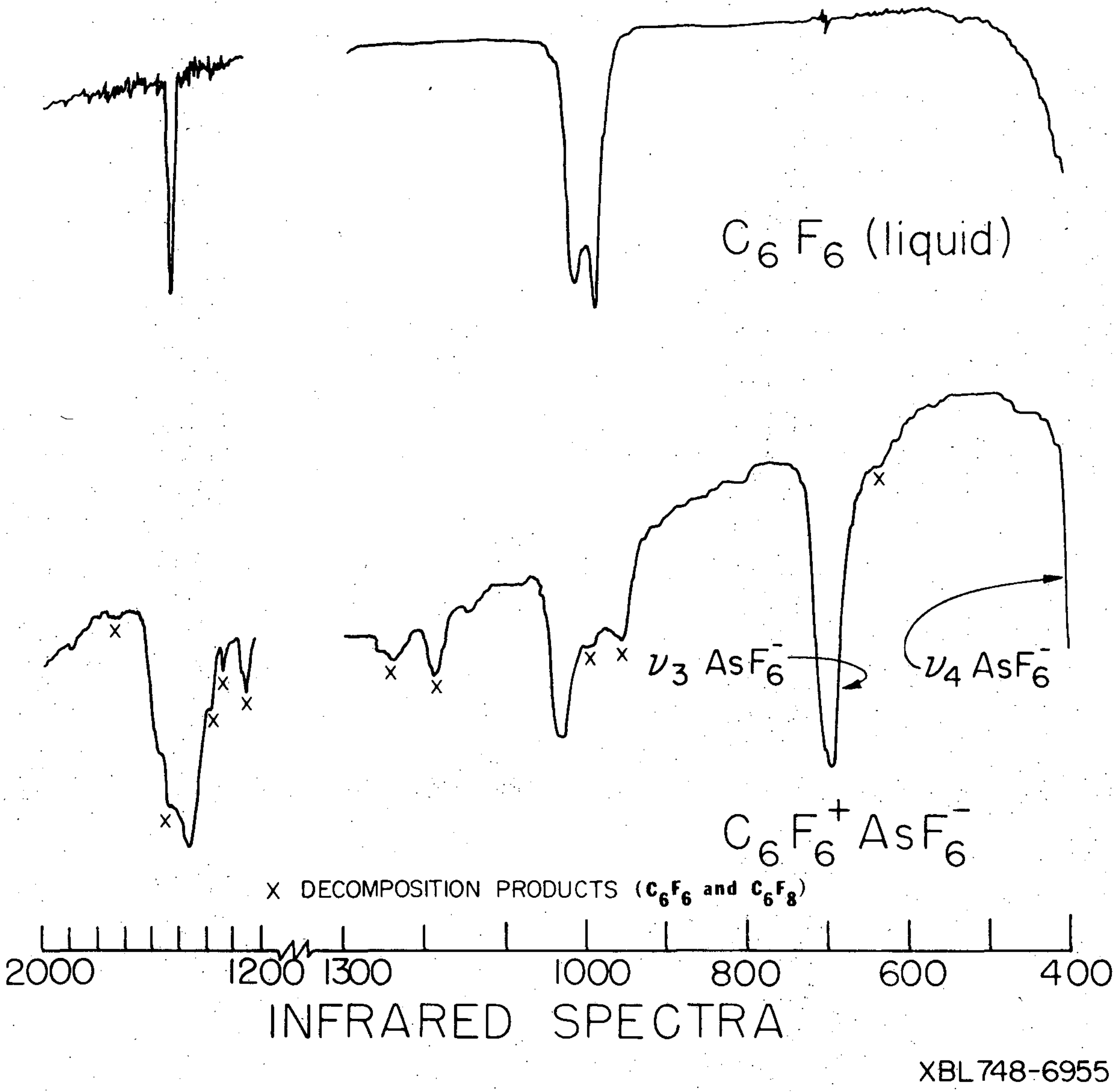
Fig. VI-4. $1/\chi_m$ vs T for $C_6F_6AsF_6$.



VI-5. Comparison of the infrared spectra of C_6F_6 and $C_6F_6AsF_6$.

antibonding electron[102] from the ring system should strengthen the C-C bonds and increase their stretching frequency, as is the case.

Repeated attempts to record Raman spectra of $C_6F_6AsF_6$ powders, crystals, and HF solutions met with no success. A high level of fluorescence was always observed, regardless of the wavelength of the laser exciting line, and at high intensities of excitation, decomposition was rapid even with efficient cooling. A dark green sample of the product of C_6F_6 and O_2SbF_6 gave the spectrum shown in Fig. VI-6. The laser wavelength here was 647.1 nm, and the sample was kept at -15° by a stream of cold nitrogen. Some decomposition of this material was apparent, as the solid was wet. Only a small quantity of hexafluorobenzene is present, however, evidenced by the peaks at 559, 443 and 370 cm^{-1} (Ref. 100). The strong peak at 655 cm^{-1} is probably the Sb-F stretching frequency of the anion, which could be SbF_6^- or $Sb_2F_{11}^-$, as side reactions in the preparation result in the presence of SbF_5 in the product.

Solubility and Recrystallization of $C_6F_6^+$ Salts

Salts of the hexafluorobenzene cation were found to be insoluble in many solvents, reactive toward a few, and soluble in three, though thermal decomposition was more rapid in solution than in the dry solids. Fluorocarbon and chlorofluorocarbon solvents trichlorofluoromethane ($CFCl_3$), perfluoropropane (C_3F_8), hexafluorobenzene (C_6F_6), and carbon tetrachloride (CCl_4), and non-polar tungsten hexafluoride (WF_6) dissolved $C_6F_6^+$ salts sparingly or not at all, but showed no tendency to react with them. Acetonitrile (CH_3CN), chloroform ($CHCl_3$)

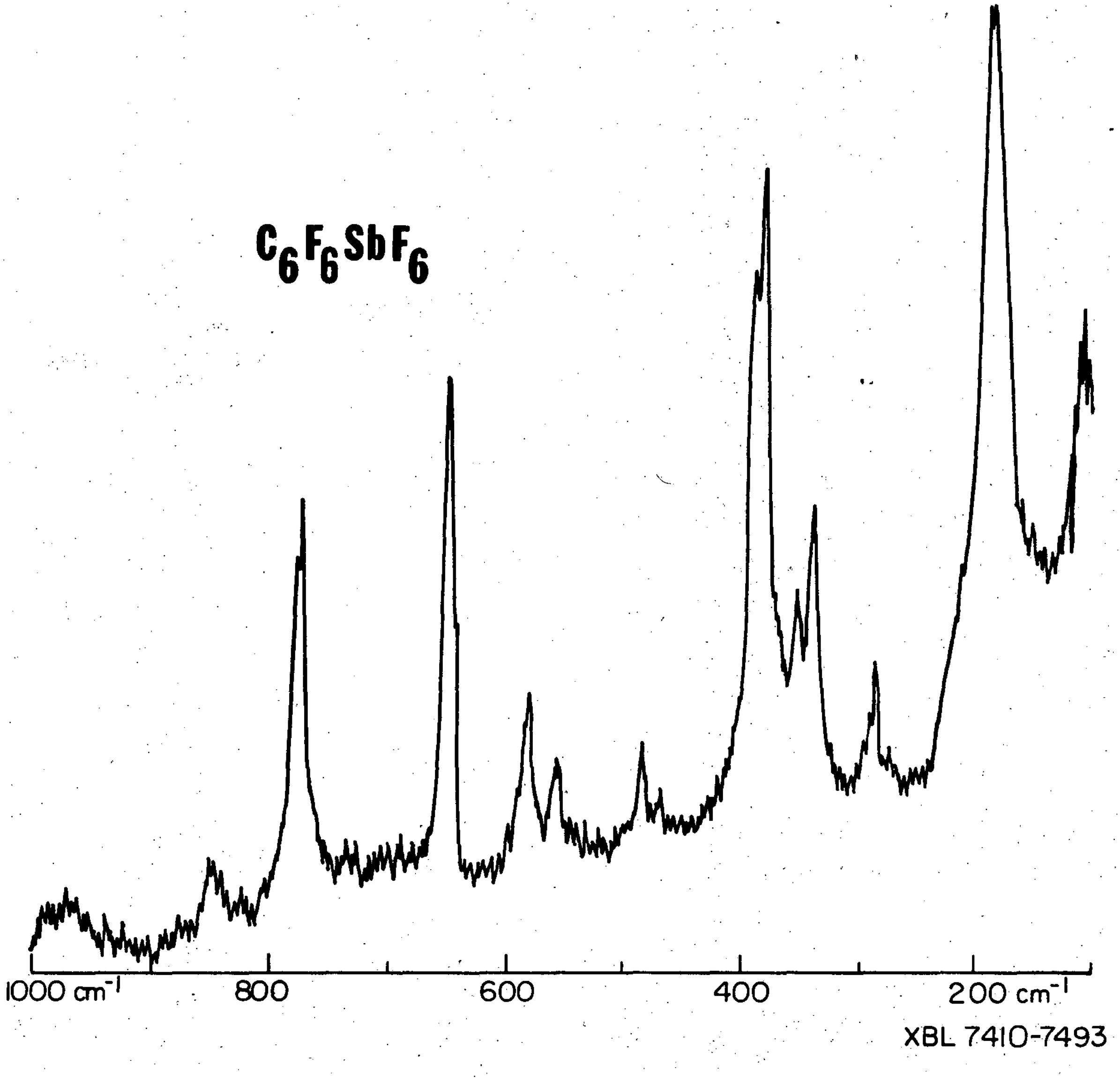


Fig. IV-6. Raman spectrum of $C_6F_6SbF_6$.

and water (H_2O) reacted rapidly to decompose the solids, though in each case some dissolution was evident.

Iodine pentafluoride (IF_5), antimony pentafluoride (SbF_5) and anhydrous hydrogen fluoride (HF) were found to dissolve large quantities of the $C_6F_6^+$ salts. They could be recovered from IF_5 and from HF, though in low yield from the former. Decomposition occurred too rapidly at room temperature to permit recovery from SbF_5 solutions. In each case, the resulting solutions were similar in color to the solute powders, bright yellow for the hexafluoroarsenates, yellow green to dark green for the fluoroantimonates.

When a solution of $C_6F_6^+AsF_6^-$ in anhydrous HF was cooled slowly to 0°, needle-like yellow-orange crystals of the solute grew from the sides of the Teflon FEP tube toward the center of the solution. Very little of the salt remained in solution at 0°, and on cooling to -78°, the solvent could be removed under vacuum without disturbing the freshly-grown crystals. By varying the rate at which they were grown from a few seconds to several minutes (the solution is relatively unstable and slower cooling resulted in poor yields and a contaminated product), crystals as large as 3 mm × 0.3 mm × 0.3 mm could be grown. When cooling, and hence crystal growth, was rapid, clumps of very small crystals were formed, which could not easily be separated.

Like the powder from which they originated, the crystals of $C_6F_6^+AsF_6^-$ were heat, moisture, and pressure sensitive. They were quite fragile, tending to splinter along the needle axis, and required extreme care in handling. They were observed to decompose fully in

6 or 7 hours after preparation when kept at room temperature. Their crystallographic quality, as evidenced by X-ray diffractometer omega-scans, however, deteriorated even more rapidly, rendering them useless for data collection beyond 45 minutes to one hour at ambient temperatures. Weissenberg photographs and diffractometer examination showed them to be single crystals in many cases. Exposure to X-rays significantly reduced their lifetimes.

When the yellow-green product of the reaction of $O_2Sb_2F_{11}$ with C_6F_6 in WF_6 was dissolved in anhydrous HF and recrystallized in the same fashion, pale greenish-yellow crystals, of similar morphology, but shorter and thicker, were obtained. These, like the powder from which they were prepared, were much more thermally stable than the hexafluoroarsenate, persisting for several days at 20°. These were invariably of poor crystallographic quality, however, and were badly twinned. A Weissenberg oscillation photograph of one apparently single crystal showed it to be a conglomerate of a large number of small crystals. In one instance a single crystal of otherwise poor quality gave indications of hexagonal symmetry, but no cell constant or further information was obtained from this material, and its exact composition is unknown.

Crystallographic Data for $C_6F_6^+AsF_6^-$

Zero- and first-layer Weissenberg oscillation photographs of a large (0.2 × 0.2 × 1.5 mm, approximately) single crystal of $C_6F_6^+AsF_6^-$ recrystallized from anhydrous hydrogen fluoride solution confirmed the hexagonal symmetry suggested by a powder pattern of the freshly prepared salt (see below). They established the space group as $R\bar{3}$ (C_{3i}^2), No. 148. The cell constants for the hexagonal setting are a_0 = 10.55(1)Å, c_0 = 7.66(1)Å. For the rhombohedral setting, a_0 = 6.60(1)Å,   = 106.0(1)°. The hexagonal unit cell volume is 738.3Å^3, with three molecules per unit cell. With a formula weight of 374.9 gm/mole, the calculated density is 2.53 cm/cm^3.

Repeated attempts to obtain X-ray diffraction intensity data using a Picker automatic four cicle diffractometer were unsuccessful due to the high thermal instability of the compound. Samples of $C_6F_6^+AsF_6^-$ were prepared in Teflon FEP reaction tubes and immediately dissolved in anhydrous HF, recrystallized, the solvent removed under vacuum at -78°, and transferred as quickly as possible to a Vacuum Atmospheres drybox. With experience, the time during which the product was at room temperature could be reduced to as little as 20-25 min. The crystals were loaded into 0.2 mm O.D. quartz capillaries which were plugged with Kel-F grease and sealed in a small flame on removal from the drybox. These capillaries were maintained in dry ice or liquid nitrogen until ready for use. They were quickly studied under a polarizing microscope (the single crystals exhibited good extinction in crossed polarizers), and mounted on a goniometer head. Once the head was in its place on the diffractometer, the capillary was bathed in cold nitrogen gas by means of an Enraf-Nonius Low Temperature Device which automatically maintained a constant temperature, generally in the neighborhood of -130° to -150°.

In spite of the great care taken to avoid thermal decomposition, which in the powder produces impurities, and in the crystals causes fracturing due to the escape of arsenic pentafluoride gas, each of at least 40 crystals so studied was found to be of insufficient quality for detailed structural analysis.

The powder pattern of the fresh product was indexed with the help of the single-crystal photographs mentioned above, demonstrating the identity of the canary-yellow powder and yellow-orange crystals. The pattern appears in Fig. VI-7. Table VI-2 contains the crystal data, powder pattern, and indexing.

The Crystal Structure of $C_6F_6^+AsF_6^-$

From the space group and unit cell data which have been obtained from the powder pattern and single-crystal photographs, it is possible to draw an approximate structure for $C_6F_6^+AsF_6^-$. The precise geometry of the $C_6F_6^+$ ion cannot be determined from the available information, but it appears to be planar or nearly so. It lies upon a three-fold rotation axis in the $R\bar{3}$ unit cell, but the structure could be disordered. Indeed, the tailing off of the intensities of the higher-angle reflections (see Table VI-2) is typical of a disordered structure.

The coordination of $C_6F_6^+$ units about the AsF_6^- octahedron is shown in Fig. VI-8. This is essentially a trigonally distorted cesium chloride structure, with 8-coordination of both anion and cation. Not shown in Fig. VI-8 are $C_6F_6^+$ rings immediately above and below the AsF_6^- which is at the center of the rhombohedral cell.

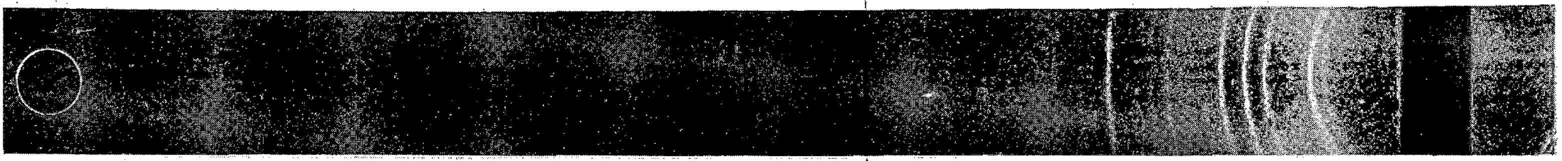


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Fig. VI-7. X-Ray Powder Photograph of $C_6F_6^+ AsF_6^-$

Table VI-2. The X-ray powder pattern of $C_6F_6^+AsF_6^-$.

Space Group $R\bar{3}$

Hexagonal Setting, a_o = 10.55(1), c_o = 7.66(1)Å

V = 738.4Å^3, Z = 3, N.W. = 374.9 g-mole^{-1}, d_c = 2.53 g-cm^{-3}.

Observed reflections obey the rule:

-h + k + 1 = 3n

Rhombohedral Setting, a_o = 6.60(1)Å, α = 106.0(1)°

V = 246.1Å^3, Z = 1, no systematic absences.

Hex. hkℓ	Rhomb. hkℓ	$d_{hk\ell}$	$10^4/d^2$(calc)	$10^4/d^2$(obs)	Relative Intensity
101	010	5.84	290	293	w
110	$01\bar{1}$	5.29	359	357	vvs
021	$11\bar{1}$	3.294	650	650	s
012	110	3.532	802	802	vs
211	$02\bar{1}$	3.151	1009	1007	vs
300	$\bar{1}2\bar{1}$	3.054	1078	1072	vvw
202	020	2.948	1161	1151	vw
122,003	$12\bar{1}$,111	2.550	1520,1534	1537	w
131	$12\bar{2}$	2.408	1728	1725	w
113	120	2.308	1893	1877	vvw
312	$03\bar{1}$	2.118	2239	2229	m
321	$03\bar{2}$	2.021	2447	2448	w
303	030	1.955	2612	2615	w

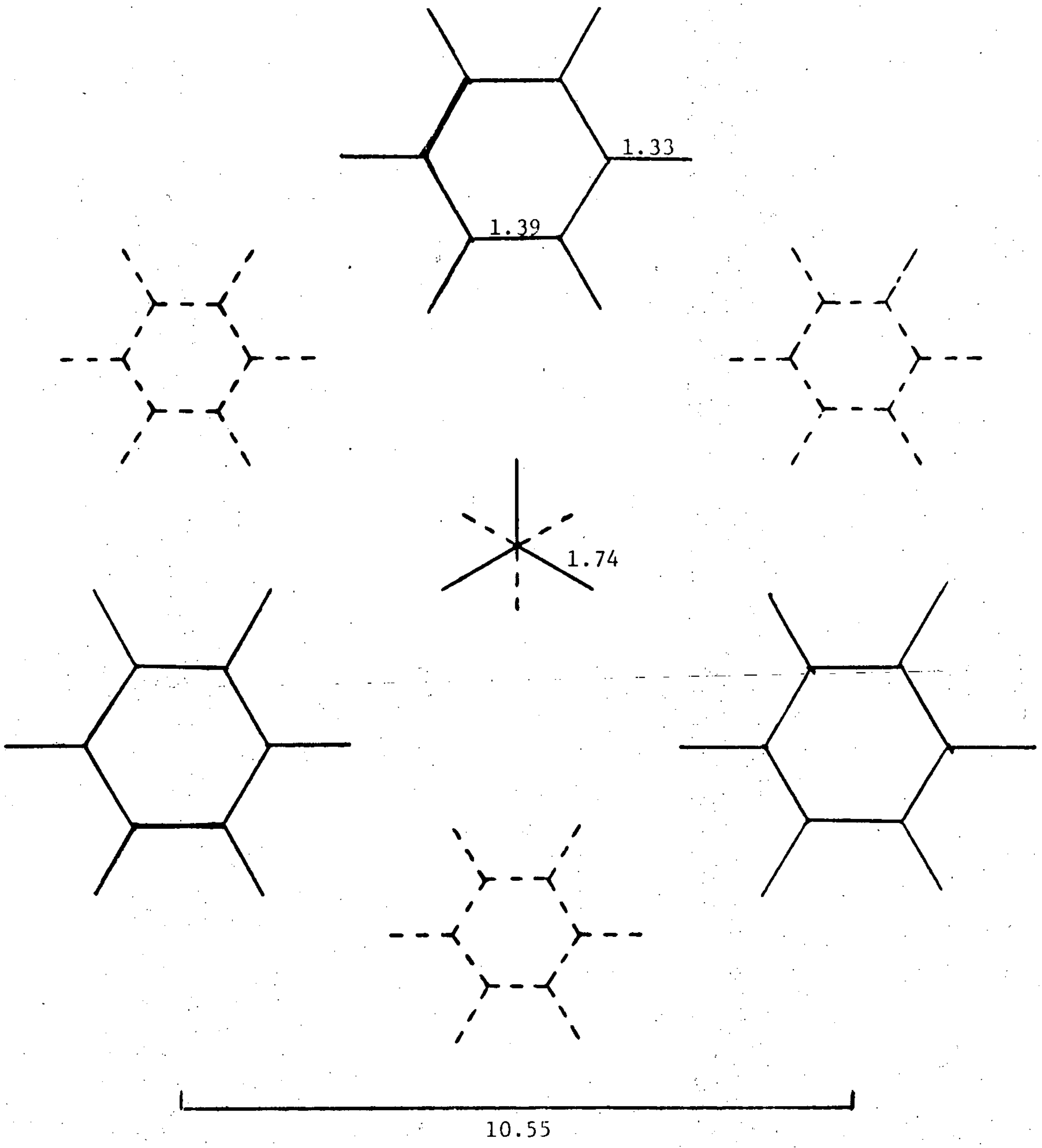
Table VI-2. Continued.

Hex. hkℓ	Rhomb. hkℓ	$d_{hk\ell}$	$10^4/d^2$(calc)	$10^4/d^2$(obs)	Relative Intensity
104	121	1.871	2847	2858	vvw
232,223	$13\bar{2},13\bar{1}$	1.840	2958,2971	2955	w
		1.688		3508	vvw
502	$\bar{1}4\bar{1}$	1.652	3677	3662	vvw
		1.608		3867	vvw
		1.574		4036	vw
		1.534		4249	vvw

Three $C_6F_6^+$ ions surround the anion at a height of one-third of the body diagonal of the $\bar{R}$ cell, and pack with three of the fluorine atoms attached to arsenic. Another three cations lie at two-thirds of the body diagonal, packing with the remaining three AsF_6^- fluorine ligands. The bond distances given in Fig. VI-8 are taken from the molecular structure of hexafluorobenzene[86] and the crystal structure of $ClF_2^+AsF_6^-$ (Ref. 87).

The cation is similarly eight-coordinate, with an AsF_6^- centered above and below the ring, and two sets of three surrounding it, alternately above and below the ring. In the idealized structure, there is an approximate close-packing of fluorine atoms, with vacant "holes" halfway between the centers of adjacent coplanar rings, and filled "holes" occupied by the six-membered carbon rings. Thus each unit cell contains 12 F atoms and 2 F atom-sized "holes", in a total volume of 246.1Å.^{3} This gives a volume of 17.58Å^3 per F atom, in good agreement with Zachariason's rule[88] for close-packed fluoride lattices.

Using a fluoride ion radius of 1.3Å and the bond distances in Fig. VI-8, the unit cell dimensions for the idealized structure are a_o = 10.34 and c_o = 7.23Å, 0.21 and 0.43Å smaller than the experimental values. These are, of course, only lower limits, and do not take into account the "thickness" of the aromatic ring system or possible puckering in $C_6F_6^+$. An upper limit on the cell constant a_o may be estimated by assuming free rotation of the ions about the three-fold axis in the crystal, so that each unit sweeps out a cylinder of radius equal to its greatest dimensions. This would require a_o to be 11.5Å. Thus, it



XBL 7411-7565

Fig. VI-8. The crystal structure of $C_6F_6AsF_6$.

is possible that there is some departure from the ideal, ordered structure, but not enough to allow free rotation. A further, but slight, expansion of a_o may be the result of a longer C-F bond in $C_6F_6^+$, indicated by a decrease in stretching frequency of about 40 cm^{-1} from the neutral molecule.

The major crystallographic axis is coincident with the needle axis of the crystals. One can envision the growth of these crystals as layers of $C_6F_6^+$ plates and AsF_6^- octahedra can align and add to the crystal most favorably at the 001 face. Thus, the crystal grows fastest in the c-direction, producing a needle.

It is to be hoped that an accurate crystal structure determination will result from further efforts to obtain and preserve high-quality crystals of $C_6F_6AsF_6$.

The Reaction of $C_6F_6^+AsF_6^-$ with NO

The ionization potential of hexafluorobenzene is 9.97 eV, that of nitric oxide 9.25 eV.[82] This suggested the redox reaction:

$$C_6F_6^+AsF_6^- + NO \longrightarrow NO^+AsF_6^- + C_6F_6$$

Nitrosyl hexafluoroarsenate would, additionally, be expected to have a greater lattice energy than the $C_6F_6^+$ salt, making the reaction more favourable.

The gas-solid reaction is instantaneous at room temperature, the products being hexafluorobenzene and $NOAsF_6$, the former identified by its gas phase infrared spectrum, the latter by its X-ray powder diffractometer pattern and Raman spectrum. Due to the exothermic nature of the reaction, and the relative thermal instability of $C_6F_6^+AsF_6^-$, however, the process is not quantitative according to Eq. 1. Thermal decomposition of $C_6F_6^+AsF_6^-$ produces, among other things, arsenic pentafluoride, which reacts with nitric oxide as well:[83]

$$3AsF_5 + 2NO \rightarrow 2NOAsF_6 + AsF_3.$$

Some attack on the benzene ring also occurs in the decomposition, further reducing the yield of $NOAsF_6$, as shown by the following table:

Expt.	$C_6F_6^+AsF_6^-$ Reacted (m-moles)	$NOAsF_6$ Produced (m-moles)	Ratio
1	0.40	0.21	52.5%
2	0.072	0.047	65.3%
3	0.119	0.072	60.5%
4	0.656	0.639	97.4%

In the last experiment, nitric oxide was admitted to the reaction vessel very slowly and not in excess until all the solid appeared to have reacted.

Thermal Decomposition of $C_6F_6AsF_6$ and the Reaction of $C_6F_6AsF_6$ with CsF

$C_6F_6^+AsF_6^-$ decomposes in a few hours on standing at room temperature. If heated to 50-60°, the decomposition becomes very rapid. The products are the same in each case: arsenic pentafluoride, hexafluorobenzene, and a material of similar volatility to C_6F_6, with infrared absorptions in the same regions as C_6F_6, identified[84] as octafluorocyclohexa-1,4 diene, C_6F_8 (Fig. VI-9).

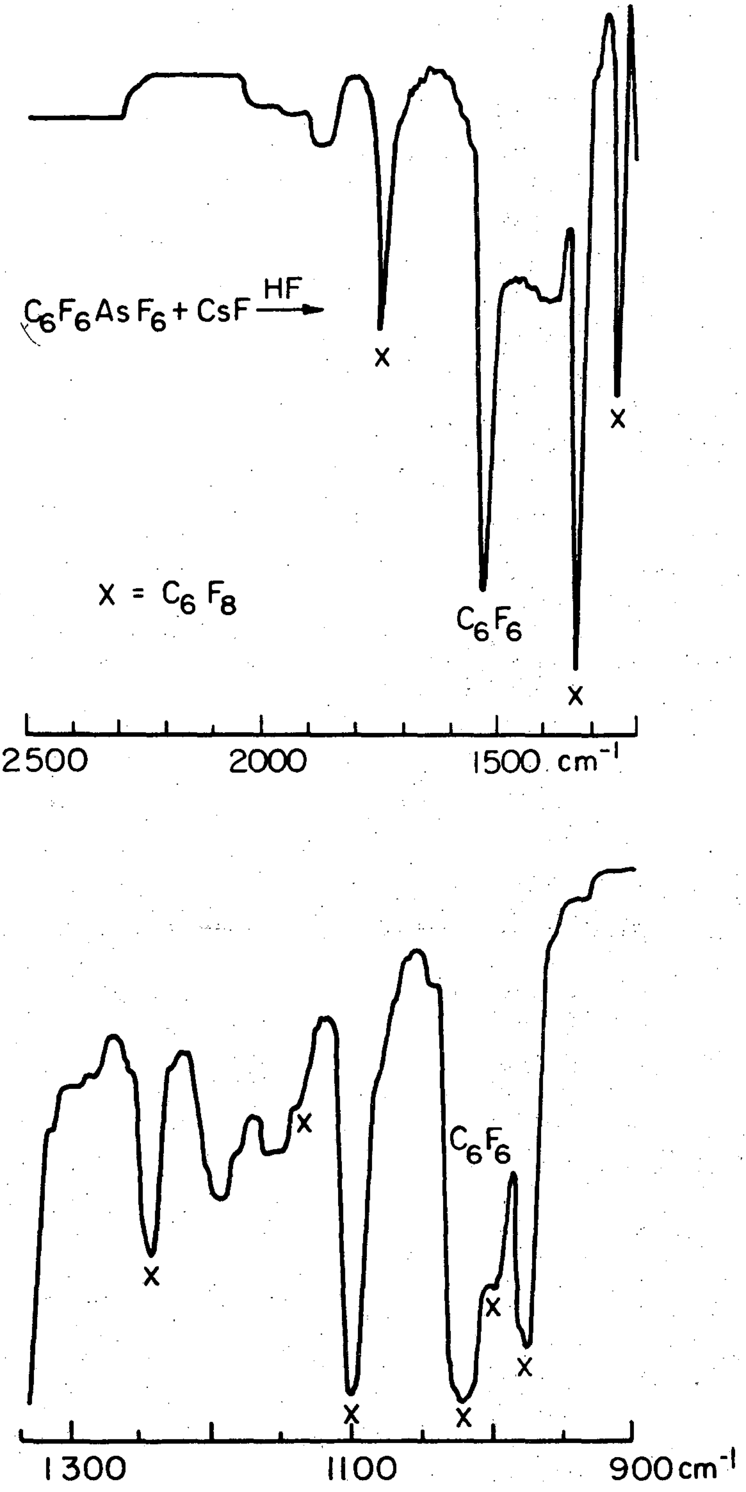


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Fig. VI-9. Infrared spectra of the volatile products of the reaction of $C_6F_6AsF_6$ with CsF.

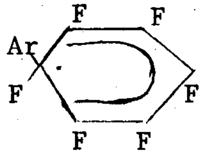
The decomposition may be described in terms of stepwise dissociation of the salt into arsenic pentafluoride and the ion pair $C_6F_6{}^+F^-$, which then disproportionates to C_6F_6 and C_6F_8 through an intermediate neutral radical, $C_6F_7{}^{\cdot}$. That arsenic pentafluoride does not enter into the disproportionation is born out by the results of a study of the reaction of $C_6F_6AsF_6$ with cesium fluoride, both neat and in HF solution. Again, the end products are C_6F_6 and C_6F_8 in approximately equimolar proportions, along with $Cs^+AsF_6{}^-$. This reaction may be written:

$$C_6F_6{}^+AsF_6{}^-{}_{(s)} + Cs^+F^-{}_{(s)} \rightarrow Cs^+AsF_6{}^-{}_{(s)} + C_6F_6{}^+F^-$$

The neat solid-solid reaction begins at about 40° and continues to completion without further heating, producing a dirty-brown solid whose powder pattern is diffuse, but contains only lines due to $CsAsF_6$. An infrared spectrum of the powder pressed between AgCl windows exhibits only a strong, broad absorption centered at 700 cm^{-1} (ν_3 $AsF_6{}^-$). The gaseous products are identical with those from the thermal decomposition except for the absence of AsF_5.

The reaction of $C_6F_6AsF_6$ and CsF in anhydrous hydrogen fluoride solution proceeds at a temperature slightly below 0°, and is sufficiently exothermic to cause the liquid to boil in the reaction vessel. Here again, the same gaseous products were observed; however, the solid remained wet even after a long period of evacuation at room temperature, and was not further examined.

Claret, Williams and Coulson[85] have studied the arylation of hexafluorobenzene by diaroyl peroxides and proposed a mechanism involving hepta-substituted radical species:

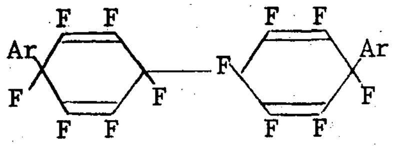
$Ar^{\cdot} + C_6F_6 \rightarrow$ 

These are somewhat unstable, and decompose by routes involving both fluorine radical elimination:

$$ArC_6F_6^{\cdot} \rightarrow ArC_6F_5 + F^{\cdot}$$

$$ArC_6F_6^{\cdot} + F^{\cdot} \rightarrow 1,4\ ArC_6F_7 \quad ,$$

and dimerization:

$ArC_6F_6^{\cdot} \rightarrow$  .

In the case of $C_6F_7^{\cdot}$, the dimer may not be sufficiently stable to persist (although a small amount of $C_{12}F_{14}$ would not have been detected), and may undergo further rearrangement to form C_6F_6 and C_6F_8.

The Reaction of $C_6F_6AsF_6$ with C_6H_6

$C_6F_6AsF_6$ was prepared in tungsten hexafluoride as described previously. Benzene was shown to be free of gross impurities by infrared spectroscopy, and was used without further purification. About 100 mg $C_6F_6AsF_6$ in a Teflon FEP tube was exposed to benzene vapor for several minutes with only a slight darkening in the color of the solid. A small quantity of benzene was then condensed onto the solid at -196° and allowed to warm in an ice bath (0°). The reaction proceeded smoothly as the benzene melted, with little change in pressure. The solid became first blue, and then gray-black. An infrared spectrum of the gases produced shows mainly hexafluorobenzene, along with some benzene. No arsenic pentafluoride and no other carbon-fluorine bands were seen. The black solid residue has the appearance of graphite. It is thermally stable at room temperature, and does not react with water. An infrared spectrum of the solid, pressed between silver chloride windows, shows only a weak, broad absorption centered around 710 cm^{-1}, which may be due to residual As-F bonds. No Raman spectrum could be obtained due to the very dark color.

The reaction produced a like material when carried out in anhydrous hydrogen fluoride solution. Both reactions (neat and HF solution) were studied gravimetrically. The data are as follows:

	$C_6F_6AsF_6$	Product
Neat Reaction	0.2148g(0.57 m-mol)	0.0684g
HF Solution	0.4179g(1.11 m-mol)	0.1520g

The black, unreactive solid is insoluble in HF, and precipitates immediately when benzene contacts the liquid containing $C_6F_6AsF_6$. No AsF_6 is provided. The product does not react with nitric oxide. When exposed to 100 to 300 mm Hg of fluorine gas, the solid takes up F_2. If the pressure is raised above 300 mm Hg, sparking occurs in the powder, with emission of orange-red light. CF_4 is produced, and the solid becomes light gray in color.

An x-ray powder pattern was obtained for the solid prepared in the neat reaction. It is complex and may contain more than one phase. The powder pattern is given in Table VI-3.

Table VI-3. X-ray powder pattern of the black solid product of the of $C_6F_6AsF_6$ with benzene (film No. 641).

$d_{hk\ell}$	$10^4/d^2$	Relative Intensity
8.15	151	MS
6.93	208	M
6.27	254	MS
5.87	290	W
5.50	331	S
5.03	395	M
4.813	432	M
4.282	546	M
4.171	575	MW
4.065	605	W
3.965	636	VS
3.792	695	W
3.717	724	W
3.577	782	W
3.467	832	M
3.099	1041	W
3.018	1098	W
2.940	1157	W
2.699	1373	S
2.260	1959	S
2.001	2498	M
1.758	3236	M
1.659	3633	M

$C_6F_6^+$ Salts of the Fluoroantimonates

The investigation of $C_6F_6^+$ salts has centered around $C_6F_6AsF_6$ for several reasons. Because the preparations do not proceed in 100% yield, by-products which are not volatile remain in the reaction vessel and contaminate the product. In the case of $C_6F_6AsF_6$, the by-products are O_2, AsF_5, and fluorination products of C_6F_6, mostly C_6F_8, all of them sufficiently volatile to allow their removal under vacuum at room temperature. In the case of the fluoroantimonates O_2SbF_6 and $O_2Sb_2F_{11}$, however, SbF_5 is a by-product which is not sufficiently volatile to be removed in the limited time available before decomposition occurs. Furthermore, SbF_5 tends to form fluorine-bridged polyanions[103] such as $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ with SbF_6^- and $Sb_2F_{11}^-$, which results in a product which may contain more than one $C_6F_6^+$ salt. These difficulties make the hexafluoroarsenate salt more amenable to gravimetric study in spite of the fact that the yields in the fluoroantimonate reactions appear to be greater, perhaps as high as 80%.

In addition, the materials prepared from C_6F_6 and O_2SbF_6 or $O_2Sb_2F_{11}$ are sufficiently stable that they do not interact quickly and smoothly at room temperature with nitric oxide, which reaction has proved invaluable in elucidating the composition and stoichiometry of $C_6F_6AsF_6$.

Preparations of the fluoroantimonate salts of $C_6F_6^+$ were carried out in essentially the same manner as those of $C_6F_6AsF_6$. O_2 evolution was consistent with complete reduction of O_2^+ to molecular oxygen, and vibrational and epr spectra were similar to those for $C_6F_6AsF_6$. The material prepared from $O_2Sb_2F_{11}$ was nearly identical in color with

$C_6F_6AsF_6$, bright yellow-green. That made from O_2SbF_6, however, varied from deep forest green to yellow-green, often containing an inhomogeneous mixture of yellow and green solids. This is most likely due to the presence of a limited quantity of SbF_5, produced in side-reactions, which combines with some or all of the SbF_6^- available to form $Sb_2F_{11}^-$, the $C_6F_6^+$ salt of the former being green, of the latter, yellow.

The fluoroantimonate salts also react with octafluoronapthalene to form blue-green materials, similar in appearance and stability to $C_{10}F_8^+AsF_6^-$ (see the following section), but these were in each case, wet and untractable.

B. The Octafluoronapthalene Cation, $C_{10}F_8^+$

Because of the relative involatility of octafluoronapthalene (m.p. 87-88°, vapor pressure 15 mm at 80°),[89] it was necessary to introduce it into reaction vessels as a solid. When $C_{10}F_8$ crystals and dioxygenyl hexafluoroarsenate were mixed in the dry box, they reacted exothermically on contact to form a wet green mass which was quickly removed from the dry box so as to minimize contamination of the nitrogen atmosphere.

In hope of obtaining a slower reaction, which would favor higher yields and greater purity, the reaction of $C_{10}F_8$ with hexafluorobenzene cation salts was investigated. The dry solids $C_{10}F_8$ and $C_6F_6AsF_6$ were combined in the dry box, whereupon the yellow $C_6F_6^+$ salt turned blue wherever it contacted a crystal of octafluoronapthalene, which appeared to dissolve and consume the powder. When the reaction was complete, a very wet, deep green mud remained. If the mixture were quickly transferred to a reaction vessel and removed to the vacuum line, the greater part of the liquid could be removed under vacuum, and examined, along with the gaseous product, by infrared spectroscopy. Seen in the spectrum thus obtained were hexafluorobenzene and arsenic pentafluoride, along with octafluorocyclohexa-1,4 diene, which is produced in the thermal decomposition of $C_6F_6AsF_6$.

When the solids were kept separate in the reaction vessel until it could be removed from the dry box and cooled in liquid nitrogen to prevent interaction, a small quantity of the material reacted due to the $C_{10}F_8$ vapor reaching the $C_6F_6AsF_6$. Tungsten hexafluoride or anhydrous hydrogen fluoride could then be condensed onto the cold mixture, and on warming, the reaction was immediate, producing very little of the above-mentioned by-products, especially when WF_6 was used as the solvent/moderator.

The reaction may be written simply,

$$C_6F_6^+AsF_6^-{}_{(s)} + C_{10}F_8{}_{(s)} \rightarrow C_{10}F_8^+AsF_6^-{}_{(s)} + C_6F_6{}_{(\ell)}$$

The behavior of the solid-solid reaction is easily explained by dissolution of the crystalline $C_{10}F_8$ in the liquid C_6F_6 produced at the reaction front.

$C_{10}F_8^+AsF_6^-$ is a soft, forest green solid, m.p. 122° ± 3°, often containing octafluoronapthalene as an impurity (evacuation for extended periods eventually removes $C_{10}F_8$). It is stable at room temperature in quartz tubes, but has been observed to decompose in a day or two when stored in pyrex, faster if prepared in or treated with anhydrous HF. It is quite soluble in HF, but attempts to grow crystals from HF solution have failed, and the material recovered is generally wet and untractable, although unchanged in color.

Gravimetric studies of the preparation are hampered by both the presence of $C_{10}F_8$ in the product and the side reaction which involves decomposition of the less stable $C_6F_6^+AsF_6^-$. The data obtained indicate a low yield of $C_{10}F_8^+AsF_6^-$ based on $C_6F_6^+AsF_6^-$.

Exposure of the octafluoronapthalene cation salt to one atmosphere of nitric oxide resulted in no reaction at room temperature. With strong heating, partial reaction was achieved, probably the result of thermal decomposition of the $C_{10}F_8^+AsF_6^-$ and subsequent reaction of AsF_5 with NO.

Several attempts to obtain Raman spectra of this intensely colored material were unsuccessful.

When the green $C_{10}F_8^+$ materials are exposed to moist air, they quickly become pale yellow, with no change in texture. The resulting yellow powder deliquesces slowly on standing in air.

EPR Spectrum of $C_{10}F_8^+AsF_6^-$

The *epr* spectrum of $C_{10}F_8^+AsF_6^-$ powder at room temperature consists of a single, unresolved, symmetric resonance at $g = 2.004_9$. It is a very intense signal, with a line width of 8 gauss, considerably narrower than those observed in $C_6F_6^+$ salts and solutions.

X-Ray Diffraction Powder Pattern of $C_{10}F_8^+AsF_6^-$

A sample of the deep green solid prepared from $C_6F_6AsF_6$ and $C_{10}F_8$ in WF_6 was loaded into a 0.5 mm quartz capillary and examined by x-ray powder photography using unfiltered CuK_α radiation. The resulting pattern, with a tentative indexing, appears in Table VI-4.

Table VI-4. Powder Pattern of $C_{10}F_8^+AsF_6^-$ (Film No. 679)

Tetragonal: $a_o = 8.27(5)$, $c_o = 18.57(5)$Å

$V = 1270\text{Å}^3 = z = 4$

hkl	d_{hkl}	$10^4/d^2$(obs.)	$10^4/d^2$(calc.)	Rel. Intensity
100	8.21	148	146	s
101	7.54	176	175	s
110	5.90	287	292	ms
112,103	4.963	406	408,407	s
004	4.673	458	464	MW
113	4.249	554	553	S
201,104	4.051	609	613,610	S
202	3.779	700	700	VS
211,114	3.634	757	759,756	VS
212,203	3.436	847	846,855	S
213	3.177	991	991	MS
220	2.918	1175	1168	M
301	2.731	1341	1343	W
310	2.631	1444	1460	VW
312,303	2.517	1578	1574,1575	MS
314,321	2.282	1921	1924,1927	VW
322	2.230	2011	2014	VW
323	2.153	2158	2159	M
400,324	2.063	2350	2336,2362	M
	1.955	2615		W
420	1.845	2937	2920	VW
	1.513	4370		VW

VII. THE HYDROLYSIS OF $Xe_2F_3^+RuF_6^-$ AND $Xe_2F_3^+IrF_6^-$

Only three binary tetroxides are presently known, those of osmium, ruthenium and xenon. OsO_4 and RuO_4 were discovered soon after the elements were isolated, and were characterized[90] by Draus and Schrader in 1928. OsO_4 is prepared by burning the metal, or by oxidation of osmium solutions with nitric acid. RuO_4, the less stable of the two, is prepared by heating acid solutions containing ruthenium with strong oxidizers such as periodate, permanganate, or bromate.[91] Xenon tetroxide, XeO_4, was produced[92] in 1964 by Selig et al., in the reaction of sulfuric acid with the perxenate salts Na_4XeO_6 and Ba_2XeO_6. All three tetroxides have been shown to be tetrahedral molecules in the gas phase.

The highest known oxide of iridium is the dioxide, IrO_2. Oxidation states higher than Ir(IV) have thus far been found only in the fluorides and in IrF_6^-. Since iridium (0) has a d^7s^2 configuration, the tetroide would be expected to be d^1, and paramagnetic. The epr spectrum of such a species should exhibit hyperfine splittings due to ^{191}Ir (natural abundance 38.5%) and ^{193}Ir (61.5%), both with spin3/2. It is possible that dimerization of this molecule could occur via a peroxygen bridge, thereby lowering the effective oxidation state to +7. This would probably still be a paramagnetic species, however, with the two d-electrons in different orbitals.

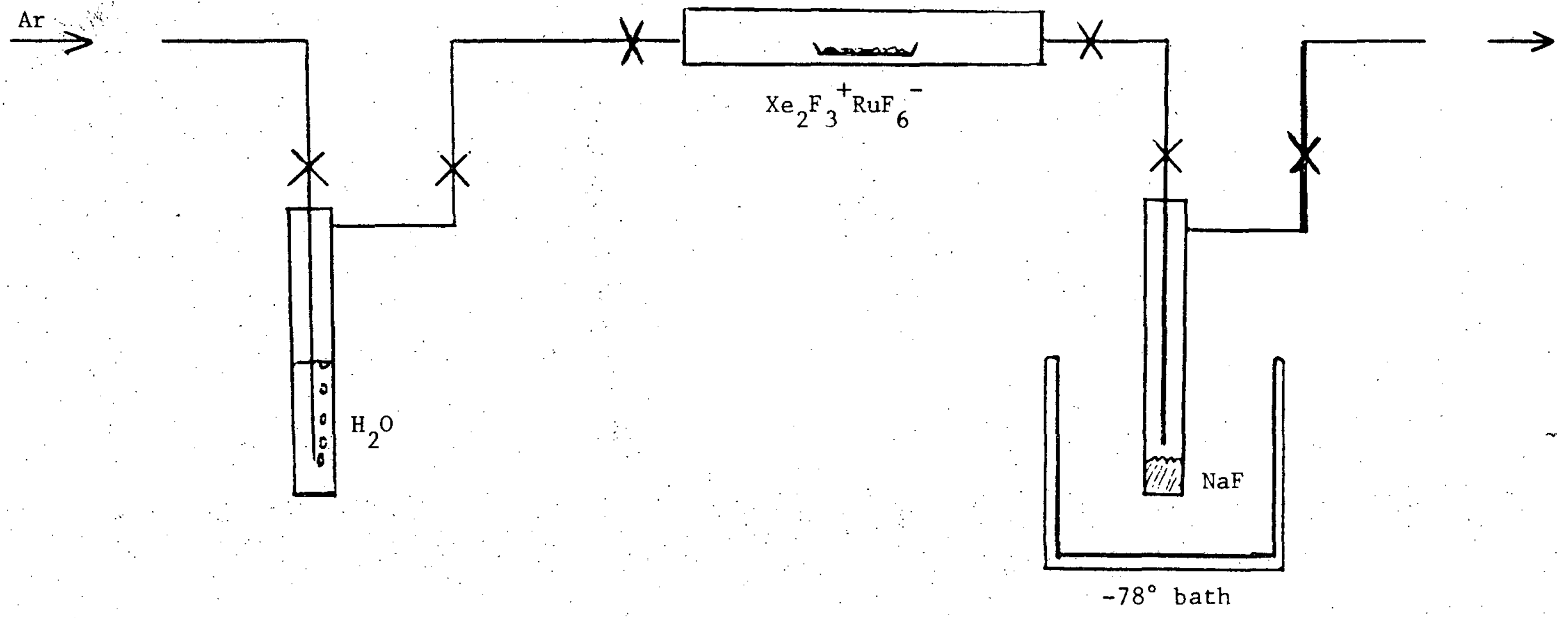
In an attempt to prepare the tetroxide of iridium, the hydrolysis of the 2:1 xenon difluoride-iridium pentafluoride adduct was investigated. In order to ascertain the feasibility of the reaction, and the best method for carrying it out, the known compound ruthenium tetroxide was prepared by hydrolysis of the analogous xenon difluoride-ruthenium pentafluoride adduct.

Both compounds, properly formulated as the salts $Xe_2F_3^+IrF_6^-$ and $Xe_2F_3^+RuF_6^-$, respectively,[93] were prepared by the room temperature interaction of a 3:1 mole ratio of XeF_2 and the corresponding pentafluoride in bromine pentafluoride solution. The reaction is quantitative, producing small crystals of the pale green ruthenium salt and the paler yellow-green iridium salt. Raman spectra of these compounds showed them to be pure, except for a very small (<3%) quantity of the 1:1 adducts, XeF^+RuF_6 and XeF^+IrF_6.

Hydrolysis of the ruthenium salt was first carried out in the flow system depicted in Fig. VII-1. $Se_2F_3^+RuF_6^-$, contained in a platinum boat, was placed in a quartz reaction tube with a valve at each end, which was evacuated and removed to the dry box for this purpose. A wet stream of argon gas was passed over the sold, which immediately became dark brown, then black. An infrared spectrum of the contents of the cold trap shows absorption maxima at 1220 cm^{-1} (PQR), 1360 cm^{-1}, and 1735 cm^{-1} (PQR).

Next, the reaction of $Xe_2F_3^+RuF_6^-$ with water was carried out in a static system. Water was condensed into a Kel-F tube containing the ruthenium salt at -196°.

The contents were allowed to warm to room temperature, and the volatile products collected in a Kel-F trap held at -196°. A volatile yellow material appeared in the cold trap and was identified by its infrared spectrum as RuO_4 [ν_3 = 920 cm^{-1} (PQR)].[94,95] In this experiment, no other absorptions were seen in the spectrum of the gases from the cold trap. The absence of HF is explained by adsorption of the small



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VII-1. Apparatus used in hydrolysis of $Xe_2F_3^+RuF_6^-$.

amount present onto the prefluorinated silver plate walls of the infrared sample cell. The reaction may be written:

$$2Xe_2F_3^+RuF_6^- + 9H_2O \rightarrow 2RuO_4 + 4Xe + 18HF + \frac{1}{2}O_2$$

Having succeeded in preparing RuO_4 in this manner, the hydrolysis of $Xe_2F_3^+IrF_6^-$ was undertaken in a like fashion. Again, a volatile light brown material was collected in the -196° trap. This time, however, on expanding the gas into the infrared cell, no absorption was detected.

A large quantity of the iridium salt was hydrolyzed in the same way. The volatile light brown substance was again formed and caught in the cold trap, but no infrared absorption seen.

Subsequent hydrolyses were carried out in pyrex, quartz and Kel-F apparatus, with and without sodium fluoride present to take up hydrogen fluoride and liquid H_2O. In each case, as in the first two experiments, iridium residues were found in the area where the products were condensed. When pyrex apparatus was used, the product attacked the glass immediately upon warming toward room temperature, and the purple residue appeared.

It is evident that a volatile, iridium-containing material is produced in the hydrolysis of $Xe_2F_3^+IrF_6^-$. This compound is unstable in the presence of NaF, and decomposes on expansion into a silver-plated infrared cell with prefluorinated silver chloride windows.

The hydrolysis was, therefore, run <u>in situ</u>, within a solid Kel-F infrared cell equipped with silver chloride windows and having no metallic surfaces on its interior. $Xe_2F_3^+IrF_6^-$ was introduced into the cell cavity through a hole in the side which was closed by a threaded

Teflon plug. The cell was removed from the dry box and evacuated. A quantity of water insufficient to effect complete hydrolysis was introduced into the tubing between two valves connected in series to the cell, and then forced by air pressure into the evacuated cell on opening of the valve on the cell body. The reaction was monitored by repeated recording of infrared spectra.

Initially, a strong PQR band, centered around 1110 cm^{-1} appeared when the water wad admitted to the cell. Over a period of 20 min, its intensity had diminished by half, and in a little over an hour, had disappeared entirely. This band has been assigned to chlorine dioxide, ClO_2. The apparent PQR structure is in fact due to isotopic chlorine splitting of ν_3 of this C_{2v} molecule.[96,97]

Preparation of Chlorine Dioxide

In order to confirm the assignment of this absorption to chlorine dioxide, a small quantity of ClO_2 was prepared by the method of McHale and von Elbe.[98] Potassium chlorate (0.025 g, 0.20 m-mol) and oxalic acid dihydrate (0.028 g, 0.22 m-mol) were mixed in a Teflon FEP reaction tube. The solids were moistened with water, the tube was connected to the vacuum line, evacuated, and opened to a monel infrared cell and to the Helicoid gauge. The mixture was heated gently until the pressure in the entire volume had risen to 25 mm Hg. The pressure was kept low to avoid decomposition and possible detonation of the gaseous ClO_2 .

The reaction proceeds according to the equation:

$$2KClO_3 + 2\ H_2C_2O_4 \cdot 2H_2O \xrightarrow[\Delta]{H_2O}$$

$$K_2C_2O_4 + 2CO_2 + 6H_2O + 2\ ClO_2.$$

An infrared spectrum of the product of this reaction was found to correspond precisely to that obtained in the hydrolysis of $Xe_2F_3^+IrF_6^-$.

The Origin of ClO_2 in the Hydrolysis of $Xe_2F_3^+IrF_6^-$

ClO_2 may have been formed from the reaction of the silver chloride windows of the infrared cell with an active oxygen species such as IrO_4 or XeO. To investigate this further, a low-temperature cell with a liquid nitrogen-cooled AgCl window in the center, and potassium bromide windows on the ends was utilized. The central AgCl window was mounted on a copper cold finger, which could be rotated 90° to receive vapors from an inlet nozzle, and at right angles to this, to record the spectrum.

$Xe_2F_3^+IrF_6^-$ was hydrolysed in a Kel-F tube connected directly to the evacuated low-temperature cell by a 6 cm length of Kel-F tubing which terminated ~1.5 cm from the cold window. The only bands observed in the infrared spectrum thus obtained were due to water and hydrogen fluoride.

The Hydrolysis of $XeF_2 \cdot IF_5$

In order to determine whether XeO might be an important intermediate in the hydrolysis of XeF_2 compounds, an investigation of the reaction of the xenon difluoride-iodine pentafluoride molecular adduct[99] with water was undertaken. The formation of IOF_5 in this reaction would be indicative of such an XeO species.

$XeF_2 \cdot IF_5$ was prepared by the room temperature interaction of xenon difluoride and a slight excess of iodine pentafluoride. The reaction is rapid and quantitative. Excess IF_5 was removed under vacuum, leaving the finely powdered white solid, $XeF_2 \cdot IF_5$.

This material was introduced into the Kel-F infrared cell previously used for hydrolysis of $Xe_2F_3^+ IrF_6^-$. A spectrum recorded before admitting water to the cell showed the presence of dissociated XeF_2 and IF_5. Another spectrum immediately following the addition of water showed a disappearance of the XeF_2 absorptions, and no change in that of IF_5. No bands due to IOF_5 were observed.

The Reaction of $XeF_2 \cdot IF_5$ with N_2O_4

In a further attempt to determine whether XeO might be present in oxidations by XeF_2, the iodine pentafluoride complex was exposed to liquid dinitrogen tetroxide, with the hope of producing IOF_5.

An infrared spectrum of commercial dinitrogen tetroxide, N_2O_4, showed no impurities and it was used without purification. 0.1 g (0.26 mmol) $XeF_2 \cdot IF_5$ was placed in a Kel-F trap and liquid N_2O_4 (2 ml) was transferred onto the solid. The mixture was shaken at room temperature and heated gently. No gas evolution was observed, and cooling to -196° showed the presence of no non-condensible gas. The infrared spectrum of the vapor above the mixture was identical with that of pure N_2O_4, i.e. no evidence was found for IOF_5.

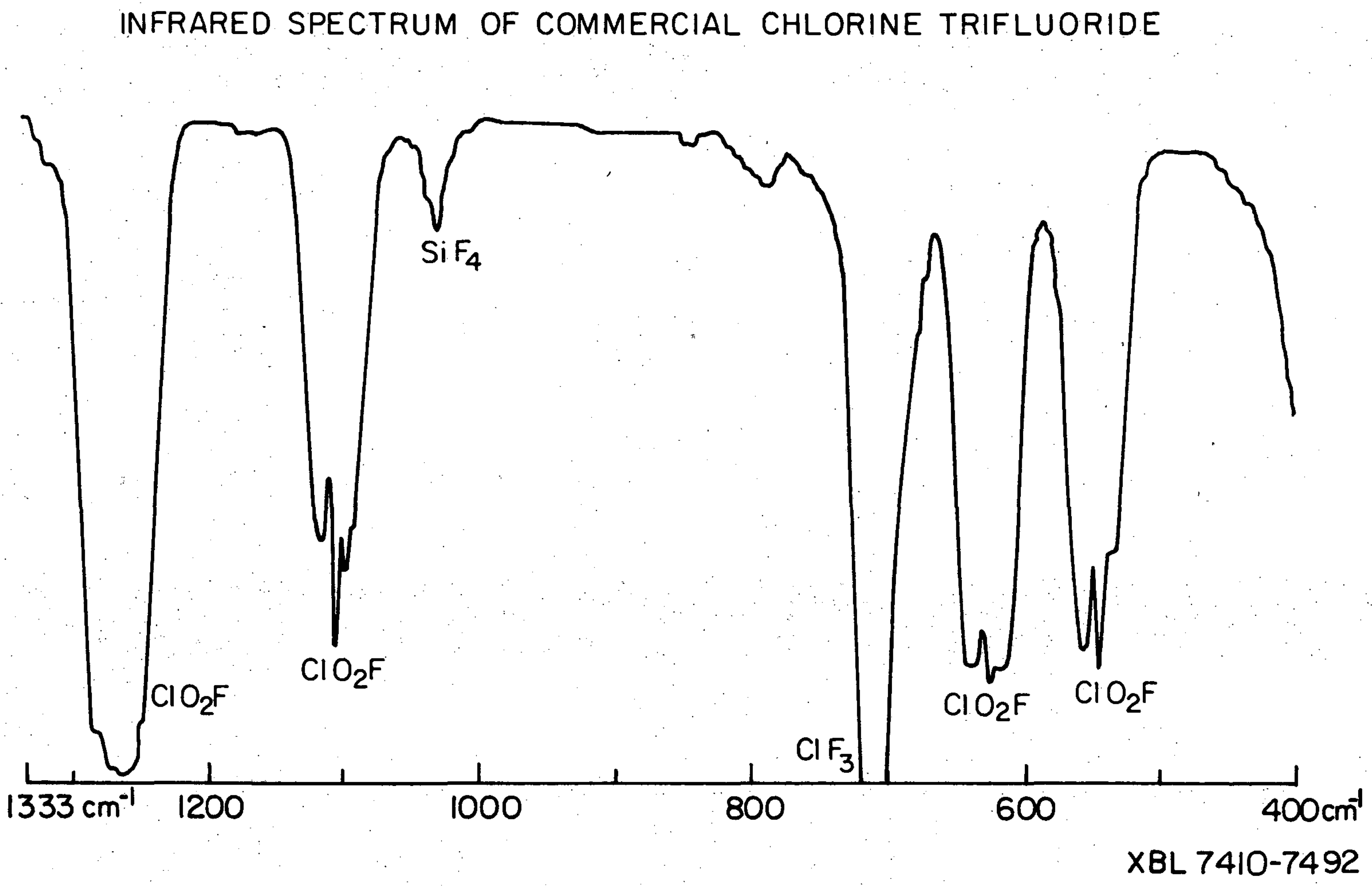
Conclusions

An unstable, volatile, iridium-containing compound has been produced in the hydrolysis of $Xe_2F_3^+IrF_6^-$. This compound is almost certainly not IrF_6, which is rapidly hydrolysed itself. It may be an unknown oxide, an oxyfluoride, or an oxy-acid such as $HIrO_4$. Further investigation of this system by means of mass spectrometry will be undertaken.

VIII. THE CATIONS ClF_2^+ and ClO_2^+

The compounds $ClF_3 \cdot AsF_5$ and $ClF_3 \cdot SbF_5$ were first reported[104,105] in 1958 and 1959 by Seel and Detmer. Subsequent vibrational[106-108] and crystallographic[87,109] studies have confirmed the ionic character of these the other ClF_3-Lewis acid adducts.[111-113] The difluorochlorinium (III) ion, ClF_2^+, has C_{2v} symmetry, with a bond angle of 95.9 (3.1)° in the SbF_6^- salt,[109] and 103.17 (0.70)° in $ClF_2^+AsF_6^-$.[87] The corresponding Cl-F bond distances are 1.57(3)Å and 1.54(14)Å, respectively.

Woolf prepared[114] ClO_2F adducts with BF_3, AsF_5, SbF_5, etc and correctly identified them as salts of the chloryl ion, ClO_2^+. This formulation was confirmed by Christe et al.[115] who obtained infrared and Raman spectra along with X-ray powder patterns. They pointed out that ClO_2F is the most stable product of reactions of water or oxides with chlorine fluorides of all oxidation states, and is hence a common impurity in these reagents. The spectrum of commercially obtained chlorine trifluoride is shown in Fig. VIII-1. In a-dition to the large ClO_2F impurity, a significant amount of HF is present, which facilitates the attack of ClF_3 on glass, producint more ClO_2F and SiF_4. Edwards and Sills have recently reported[117] the crystal structure of chloryl μ-fluorobis [pentafluoroantimonate (V)], $ClO_2^+Sb_2F_{11}^-$. The crystals from which this structure was obtained were prepared from chlorine, chlorine trifluoride, and antimony pentafluoride stored together in pyrex glass at room temperature for several months. The mean Cl-O distance in the cation is 1.31(3)Å, with an O-Cl-O bond angle of 121.9(1.5)°.



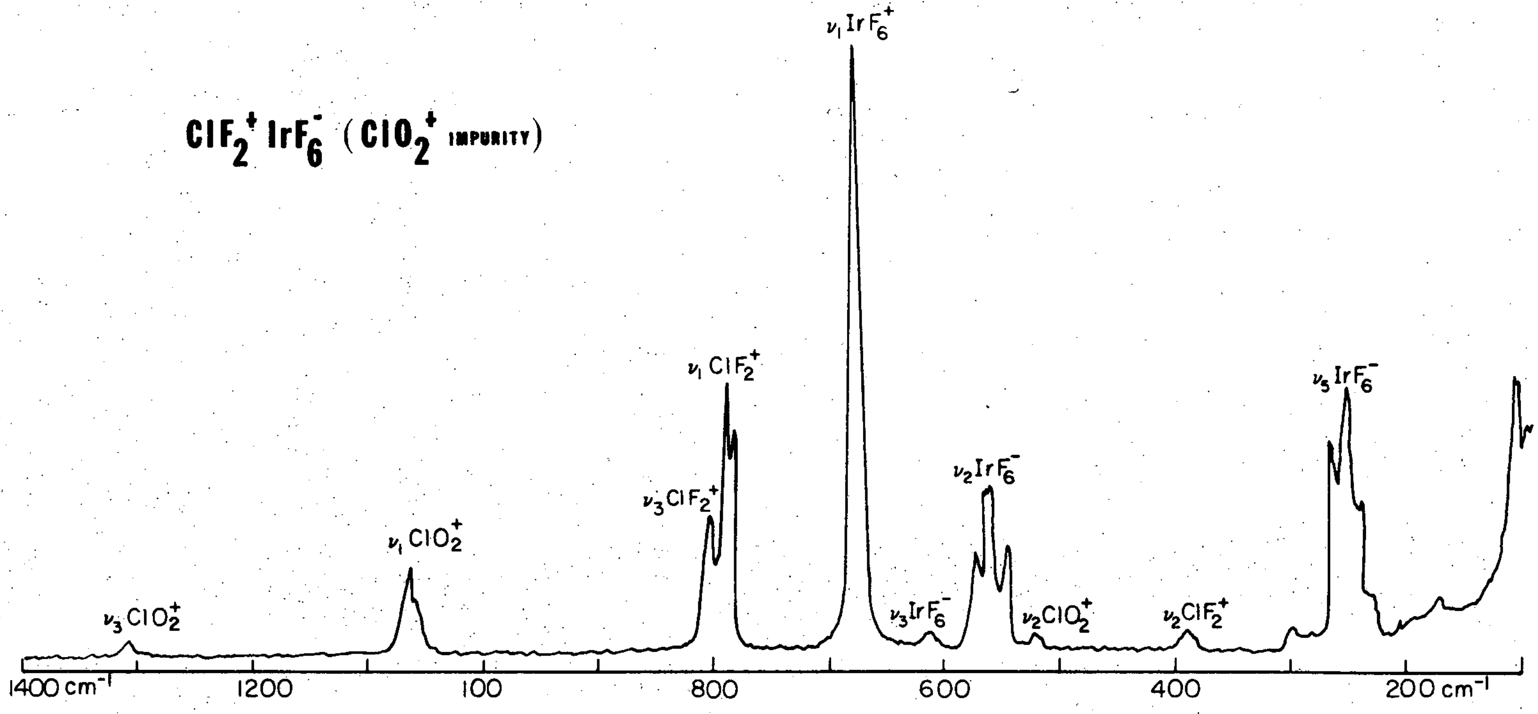
VIII-1. Infrared spectrum of commercial chlorine trifluoride.

A single crystal X-ray determination of the structure of the adduct prepared from ClF_3 and IrF_5 was carried out by Passmore.[4] The results were interpreted assuming the composition $ClF_2^+IrF_6^-$. The Cl-F bond distances were, however, very short (1.23Å); and the F-Cl-F bond angle quite large (128°). Because of uncertainty in agreement between calculated and observed structure factors, and the small number of reflections measured, the structure was not published, work was undertaken on the $ClF_3 \cdot AsF_5$ adduct, and a structure was reported[87] with the more acceptable Cl-F distance of 1.54Å. It now appears likely that the single crystal from which the X-ray data were collected[4] was actually $ClO_2^+IrF_6^-$, as there is close agreement with the parameters of Edwards and Sills.

The crystals in the original study were prepared by sublimation of the adduct in the presence of 2 atm chlorine trifluoride and 3 atm fluorine gas at a temperature of 160°. Under such conditions any ClO_2F present in the ClF_3 or arising from oxides on the walls of the monel reactor or from reaction with O_2 impurity in the F_2 would almost certainly have displaced ClF_3 in the adduct to form $ClO_2^+IrF_6^-$. Although an elemental analysis of the bulk material favored the formulation $ClF_3 \cdot IrF_5$, selection of good single crystals may well have preferred the separation of $ClO_2^+IrF_6^-$.

In order to confirm this hypothesis, a new preparation of $ClF_2^+IrF_6^-$ was undertaken. Chlorine trifluoride was partially freed of chloryl fluoride by holding several ml ClF_3 at -78° (where it is a solid when pure), and pumping to remove the slightly more volatile ClO_2F (vapor pressure ~10 mm at -78°). Infrared spectra of the ClF_3 showed that it still contained a trace of ClO_2F. ClF_3 (1.6 mmol) and IrF_6 (1.6 mmol) were combined in a prefluorinated monel can with a Teflon gasket and water-cooled removable lid. The bottom of the can was maintained at 190° overnight. An infrared spectrum of the residual gases contained absorptions due to IrF_6 and ClF_3, but no trace of ClO_2F, indicating the greater stability of the $ClO_2F \cdot IrF_5$ adduct relative to that of $ClF_3 \cdot IrF_5$.

On opening the can in the drybox, a considerable quantity of bright yellow crystals were found on the lid. The Raman spectrum of a representative sampling of this material is shown in Fig. VIII-2. It is seen to consist mainly of $ClF_2^+IrF_6^-$, but with a large impurity of $ClO_2^+IrF_6^-$.[110] An X-ray powder pattern of the same sample was obtained and compared with those of Passmore, and with the powder pattern of $ClF_2^+PtF_6^-$, prepared by N. K. Jha.[116] Due to the nearly identical unit cell cimensions of the two iridium compounds, the patterns are very similar. Slight differences are observed, however, and the pattern of $ClF_2^+IrF_6^-$ prepared in this work more nearly resembles that of the corresponding platinum compound. Table VIII-1 summarizes the powder data, and the patterns of $ClF_2^+IrF_6^-$, $ClO_2^+IrF_6^-$ and $ClF_2^+PtF_6^-$ are shown in Fig. VIII-3.



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VIII-2. Raman spectrum of $ClF_2^+IrF_6^-$ (containing some $ClO_2^+IrF_6^-$).

Table VIII-1. The X-ray powder patterns of $ClO_2^+IrF_6^-$ (Passmore) and $ClF_2^+IrF_6^-$ (this work).

	$ClO_2^+IrF_6^-$		$ClF_2^+IrF_6^-$
$hk\ell$	$10^4/d^2$ obs	$10^4/d^2$ calc	$10^4/d^2$ obs
100	315	308	311
011	381	386	361
			406
101	477	500	485
110	501	501	529
	575		
	640		
111	691		681
			724
002	757	768	767
020		774	
	904		847
			996
102	1075	1076	1069
120		1082	
			1163
112	1247	1269	1272
		1274	
201		1425	1431
210		1427	
211	1619	1619	1626
013	1996	1922	1996
031		1933	
			2127
113	2213	2230	2205
		2241	
			2309
123	2787	2811	2796
132		2817	
			3045

Single crystal data (passmore) $ClO_2^+IrF_6^-$ a_o=5.69, b_o=7.19, c_o=7.22Å, V=295.4Å^3 M.W. 373.7 gm mol^{-1}, Z=2, $\underline{d}_c$=4.20 gm cm^{-3}. Space group: P_{nmm}, systematic absences: $ok\ell$, when $k + \ell = 2n + 1$.

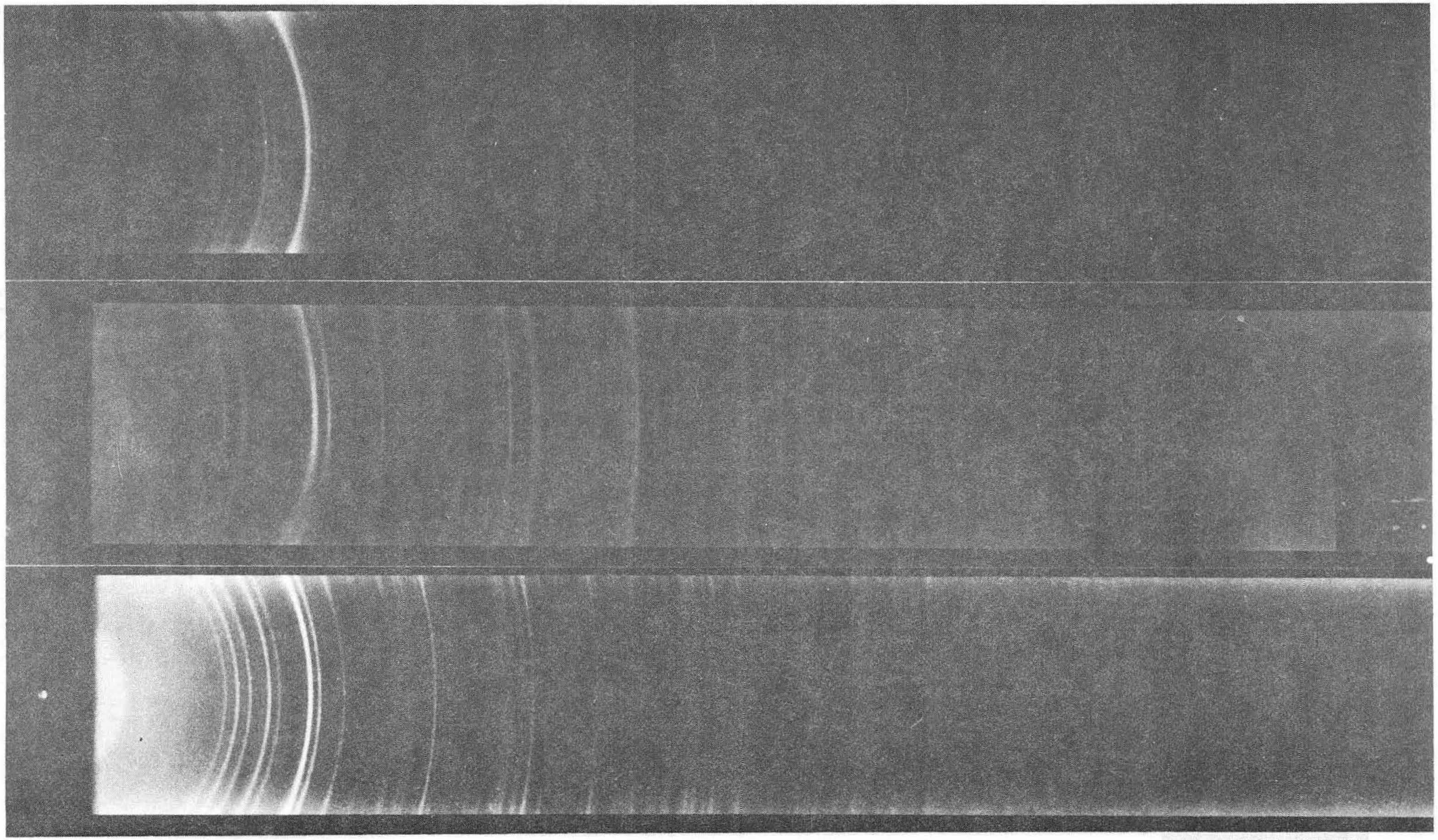

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Fig. VIII-3. X-ray powder patterns of ClF_2IrF_6, ClO_2IrF_6 and ClF_2PtF_6.

IX. CONCLUSIONS

The identity of the yellow solids obtained from the reaction of hexafluorobenzene with dioxygenyl salts in tungsten hexafluoride has been established, and much has been done to characterize the hexafluorobenzene cation. The octafluoronapthalene cation has also been prepared and characterized, though much less fully. An accurate crystal structure is necessary to elucidate the precise nature of these materials.

Further investigation into the deeply-colored adducts of chlorine and the dioxygenyl salts should clear up their composition and structure. More spectroscopic evidence is required, such as visible uv spectra of HF solutions, resolved epr spectra of dilute solutions, and better infrared and Raman data. It should also be possible to obtain an X-ray powder photograph, and possible single crystals.

There is still hope for synthesis of many or all of the inorganic radicals attempted in Chapters III and IV. A good solvent system is definitely needed here, and the techniques of cryogenic isolation of metastable products will no doubt be useful, as would availability of a molecular-beam mass spectrometer.

The hydrolysis of $Xe_2F_3^+IrF_6^-$ and other reactions may yet lead to IrO_4, or at least a new oxyfluoride or oxy acid of iridium, and the oxidizing capability of Xe (II) should be exploited in other systems.

The research described in this thesis is a patchwork of success and disappointment, but in every part of it there is some promise of future development.

ACKNOWLEDGEMENTS

I would like to thank Professor Neil Bartlett for his guidance and encouragement throughout my graduate career. His experience, imagination and insight into chemical systems lit the way through many dark moments of failure. It has been a great pleasure to be associated with a man of such integrity, brilliance and warm friendhsip.

My many friends among the graduate students and post-doctoral fellows in inorganic and physical chemistry supplied invaluable advice and companionship. I would particularly like to acknowledge my closest co-worker, Kevin Leary. Thanks also to Richard Wilson for help with *epr* spectra, to Dr. Allan Zalkin for assistance with a difficult crystal structure, to Dr. Norman Edelstein for help in obtaining magnetic susceptibilty data, and to the group headed by Dr. Jim Scherer at WRRL for their time and aid in recording Raman spectra.

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REFERENCES

1. D. F. Shriver, The Manipulation of Air-Sensitive Compounds (McGraw-Hill, N. Y., 1969).
2. S. P. Beaton, Ph. D. Thesis, University of British Columbia (1966).
3. T. A. O'Donnell and D. F. Stewart, Inorg. Chem. 5, 1434 (1966).
4. J. Passmore, Ph. D. Thesis, University of British Columbia (1967).
5. N. Bartlett, Angew. Chem. Int. Ed. 7, 433 (1968).
6. N. K. Jha, Ph. D. Thesis, University of British Columbia (1965).
7. R. D. Peacock in Progress in Inorganic Chemistry, F. A. Cotton, ed. (Interscience, N. Y., 1960), Vol. 2, p. 224.
8. R. A. Ogg, J. Chem. Phys. 15, 337 (1947); 18, 572 (1950).
9. H. S. Johnston, J. Amer. Chem. Soc. 73, 4542 (1951).
10. T. W. Martin, A. Henshall and R. C. Gross, J. Amer. Chem. Soc. 85, 113 (1963).
11. D. E. Wood and T. M. Pietrzak, J. Chem. Phys. 46, 2973 (1967).
12. T. W. Martin, L. L. Swift and J. H. Venable, Jr., J. Chem. Phys. 52, 2138 (1970).
13. R. Livingston and H. Zeldes, J. Chem. Phys. 41, 4011 (1964).
14. E. Mayon and E. Saito, J. Chem. Phys. 43, 4314 (1965).
15. J. F. Olsen and L. Burnelle, J. Amer. Chem. Soc. 92, 3659 (1970).
16. J. Berkowitz and W. A. Chupka, J. Chem. Phys. 55, 2733 (1971).
17. V. M. Dibeler and J. A. Walker, J. Chem. Phys. 44, 4405 (1966).
18. K. O. Christe, R. D. Wilson and A. E. Axworthy, Inorg. Chem. 12, 2478 (1973).
19. A. Begum, S. Subramanian and M. C. R. Symons, J. Chem. Soc. (A), 1323 (1970).

20. M. Eisenberg and D. D. DesMarteau, Inorg. Chem. 11, 1901 (1972).

21. P. A. Bernstein, F. A. Mohorst, M. Eisenberg and D. D. DesMarteau, Inorg. Chem. 10, 1549 (1971).

22. N. Bartlett and P. L. Robinson, J. Chem. Soc., 3549 (1961).

23. O. Glemser, J. Wegener and R. Mews, Chem. Ber. 100, 2474 (1967).

24. I. Noddack and W. Noddack, Z. anorg. chem. 181, 1 (1929).

25. E. Ogawa, Bull. Chem. Soc. Japan 7, 265 (1932).

26. N. Bartlett and D. H. Lohmann, Proc. Chem. Soc. 115 (1962); J. Chem. Soc. 5253 (1962).

27. A. R. Young, T. Mirata and S. I. Morrow, J. Amer. Chem. Soc. 86, 20 (1964).

28. I. J. Solmon, R. I. Brabets, R. K. Uenishi, J. N. Keith and J. M. McDonough, Inorg. Chem. 3, 457 (1964).

29. J. B. Beal, C. Pupp and W. E. White, Inorg. Chem. 8, 828 (1968).

30. J. Shamir and J. Binerbouym, Inorg. Chimica Acta 2, 37 (1968).

31. D. E. McKee and N. Bartlett, Inorg. Chem. 12, 2738 (1973).

32. K. Leary and N. Bartlett, J. Chem. Soc. Chem. Comm. 903 (1972).

33. A. J. Edwards, W. F. Falconer, J. E. Griffiths, W. A. Sunder and M. J. Vasile, J. Chem. Soc. Dalton 1129 (1974).

34. W. E. Falconer, F. J. DiSalvo, A. J. Edwards, J. E. Griffiths, W. A. Sunder and M. J. Vasile, to be published.

35. N. B. S. (U.S.A.) Natl. Stand. Ref. Data Series NBS26, 151 (1969).

36. D. D. Gibler, unpublished observation.

37. L. Stein, 7th International Fluorine Symposium, Santa Cruz, July 15-20, 1973.

38. K. O. Christe, Inorg. Chem. 12, 1580 (1973).

39. J. Shamir, J. Binenboym and H. H. Claassen, J. Amer. Chem. Soc. 90, 6223 (1968).

40. K. O. Christe and W. Sawodny, Inorg. Chem. 6, 1783 (1967).

41. C. L. Chernick, H. H. Claassen, J. G. Malm and P. L. Plurien, Noble Gas Compounds, H. H. Hyman, ed. (University of Chicago, Illinois, 1963).

42. F. Q. Roberto and G. Mamantov, Inorg. Chimica Acta 2, 317 (1968).

43. G. A. Olah and M. B. Comisarow, J. Amer. Chem. Soc. 90, 5033 (1968).

44. G. A. Olah and M. B. Comisarow, J. Amer. Chem. Soc. 91, 2172 (1969).

45. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds (Wiley-Interscience, N. Y., 1970), p. 78

46. N. Bartlett and D. D. Gibler, unpublished observation.

47. R. S. Eachus, T. P. Sleight and M. C. R. Symons, Nature 222, 769 (1969).

48. K. O. Christe and J. J. Muirhead, J. Amer. Chem. Soc. 91, 7777 (1969).

49. R. J. Gillespie and M. J. Morton, J. Chem. Soc. Chem. Comm. 1565 (1968).

50. R. J. Gillespie and M. J. Morton, J. Mol. Spectrosc. 30, 178 (1969).

51. R. D. W. Kemmit, J. Murray, V. M. McRae, R. D. Peacock, M. C. R. Symons and T. A. O'Donnell, J. Chem. Soc. A 862 (1968).

52. R. J. Gillespie and J. B. Milne, Inorg. Chem. 5, 1577 (1966).

53. V. D. Shteingarts, Yu. V. Pozdnyakovich and G. G. Yakobson, J. Chem. Soc. Chem. Comm. 1264 (1969).

54. A. J. Edwards, G. R. Jones and R. J. C. Sills, J. Chem. Soc. Chem. Comm. 1527 (1968).

55. O. Glemser and A. Smalc, Angew, Chem. Intern. Edit. 8, 517 (1969).

56. A. G. Streng and A. V. Grosse, Adv. Chem. Ser. 36, 159 (1962).

57. A. G. Streng, Chem. Rev. 63, 607 (1963).

58. D. J. Gardiner, J. Fluorine Chem. 3, 226 (1973).

59. F. J. DiSalvo, W. E. Falconer, R. S. Hutton, A. Rodriquez and J. V. Waszczak, to be published.

60. J. Shamir, J. Binenboym and H. H. Claassen, J. Amer. Chem. Soc. 90, 6223 (1968).

61. D. E. McKee and N. Bartlett, Inorg. Chem. 12, 2738 (1973).

62. G. Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand, Princeton, N. J., 1950), Vol. 1, p. 520.

63. J. Behringer in Raman Spectroscopy, H. A. Szymanski, ed. (Plenum Press, N. Y., 1967), p. 168.

64. R. D. Spratley, J. J. Turner and G. C. Pimentel, J. Chem. Phys. 44, 2063 (1966).

65. A. Arkell, J. Amer. Chem. Soc. 87, 4057 (1965).

66. A. Arkell and I. Schwager, J. Amer. Chem. Soc. 89, 5999 (1967).

67. T. C. Waddington and F. Klanberg, Z. anorg. chem. 304, 185 (1960).

68. A. M. Qureshi and F. Aubke, Can. J. Chem. 48, 3117 (1970).

69. N. M. Bazhin, Yu. V. Pozdnyakovich, V. D. Shteingarts and G. G. Yakobson, Izvest. Akab. Nauk SSSR Ser. Khim. 2300 (1969).

70. W. F. Howard and L. Andrews, J. Amer. Chem. Soc. 95, 2056 (1973).

71. J. Shamir and J. Binenboym, Inorg. Chim. Acta 2, 37 (1968).

72. P. N. Noble and G. C. Pimentel, J. Chem. Phys. 44, 3641 (1966).

73. S. W. Benson and J. H. Buss, J. Chem. Phys. 27, 1382 (1957).

74. N. M. Bachin, N. E. Akhmetova, L. V. Orlova, V. D. Shteingarts, I. N. Shchegoleva and G. G. Yakobson, Tetrahedron Lett. 4449 (1968).

75. C. Thomson and W. J. MacCulloch, Tetrahedron Lett. 5899 (1968).

76. C. Thomson and W. J. MacCulloch, Mol. Phys. 19, 817 (1970).

77. P. R. Hammond and R. R. Lake, J. Chem. Soc. Chem. Comm. 987 (1968).

78. P. R. Hammond, J. Phys. Chem. 74, 647 (1970).

79. T. J. Richardson and N. Bartlett, J. Chem. Soc. Chem. Comm. 427 (1974).

80. D. E. Wood and T. M. Pietrzak, J. Chem. Phys. 46, p. 111.

81. N. Bartlett and P. R. Rao, J. Chem. Soc. Chem. Comm. 252 (1965).

82. D. E. Wood and T. M. Pietrzak, J. Che. Phys. 46, p. 116.

83. R. D. Peacock and I. L. Wilson, J. Chem. Soc. A 2030 (1969).

84. J. C. Tatlow and R. Stephens, private communication.

85. P. A. Claret, G. H. Williams and J. Coulson, J. Chem. Soc. C 341 (1968).

86. A. Almenningen, O. Bastiansen, R. Seip and H. M. Seip, Acta Chem. Scand. 18, 2115 (1964).

87. H. Lynton and J. Passmore, Can. J. Chem. 49, 2539 (1971).

88. W. H. Zachariason, Acta Cryst. 2, 388 (1949).

89. PCR Inc., Gainesville, Florida, product information.

90. F. Kraus and G. Schrader, Z. anorg. allgem. chem. 176, 385 (1928).

91. F. A. Cotton and G. Wilkinson, Adv. Inorganic Chemistry (Interscience, N. Y., 1966), p. 1005.

92. H. Selig, H. H. Claassen, C. L. Chernick, J. G. Malm and J. L. Huston, Science 143, 1322 (1964).

93. F. O. Sladky, P. A. Bulliner and N. Bartlett, J. Chem. Soc. A 2179 (1969).

94. R. E. Dodd, Trans. Farad. Soc. 55, 1480 (1959).

95. M. H. Ortner, J. Chem. Phys. 34, 556 (1961).

96. A. H. Neilsen and P. J. H. Woltz, J. Chem. Phys. 20, 1878 (1952).

97. A. W. Richardson, R. W. Redding and J. C. D. Brand, J. Mol. Spectrosc. 29, 93 (1969).

98. E. T. McHale and G. vonElbe, J. Phys. Chem. 72, 1849 (1968).

99. F. O. Sladky and N. Bartlett, J. Chem. Soc. A 2188 (1969).

100. D. Steele and D. H. Whiffen, Trans. Farad. Soc. 55, 369 (1959).

101. G. M. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965).

102. I. D. Clark and D. C. Frost, J. Amer. Chem. Soc. 89, 244 (1967).

103. J. Bacon, P. A. W. Dean and R. J. Gillespie, Can. J. Chem. 47, 1655 (1969).

104. F. Seel and O. Detmer, Angew. Chem. 70, 163 (1958).

105. F. Seel and O. Detmer, Z. Anorg. Allgem. Chem. 301, 113 (1959).

106. K. O. Christe and W. Sawodny, Inorg. Chem. 6, 313 (1967).

107. R. J. Gillespie and M. J. Morton, Inorg. Chem. 9, 616 (1970).

108. H. A. Carter and F. Aubke, Can. J. Chem. 48, 3456 (1970).

109. A. J. Edwards and R. J. C. Sills, J. Chem. Soc. A 2697 (1970).

110. K. L. Christe, Inorg. Chem. 12, 1580 (1973).

111. N. Bartlett and D. H. Lohmann, J. Chem. Soc. 5253 (1962).

112. H. Selig and J. Shamir, Inorg. Chem. 3, 294 (1964).

113. K. O. Christe and A. E. Pavlath, Z. anorg. allgem. Chem. 335, 210 (1965).

114. A. A. Woolf, J. Chem. Soc. 4113 (1954).

115. K. O. Christe, C. J. Schack, D. Pilipovich and W. Sawodny, Inorg. Chem. 8, 2489 (1969).

116. N. K. Jha and N. Bartlett, unpublished results.

117. A. J. Edwards and R. J. C. Sills, J. Chem. Soc. Dalton 1726 (1974).

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