# Hydrolysis Reactions of Transition Metal Hexafluorides in Liquid Hydrogen Fluoride: Oxonium Salts with Pt, Ir and Ru.

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## ABSTRACT

The hydrolysis reactions of $OsF_6$, $IrF_6$, $PtF_6$, $RuF_6$ and $RhF_6$ in hydrogen fluoride have been studied. Hydrolysis of $OsF_6$ in HF leads to an improved synthesis of $OsOF_4$. Hydrolyses of $IrF_6$, $PtF_6$ and $RuF_6$ yield oxonium salts, $H_3O^+MF_6^-$, having rhombohedral cells with nearly identical dimensions. If excess water is used, the salt $(H_3O^+)_2PtF_6^=$ can also be isolated. Hydrolysis of $RhF_6$ leads to an unstable product which could not be further characterized.

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## INTRODUCTION

The hydrolysis of an inorganic hexafluoride can in principle replace two, four, or six fluorine atoms by oxygen to yield oxide-fluorides or oxides of the core atom and liberate HF. Under suitable conditions, the oxonium ion $H_3O^+$ may be stabilized with an appropriate counter-ion. Oxonium salts of hexafluoroarsenate(V) [1], hexafluoroantimonate(V) [1], and hexafluorouranate(V) [2] have been described, but no compounds of this type have been reported with anions containing transition metals.

Partial hydrolysis of $MoF_6$, $WF_6$, $UF_6$, and $NpF_6$ has been used to synthesize oxide-fluorides of these metals [3-8]. In addition, $ReOF_4$ has been prepared by the reaction of traces of moisture with $ReF_6$ in a Pyrex vessel [9]. Hydrogen fluoride liberated in the reaction regenerates water by reaction with the silica to continue the hydrolysis. This preparation is time consuming and results in side products in addition to the desired oxide fluoride. Attempts to prepare $OsOF_4$ by this method led to inconclusive results [9].

An abundance of oxide-fluorides are known for osmium and rhenium, and have been synthesized by various techniques [10]. By striking contrast there is a paucity of known oxide-fluorides for iridium, platinum, ruthenium, rhodium, and palladium [3]. Therefore, the controlled hydrolyses of the hexafluorides of iridium, platinum, ruthenium and rhodium in liquid HF were studied, and compared with the hydrolyses of $OsF_6$ and $ReF_6$ under similar conditions. In the cases of $ReF_6$ [11] and $OsF_6$, metal oxide tetrafluorides formed readily, but hydrolysis of $IrF_6$, $PtF_6$, and $RuF_6$ yields the oxonium hexafluorometallates, $H_3O^+MF_6^-$. Under appropriate reaction conditions, $(H_3O^+)_2PtF_6^=$ can also be synthesized. The reaction product from the hydrolysis of $RhF_6$ is ambiguous, but is probably a rather unstable oxonium salt of rhodium.

## EXPERIMENTAL

*Materials and Apparatus* - Volatile compounds were manipulated in a Monel vacuum line which had been well passivated with fluorine. Nonvolatile materials were handled in a Vac-Atmospheres Corp. Dri-Lab with a helium atmosphere containing less than 1 ppm water and oxygen. Reactions

were carried out in 0.75" O.D. x 0.080" wall FEP tubes which were heat sealed at one end and connected by means of a 0.75" flare to a Monel head sealed with a Nupro (M-4BW) Monel valve.

Hydrogen fluoride (The Matheson Co.) was dried by treatment with fluorine [12] followed by several freezing, pumping and thawing cycles. The hexafluorides of rhenium, osmium, iridium, platinum and ruthenium were synthesized by methods described in the literature [3]. Rhodium hexafluoride was prepared by the burning wire technique used for the preparation of platinum hexafluoride [13]. This method was considerably more efficient than the ignition of powder in a fluorine atmosphere by inductive heating [14]. Rhodium wire ($\phi = .030$ in.) was obtained from Engelhard Industries.

Methods for obtaining mass spectra, Raman spectra and x-ray powder photographs have been described in detail elsewhere [15]. Raman spectra were obtained on solid samples in a rotating cell [16] or on HF solutions in 0.25" FEP tubes sealed with Kel-F valves [17] using either 5145 Å or 6471 Å excitation. Raman spectra were generally of low quality and in all cases only spectral features of the anion were observed and identified. Infrared spectra of $(H_3O^+)_2PtF_6^=$ were obtained on KBr disks using a Perkin-Elmer Model 467 spectrophotometer.

*Analyses* - Fluorine analyses were carried out by pyrohydrolysis using a modification of a procedure described in the literature [18]. Iridium and platinum were determined gravimetrically as the metals after reduction of the pyrohydrolysis residues in a hydrogen stream at 900°. Pyrohydrolysis of $H_3O^+IrF_6^-$ led to mixtures of Ir + $IrO_2$, but the platinum salts gave pure $PtO_2$ which could also be weighed as such. Ruthenium analyses were low, probably because substantial amounts were volatized as $RuO_4$. For the iridium, platinum and ruthenium compounds, correlation of x-ray diffraction patterns, chemical analyses, Raman spectra and magnetic susceptibility data led to unequivocal identifications of the salts, although not all methods were applicable for each compound.

*Hydrolysis of* $OsF_6$ - *the Preparation of* $OsOF_4$ - In a typical hydrolysis of $OsF_6$, $H_2O$ (1.77 millimoles) was pipetted with a micropipette into a FEP tube. After the water was degassed at -196°, 0.75 cm$^3$ of HF was distilled on top of it. $OsF_6$ (1.78 millimoles) was introduced at -196° by distilla-

tion, and the contents were allowed to warm to room temperature. At first a light yellow solution resulted which gradually turned greenish-yellow. Volatile materials were removed at room temperature, leaving about 460 mg of green solid which was identified as $OsOF_4$ on the basis of its x-ray powder photograph and mass spectrometric cracking pattern [10]. Attempts to react $OsF_6$ with excess water in HF led to the isolation of a black material which could not be identified, but was not $OsO_2$.

*Hydrolysis of* $IrF_6$ - *the Preparation of* $H_3O^+IrF_6^-$ - In a typical experiment, $H_2O$ (1.43 millimoles) was pipetted into a FEP tube and after outgassing at -196°C, 0.75 cm$^3$ HF was distilled on top of it. $IrF_6$ (1.13 millimoles) was condensed on top of the mixture at -196°. Upon warming to room temperature, the solution became dark yellow. Removal of volatile material, first at -63.5° (CHCl$_3$ slush) and then at room temperature, left about 358 mg of a light yellow solid which was identified as $H_3O^+IrF_6^-$ (Found: Ir, 58.0%, F, 34.8%; calc: Ir, 59.1%, F, 35.1%). Raman spectrum (HF solution): $670cm^{-1}$(s,p), $560cm^{-1}$(w), $230cm^{-1}$(s), which is characteristic of $IrF_6^-$ [19]. Magnetic susceptibility measurements showed the compound to exhibit a temperature independent paramagnetism, comparable in magnitude to that previously reported at room temperature for $IrF_6^-$ in combination with diamagnetic cations [20,21]. Reaction with excess water also gave rise to the $IrF_6^-$ species, but not in an easily crystallizable form.

*Hydrolysis of* $PtF_6$ - *the Preparation of* $H_3O^+PtF_6^-$ - Water (2.78 millimoles) was pipetted into a 3/4" FEP tube. After transfer of about 1 cc of HF, $PtF_6$ (~2.3 millimoles) was condensed on top of it at -196°. Upon warming to room temperature, a wine-red colored solution was obtained. Removal of volatile materials under vacuum left about 672 mg of a brown solid, which was identified as $H_3O^+PtF_6^-$ on the basis of its x-ray powder pattern (isostructural with $H_3O^+IrF_6^-$) and its magnetic susceptibility (paramagnetic). A Raman spectrum of the solid gave a peak at 642 cm$^{-1}$ characteristic of $PtF_6^-$ [19]. Chemical analyses averaged between the 1:1 and the 2:1 compound and were thus inconclusive.

*Hydrolysis of* $PtF_6$ - *the Preparation of* $(H_3O^+)_2PtF_6^=$ - Water (2.78 millimoles) was pipetted into a FEP tube and, after outgassing, about 1 cc HF was condensed on top of it. $PtF_6$ (~1.08 millimoles)

was condensed in at -196°. Upon warming to room temperature, a vigorous reaction ensued as shown by strong reflux of the HF. The resulting solution was straw colored. Removal of volatile materials under vacuum left about 293 mg of a yellow to orange-yellow solid which was identified as $(H_3O^+)_2PtF_6^=$. Chemical analysis: Found: F, 32.6%, Pt, 57.8%. Calc: F, 32.8%, Pt, 56.2%. The x-ray powder photograph was complex and could not be indexed. The Raman spectrum of the HF solution showed a typical $PtF_6^=$ spectrum [19] with peaks at 604 $cm^{-1}$(s,p), 575 $cm^{-1}$(w) and 220 $cm^{-1}$(m). The infrared spectrum showed bands at 3330$cm^{-1}$(vs,br), 3150$cm^{-1}$(vs,br) and 1620$cm^{-1}$(m) which are characteristic of $H_3O^+$[1], and at 585$cm^{-1}$(vs) and 277$cm^{-1}$(m) which can be assigned to $PtF_6^=$ [22,23]. Magnetic susceptibility measurements showed the compound to be diamagnetic, as expected for $PtF_6^=$. The $^{19}F$ nmr spectra of $(H_3O^+)PtF_6^=$ were recorded in HF and $CD_3SOCD_3$ solutions. The signals in HF solution were considerably broadened, but showed a singlet-doublet at $\delta(CFCl_3,ext) = 329.1$ ppm, $J(^{195}PtF) = 2074Hz$. In DMSO corresponding values were $\delta(CFCl_3) = 327.8$ ppm, $J(^{195}PtF) = 1971Hz$. The singlet:doublet ratio was 68:32 corresponding approximately to the known abundances of platinum isotopes.

*Hydrolysis of* $RuF_6$ - *the Preparation of* $H_3O^+RuF_6^-$ - In a typical experiment, $H_2O$ (2.78 milli-moles) was pipetted into a FEP tube and after outgassing about 2 cc of HF condensed in. Ruthenium hexafluoride (~1.8 millimoles) was condensed on top of the mixture at -196°. Upon warming to room temperature the dark red color of the $RuF_6$ suddenly disappeared and an almost colorless solution with a slightly greenish tinge resulted. Approximately 0.21 millimoles of oxygen were released. The HF was removed slowly at -78° leaving a white solid behind which was identified as $H_3O^+RuF_6^-$. Analysis: found, F, 48.2%; calc, 48.7%. The x-ray powder pattern showed the material to be isostructural with $H_3O^+IrF_6^-$ and $H_3O^+PtF_6^-$ with nearly identical cell dimensions. A Raman spectrum of an HF solution showed the characteristic spectrum of $RuF_6^-$ [16] with peaks at 659 $cm^{-1}$(s,p), 580 $cm^{-1}$(m) and 261 $cm^{-1}$(s). The powder in all cases turned gradually darker and finally black. This decomposition precluded making meaningful magnetic susceptibility measurements on $H_3O^+RuF_6^-$.

*The Hydrolysis of* $RhF_6$ - Rhodium hexafluoride was reacted with water in HF under similar conditions and on the same scale as the $RuF_6$ reaction. Upon warming the reaction mixture to room

temperature, the dark red-black hexafluoride suddenly disappeared and a yellow-green solution resulted. Upon removal of the HF at -78° a yellow solid remained which rapidly became darker and could not be characterized.

## RESULTS AND DISCUSSION

This investigation has resulted in the isolation and characterization of several oxonium salts containing hexafluoro anions second and third row transition metals. Previously known compounds of this type containing the anions $[AsF_6]$, $[SbF_6^-]$ [1] and $[UF_6]$ [2] had been prepared by the reactions of the respective pentafluorides with water in HF. These reactions, which have been carried out in HF, give further evidence that such solutions moderate the hydrolysis reactions to a considerable extent. The relative moderation with which hydrolyses of $RuF_6$ and $RhF_6$ proceed bears witness to this fact. The moderated hydrolyses of $IrF_6$, $PtF_6$, and $RuF_6$ have given rise to the new oxonium salts described, but have not been routes to the still elusive oxide-fluorides of these metals*.

Direct hydrolysis in liquid HF yields $OsOF_4$ by a synthetic route considerably more convenient than previously known methods which usually lead to appreciable amounts of side products such as $OsF_5$. Attempts to prepare $OsO_2F_2$ by hydrolysis of $OsF_6$ with excess water were not successful. The identity of the osmium oxyfluoride of unknown composition for which a complete structure analysis has been performed and which has been postulated to be $OsO_2F_2$ [24], thus remains unknown.

Although the presence of $H_3O^+$ cations has been directly demonstrated in this study only with $(H_3O^+)_2PtF_6^=$, the absence of other than well-known anion peaks in the Raman spectra combined with chemical analyses (especially for $H_3O^+IrF_6^-$) eliminate other possibilities such as $H^+$ or $H_2F^+$ cations. Furthermore, the latter has been observed only at low temperatures [25]. These reactions thus involve oxidation of water by the hexafluoride, the reaction scheme probably being the following:

$$MF_6 + \frac{3}{2}H_2O \longrightarrow H_3O^+MF_6^- + \frac{1}{4}O_2. \tag{1}$$

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* Gas phase reactions between water vapor and iridium hexafluoride diluted with sulfur hexafluoride yielded a product identical to that formed in HF solutions.

Oxygen is liberated in all cases except the hydrolysis of $OsF_6$, and rough tensimetric measurements confirm this stoichiometry based on amount of water taken. The stoichiometry with respect to hexafluorides is difficult to confirm, because the reactive fluorides, particularly of platinum and ruthenium, cannot be quantitatively transferred, but react with the transfer tubes [13]. In the case of platinum hexafluoride, further reaction takes place if excess water is used leading to the kinetically stable $(H_3O^+)_2PtF_6^=$, according to

$$PtF_6 + 3H_2O \rightarrow (H_3O^+)_2PtF_6^= + \frac{1}{2}O_2. \tag{2}$$

The remarkable difference between $ReF_6$ and $OsF_6$ on the one hand, which are merely hydrolyzed, and $IrF_6$, $PtF_6$ and $RuF_6$ on the other hand, can be rationalized in terms of the higher electron affinities of the latter hexafluorides. This has been pointed out by Bartlett [26,27] for the parallel reactions of third transition series hexafluorides with nitrosyl fluoride and nitric oxide. Thus, $WF_6$ and $ReF_6$ lead only to addition products with nitrosyl fluoride, while $IrF_6$ and $PtF_6$ yield hexafluorometallate(V) salts with liberation of fluorine and/or $NOF_3$. In the case of osmium, the addition product $NOOsF_7$ is formed with some question of whether or not traces of $NOF_3$ are li-

TABLE I

X-ray Powder Data for $H_3O^+IrF_6^-$[a]

| $d_{obs.}$,angstrom | $d_{calc.}$,angstrom | Intensity | hkl |
|---|---|---|---|
| 4.84 | 4.85 | 10 | 100 |
| 3.623 | 3.64 | 8 | $\bar{1}10$ |
| 3.223 | 3.25 | 10 | 110 |
| 2.895 | 2.912 | 8 | $\bar{1}11$ |
| 2.417 | 2.424 | 6 | 200 |
| 2.275 | 2.274 | 4 | $\bar{2}01$ |
| 2.102 | 2.104 | 3 | $\bar{2}11$ |
| 2.070 | 2.075 | 4 | 201 |
| 2.018 | 2.018 | 5 | $2\bar{1}1$ |
| 1.816 | 1.822<br>1.813 | 3 | $\bar{2}02$<br>211 |
| 1.708 | 1.705 | 4 | $\bar{2}21$ |
| 1.619 | 1.624<br>1.616<br>1.616 | 5 | 202<br>$22\bar{1}$<br>300 |
| 1.591 | 1.588 | 2 | $\bar{3}10$ |
| 1.550 | 1.544 | 2 | $\bar{3}11$ |
| 1.478 | 1.483<br>1.473 | 4 | 310<br>221 |

[a]Rhombohedral, a=4.91angstrom, $\alpha$ = 95.9°, V=116.3angstrom$^3$, Cu K$\alpha$ radiation.

berated [27,28]. Since $TcF_6$ yields only addition products with NOF [28], one may predict that the poorly characterized $TcOF_4$ should be more easily prepared by hydrolysis of $TcF_6$ in HF. This compound has been reported as a minor product of the fluorination of technetium metal in a flow system, the oxygen presumably coming from oxide films on the metal [29,30].

Except for $(H_3O^-)_2PtF_6^=$, which appears to be stable, the $(H_3O^+)MF_6(V)$ salts decompose with time, turning gradually darker and finally black. The solids appear also to decompose photolytically in a laser beam both at 5145 and 6471 angstrom even when exposed in the rotating cell. In the mass spectroscopic examination of the platinum and iridium compounds, copious amounts of oxygen and HF were detected, in addition to cracking patterns consisting of $MF_x^+$ up to $x=5$. Mass spectroscopic examination of $H_3O^-RuF_6^-$ showed in addition that appreciable amounts of $RuO_4$ were formed.

TABLE II

X-ray Powder Data for $H_3O^+PtF_6^{-}$ [a]

| $d_{obs.}$,angstrom | $d_{calc.}$,angstrom | Intensity | hkl |
|---|---|---|---|
| 4.82 | 4.82 | 10 | $100$ |
| 3.63 | 3.65 | 8 | $\bar{1}10$ |
| 3.20 | 3.21 | 6 | $110$ |
| 2.90 | 2.91 | 5 | $\bar{1}11$ |
| 2.407 | 2.412 | 4 | $200$ |
| 2.277 | 2.277 | 3 | $\bar{2}10$ |
| 2.099 | 2.104 | 3 | $\bar{2}11$ |
| 2.054 | 2.055 | 4 | $210$ |
| 2.010 | 2.013 | 6 | $21\bar{1}$ |
| 1.827 | 1.826 | 2 | $\bar{2}20$ |
| 1.786 | 1.788 | 1 | $211$ |
| 1.708 | 1.708 | 3 | $\bar{2}21$ |
| 1.609 | 1.608, 1.608 | 4 | $\}22\bar{1}, 300$ |
| 1.593 | 1.588, 1.606 | 2 | $\}\bar{3}10, 220$ |
| 1.552 | 1.547 | 1 | $\bar{3}11$ |
| 1.473 | 1.472 | 2 | $31\bar{1}$ |
| 1.459 | 1.456 | 1 | $\bar{2}22$ |
| 1.427 | 1.425 | 1 | $3\bar{2}0$ |
| 1.383 | 1.380 | 1 | $\bar{3}21$ |
| 1.352 | 1.352 | 1 | $3\bar{2}1$ |
| 1.280 | 1.278 | 1 | $32\bar{1}$ |
| 1.208 | 1.206 | 3 | $400$ |
| 1.180 | 1.177 | 2 | $321$ |

[a] Rhombohedral, a =4.90angstrom, $\alpha$ = 96.5°, V =115.2angstrom$^3$, Cu $K\alpha$ radiation.

*X-ray Powder Diffraction Data* - The powder patterns of all three $H_3O^+MF_6^-$ compounds show that they are isostructural with only small differences in unit cell sizes. The powder diffraction patterns of $H_3O^+IrF_6^-$ and $H_3O^+PtF_6^-$ are listed in Tables I and II. They can be indexed as rhombohedral cells with dimensions $a_0 = 4.92$angstrom, $\alpha = 96.1^o$, $V = 116.9$angstrom$^3$ and $a_0 = 4.90$angstrom, $\alpha = 96.5^o$, $V = 115.2$angstrom$^3$, respectively. The calculated volume of $H_3O^+IrF_6$ is considerably smaller than that of $NO^-IrF_6$ $(V=129.3$angstrom$^3)$ [26]. The size of the $H_3O^+$ cation should be comparable to those of $NO^+$ and $K^-$ [26], so this discrepancy in cell volume is difficult to explain. Smaller cations such as $H^+$ and $H_2F^+$ can be ruled out on the basis of analytical data and other con-siderations. Similar inexplicable discrepancies, but in the opposite direction occur in the case of
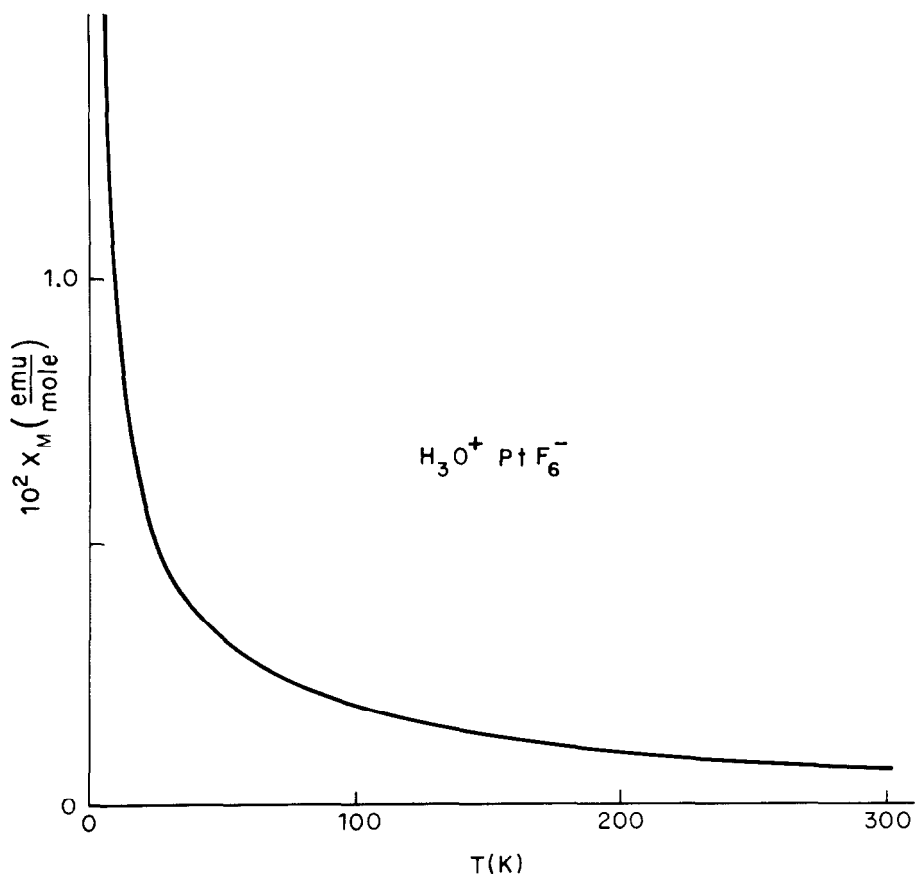


Figure 1.     Magnetic susceptibility of $H_3O^+PtF_6^-$ as a function of temperature.

$H_3O^+SbF_6^-$ (V=144.6angstrom$^3$), which has been indexed as tetragonal [1], *vis-a-vis* $NO^+SbF_6$ (V=130.4angstrom$^3$) [31].

*Magnetic Susceptibility Measurements* - The magnetic susceptibilities of $H_3O^+PtF_6^-$, $H_3O^+IrF_6$ and $(H_3O^+)_2PtF_6^-$ were measured from 4.2 to 300K by the Faraday method. The results for the first two samples are shown in Fig. 1 and 2. The last sample is diamagnetic, consistent with the electron configuration (d$^6$) and the expected octahedral crystal field. The six electrons are spin paired and $\chi_m = 66\times10^{-6}$ cmu/mole ($\pm10\%$). The Pt(V) in $H_3O^+PtF_6^-$ has a d$^5$ electron configuration, and therefore is expected to have an unpaired spin in a strong crystal field. The susceptibility results indicate that $\mu_{eff}$ decreases from $1.34\mu_B$ at 300K to $0.8\mu_B$ below 20K. These values are considerably below the spin only moment of $\mu_{eff} = 1.73\mu_B$, assuming g=2 and s=1/2. However, a reduced moment is reasonable since the spin-orbit coupling is expected to be large.



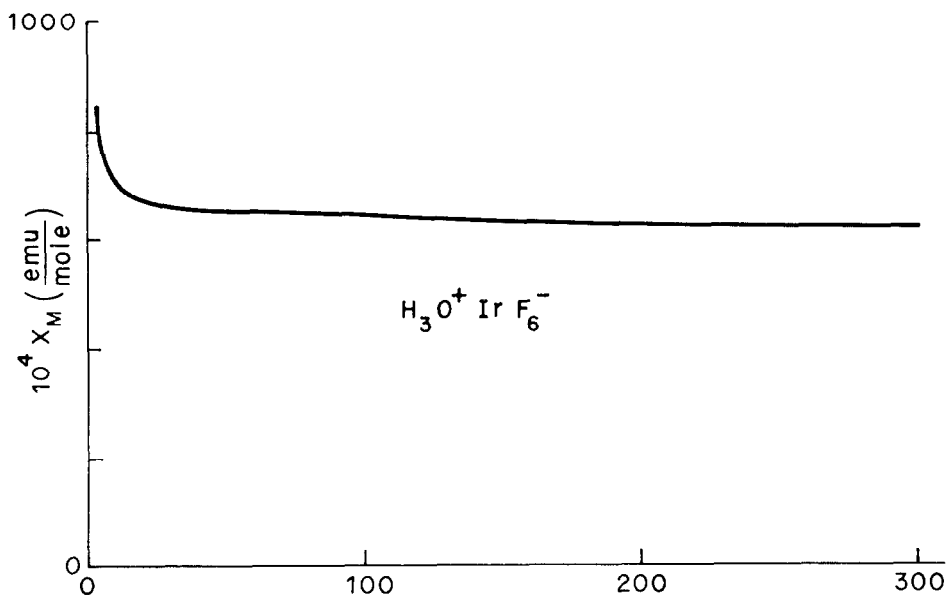Figure 2.    Magnetic susceptibility of $H_3O^+IrF_6^-$ as a function of temperature.

Finally, we see from Fig. 2 that $H_3O^+IrF_6^-$ has an almost temperature independent magnetic susceptibility of approximately $620\times10^{-6}$ emu/mole. Since Ir(V) is d$^4$, this can occur when the four occupied states are split from the rest of the $t_{2g}$ manifold by a large spin-orbit splitting. This result,

and indeed the magnitude of the susceptibility, is consistent with the results obtained for other $IrF_6^-$ compounds, such as $KIrF_6$ and $CsIrF_6$ [20,21].

## ACKNOWLEDGEMENTS

## REFERENCES

1    K. O. Christe, C. J. Schack and R. D. Wilson, Inorg. Chem. *14*, 2224 (1975).

2    J. P. Masson, J. P. Desmoulin, P. Charpin and R. Bougon, *ibid.*, *15*, 2529 (1976).

3    J. H. Canterford and R. Colton, "Halides of the Second and Third Row Transition Metals", John Wiley and Sons, New York (1968).

4    R. T. Paine and R. S. McDowell, private communication to W. E. Falconer.; see also Reference 7.

5    P. W. Wilson, J. Chem. Soc., Chem. Comm. 1241 (1972).

6    E. Jacob and W. Polligkeit, Z. Naturf. B *28*, 120 (1973).

7    R. T. Paine, R. R. Ryan and L. B. Asprey, Inorg. Chem. *14*, 1113 (1975).

8    R. D. Peacock and N. Edelstein, J. Inorg. Nucl. Chem. *38*, 771 (1976).

9    R. T. Paine, Inorg. Chem., *12*, 1457 (1973).

10    W. A. Sunder and F. A. Stevie, J. Fluor. Chem. *6*, 449 (1975).

11    H. Selig, unpublished results; see Reference [10].

12    W. E. Tolberg, R. T. Rewick, R. S. Stringham and M. E. Hill, Inorg. Chem. *6*, 1156 (1967).

13    B. Weinstock, J. G. Malm and E. E. Weaver, J. Am. Chem. Soc. *83*, 4310 (1961); N. Bartlett, private communication.

14    C. L. Chernick, H. H. Claassen and B. Weinstock, *ibid.*, *83*, 3165 (1961).

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

16    J. E. Griffiths, W. A. Sunder and W. E. Falconer, Spectrochim. Acta *31.4*, 1207 (1975).

17    M. Waldman and H. Selig, J. Inorg. Nucl. Chem. *35*, 2173 (1973).

18    J. C. Warf, W. D. Cline and R. D. Tevebaugh, Anal. Chem. *26*, 342 (1954).

19    J. E. Griffiths and W. A. Sunder, J. Fluor. Chem. *6*, 533 (1975).

20    A. Earnshaw, B. N. Figgis, J. Lewis and R. D. Peacock, J. Chem. Soc. 3132 (1961).

21    R. D. Peacock, Rec. Trav. Chim. *75*, 576 (1956).

22    R. D. Peacock and D. W. A. Sharp, J. Chem. Soc. 2762 (1959).

23    L. A. Woodward and M. J. Ware, Spectrochim. Acta *19*, 775 (1963).

24    R. D. Burbank, J. Appl. Cryst. *7*, 41 (1974).

25    M. Couzi, J. Cornut and P. V. Huong, J. Chem. Phys. *56*, 426 (1972).

26    N. Bartlett, S. P. Beaton and N. K. Jha, Chem. Comm. 168 (1966).

27    N. Bartlett, Angew. Chem. internat. Edit. *7*, 433 (1968).

28    J. H. Holloway and H. Selig, J. Inorg. Nucl. Chem. *30*, 473 (1968).

29    D. Hugill and R. D. Peacock, J. Chem. Soc. 1339 (1966).

30    A. J. Edwards, D. Hugill and R. D. Peacock, Nature *200*, 672 (1963).

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