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The Chemistry of Platinum Hexafluoride. I. Reactions with Nitric Oxide, Dinitrogen Tetroxide, Nitrosyl Fluoride, and Nitryl Fluoride

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Reactions of platinum hexafluoride with nitrosyl fluoride, nitryl fluoride, and dinitrogen tetroxide gave the compounds $NOPtF_6$, NO_2PtF_6, and $N_2O_3PtF_6$. With excess nitrosyl floride, $(NO)_2PtF_6$ was obtained. The interrelationships of these compounds are reported. Their infrared, X-ray diffraction, and epr data are reported and interpreted in terms of ionic structures. Platinum hexaflouride did not react with nitrous oxide at temperatures up to 100°

Introduction

Since the discovery of platinum hexafluoride in 1956, only a few papers on its chemistry have been published. Weinstock, Malm, and Weaver[1] described the reactions of platinum hexafluoride with bromine trifluoride, plutonium tetrafluoride, and neptunium tetrafluoride which gave bromine pentafluoride, plutonium hexafluoride, and neptunium hexafluoride, respectively. It was also observed to react rapidly at room temperature with plutonium which was prepared by the thermal decomposition of plutonium hydride. This reaction occurred with incandescense and deposited a platinum mirror on the quartz reaction vessel. Bartlett and Lohmann[2] found that platinum hexafluoride would oxidize molecular oxygen to give the dioxygenyl compound O_2PtF_6, and Bartlett[3] prepared the first inert gas compound, $XePtF_6$, by the reaction of platinum hexafluoride with xenon.

Since the first ionization potentials of nitric oxide and nitrogen dioxide are 9.5 and 11.0 ev,[4] respectively, stable nitrosonium and nitronium salts are expected to form with anions derived from strong electron-acceptor compounds; many such compounds are now known. However, no nitrosonium or nitronium derivatives of the platinum fluorides are known, and compounds of the other platinum metal hexafluorides, osmium and iridium, have not been extensively investigated. Robinson and Westland[5] reported the reactions of iridium hexafluoride with nitric oxide and dinitrogen tetroxide which gave $(NO)_2IrF_6$ and $(NO_2)_2IrF_6$, respectively. Bartlett and Lohmann[2] reported cell constants from X-ray diffraction measurements for the compounds $NORuF_6$, $NOOsF_6$, and $NOSbF_6$, but gave no other details.

We have carried out a detailed investigation of the reactions of platinum hexafluoride with nitric oxide, dinitrogen tetroxide, nitrosyl fluoride, and nitryl fluoride and have obtained structural data on the solid products of these reactions from X-ray powder diffraction data and infrared spectra.

Experimental Section

Materials and Equipment.—All reactions were carried out in a metal high-vacuum system constructed from $^3/_8$-in. nickel tubing, silver soldered to Monel Cajon fittings. Storage and measuring bulbs, obtained from Scientific Glass Corp., were of Monel. Hoke TM 440 Monel bellows valves with Teflon seats were used throughout. Pressure measurements were made using either Monel Helicoid compound gauges accurate to 3 mm or a Wallace and Tiernan gauge, Model FA 145, accurate to 0.5 mm. Volumes were calibrated using purified carbon dioxide.

The vacuum system was thoroughly passivated using chlorine trifluoride, bromine pentafluoride, and fluorine. As a final treatment the system was filled with fluorine to a pressure of 1600 mm and heated with a torch until there was no significant drop in pressure, thus indicating complete passivation of the interior. This procedure was repeated periodically to ensure absence of troublesome side reactions with the system.

Reactors were constructed from $^3/_8 \times 8$ in. nickel tubing with a welded bottom and flanged top. The vacuum seal to the valve assembly was made with a Viton "O" ring. Nickel screw caps were also provided for the reactors. After vacuum transfer of platinum hexafluoride by condensation at −196°, the reactor could be filled with helium, removed from the vacuum system, and capped in a drybox for weighing. Quantities of platinum hexafluoride taken for reaction were determined both by weight and *PVT* measurements.

Platinum Hexafluoride.—About 10 g of platinum wire, 0.030 or 0.050 in., was wound into a coil and burned in a fluorine atmosphere at pressures between 300 and 400 mm. The procedure and design of the brass reactor were those reported by Weinstock, *et al.*[1] The material so prepared was purified by trap to trap distillation[6] and stored in a prefluorinated Monel storage bulb. The vapor pressure and infrared spectrum of the purified material agreed well with the published values.[1,7]

Nitrosyl Fluoride.—This compound was prepared by allowing an excess of purified nitric oxide and fluorine to diffuse together according to a procedure previously described.[8] After extensive purification by trap to trap distillation, the vapor pressure[9] and infrared spectrum[10] were in agreement with published values.

Nitryl Fluoride.—Purified dinitrogen tetroxide was allowed to react with an excess of fluorine according to the procedure described by Geichman, Smith, and Ogle.[11] The vapor pressure[9] and infrared spectrum[12] of the purified product were in excellent agreement with literature values.

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(11) J. R. Geichman, E. A. Smith, and P. R. Ogle, *Inorg. Chem.*, **2**, 1012 (1963).

(12) R. E. Dodd, J. A. Rolfe, and L. A. Woodward, *Trans. Faraday Soc.*, **52**, 145 (1956).

Nitrous Oxide, Nitric Oxide, and Dinitrogen Tetroxide.—These materials were obtained from the Matheson Co. and were purified by trap to trap distillation until vapor pressure measurements and infrared analyses[13] showed negligible quantities of contaminants.

Fluorine.—The 98% pure material was obtained from the General Chemical Division, Allied Chemical Co. The gas was passed through a tower containing activated sodium fluoride pellets to absorb hydrogen fluoride.[14]

Platinum.—The metal was obtained as 0.030- or 0.050-in. wire from Engelhard Industries, Inc. The assay was 99.95% platinum.

X-Ray Diffraction Measurements.—X-Ray diffraction studies were carried out using the powder technique, with samples sealed in 0.3-mm thin-wall (0.01-mm) quartz capillary tubes. Samples were loaded into the capillaries in a drybox flushed with dry nitrogen, sealed with a microflame, and loaded in a 5.73-cm Debye–Scherrer camera. Measurements were made using Cu Kα radiation with a nickel filter. Exposure times varied from 2 to 3 hr. The Staumanis film technique was used and all films were corrected for shrinkage. Intensities were estimated visually.

Analyses.—Chemical analyses for platinum, fluorine, and nitrogen were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Density Measurements.—The densities of powdered solid samples were measured with a 1-ml pycnometer equipped with a thermometer. A fluorocarbon oil (No. FC-43, 3M Co.) was used as the displacement liquid. All measurements were made at 25 ± 1°. The pycnometer was calibrated with distilled water.

Infrared Spectra.—Infrared spectra were obtained with Beckman IR-10 and IR-5A recording spectrophotometers calibrated with polystyrene, using either the KBr disk or Nujol mull technique. In many cases the sample appeared to react with KBr to liberate bromine and nitrogen dioxide. In Nujol, decomposition of the sample appeared to be nonexistent or very slow. The significant features of the spectra were in good agreement with either technique. In some cases, measurements also were made on films deposited on silver chloride windows of a nickel infrared cell.

Preparation of Nitrosonium Hexafluoroplatinate. (a) **Reaction of Platinum Hexafluoride with Nitrosyl Fluoride.**—Platinum hexafluoride (3.56 mmoles, 1.102 g) was condensed into a nickel reactor containing nitrosyl fluoride (3.88 mmoles) at −196°. The mixture was allowed to warm slowly for a period of 12 hr in a dewar precooled to −196° with liquid nitrogen. The products were 1.70 mmoles of fluorine (identified by its vapor pressure and reaction with mercury[15]) and 1.207 g (3.56 mmoles) of a nonvolatile yellow solid, identified as $NOPtF_6$. The excess nitrosyl fluoride (0.32 mmoles) was trapped at −196°. *Anal.* Calcd for $NOPtF_6$: Pt, 57.5; F, 33.6; N, 4.13. Found: Pt, 57.3; F, 33.1; N, 4.65.

(b) **Reaction of Platinum Hexafluoride with Nitric Oxide.**—Nitrosonium hexafluoroplatinate was also prepaerd by the direct reaction of PtF_6 with nitric oxide. This reaction proceeded explosively, even at a very low temperature, and the product was usually impure. The gross stoichiometry of the reaction, as well as the X-ray and infrared data, clearly indicates that the principal product was identical with the $NOPtF_6$ obtained from the reaction of nitrosyl fluoride and platinum hexafluoride.

Preparation of Nitronium Hexafluoroplatinate.—Platinum hexafluoride (3.75 mmoles, 1.160 g) was condensed into an evacuated reactor with nitryl fluoride (4.13 mmoles) at −196°. The reactants were left in contact for 18 hr while the vessel was slowly warmed in a dewar precooled to −196°. Found: 1.61 mmoles of fluorine and 1.341 g (3.77 mmoles) of a yellow solid identified as NO_2PtF_6. Excess nitryl fluoride was detected by trapping at −196° but not measured. *Anal.* Calcd for NO_2PtF_6: Pt, 54.9; F, 32.1; N, 3.95. Found: Pt, 55.3; F, 31.2; N, 3.94.

Preparation of Nitrosonium Nitronium Hexafluoroplatinate. (a) **Reaction of Platinum Hexafluoride with Dinitrogen Tetroxide.**—Platinum hexafluoride (3.84 mmoles, 1.185 g) was condensed into a reactor with dinitrogen tetroxide (5.71 mmoles) at −196°. The pressure correction of the gas measured as undissociated N_2O_4 was calculated using the NO_2–N_2O_4 equilibrium data of Verhoek and Daniels.[16] The reaction mixture was warmed slowly from −196 to 25° during a period of 18 hr by enclosing the reactor in a precooled dewar. Found: 1.95 mmoles of oxygen (identified by vapor pressure measurements); 1.501 g (3.90 mmoles) of a pale yellow solid shown to be $N_2O_3PtF_6$. The excess dinitrogen tetroxide was trapped at −196° but was not measured. *Anal.* Calcd for $N_2O_3PtF_6$: Pt, 50.7; F, 29.6; N, 7.28. Found: Pt, 51.2; F, 28.4; N, 6.68.

(b) **Reaction of Nitronium Hexafluoroplatinate with Dinitrogen Tetroxide.**—An excess of dinitrogen tetroxide was condensed onto a powdered sample of nitronium hexafluoroplatinate (2.17 mmoles, 0.771 g). The reactor was kept at room temperature for 2 days. The products were 1.10 mmoles of oxygen and 0.879 g (2.28 mmoles) of a yellow solid shown by infrared and X-ray diffraction analysis to be nitrosonium nitronium hexafluoroplatinate.

(c) **Reaction of Nitronium Hexafluoroplatinate with Nitric Oxide.**—Nitric oxide (2.01 mmoles) was condensed onto powdered nitronium hexafluoroplatinate (1.56 mmoles, 0.544 g), and the reaction was allowed to proceed for 12 hr at 25°. Found: 0.592 g (1.54 mmoles) of a substance shown by infrared and X-ray diffraction analyses to be nitrosonium nitronium hexafluoroplatinate. The solid changed color from bright yellow to pale yellow during the reaction.

In a similar experiment in which the pressure decrease was followed visually, approximately 1 hr was required for complete reaction. Addition of more nitric oxide to the reactor gave no further increase in weight of the solid product after 3 hr.

Preparation of Dinitrosonium Hexafluoroplatinate. (a) **Reaction of Nitrosonium Hexafluoroplatinate with Dinitrogen Tetroxide.**—Dinitrogen tetroxide (0.680 mmole) was condensed onto nitrosonium hexafluoroplatinate (1.24 mmoles, 0.420 g), and the reactor was heated at 70° for 12 hr. The products consisted of oxygen (not measured) and 0.452 g (1.22 mmoles) of pale yellow dinitrosonium hexafluoroplatinate. The solid was heated *in vacuo* at 70° before chemical analysis to rid the compound of adsorbed gases. *Anal.* Calcd for $(NO)_2PtF_6$: Pt, 52.9; F, 30.9; N, 7.59. Found: Pt, 52.9; F, 29.4; N, 7.28.

(b) **Reaction of Platinum Hexafluoride with an Excess of Nitrosyl Fluoride.**—A mixture of platinum hexafluoride (2.52 mmoles, 0.781 g) and nitrosyl fluoride (16.3 mmoles) was kept at room temperature for 3 days. Infrared examination of the condensable gaseous products showed the presence of nitrosyl fluoride and dinitrogen tetroxide. The noncondensable gas was shown to be fluorine by its reaction with mercury. The pale yellow solid product, 0.931 g (2.52 mmoles), was shown by chemical analysis to be dinitrosonium hexafluoroplatinate. *Anal.* Calcd for $(NO)_2PtF_6$: Pt, 52.9; F, 30.9; N, 7.59. Found: Pt, 53.6; F, 29.6; N, 7.03.

Although X-ray diffraction and chemical analyses indicated that this material was essentially the same as that prepared by the reaction of nitrosonium hexafluoroplatinate with dinitrogen tetroxide, infrared studies indicated some differences.

Attempted Reaction of Platinum Hexafluoride with Nitrous Oxide.—Platinum hexafluoride (3.48 mmoles, 1.076 g) and nitrous oxide (3.84 mmoles) were condensed into an evacuated nickel reactor at −196°. The reaction mixture was allowed to warm to room temperature slowly. The volatile products were then recovered and separated. All of the nitrous oxide and 98.6% of the platinum hexafluoride were recovered unchanged. The solid residue in the reactor (0.0257 g) was identified by X-ray

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TABLE I
STOICHIOMETRIC DATA

A		B		C		D	C/B	D/B	No. of runs
NO	+	PtF_6	→	$NOPtF_6$			0.95 ± 0.03		3
NOF	+	PtF_6	→	$NOPtF_6$	+	$^1/_2F_2$	0.97 ± 0.4	0.46 ± 0.07	11
NO_2F	+	PtF_6	→	NO_2PtF_6	+	$^1/_2F_2$	1.00 ± 0.01	0.44 ± 0.03	5
N_2O_4	+	PtF_6	→	$N_2O_3PtF_6$	+	$^1/_2O_2$	1.01 ± 0.03	0.50 ± 0.02	6
2NOF	+	PtF_6	→	$(NO)_2PtF_6$	+	F_2	0.99 ± 0.05	1.1 ± 0.2	2
$^1/_2N_2O_4$	+	$NOPtF_6$	→	$(NO)_2PtF_6$	+	$^1/_2O_2$	1.04 ± 0.03		4
NO	+	NO_2PtF_6	→	$N_2O_3PtF_6$			0.98 ± 0.01		4
$^1/_2N_2O_4$	+	NO_2PtF_6	→	$N_2O_3PtF_6$	+	$^1/_2O_2$	1.01 ± 0.02	0.51 ± 0.02	2

diffraction to be platinum tetrafluoride. The reactants were then recondensed into the reactor and heated to 100° for 12 hr. Under these conditions, there was essentially no reaction, and 98% of the nitrous oxide was recovered.

Results

Stoichiometry.—The experimental reactant and product ratios determined for each reaction system are summarized in Table I. These data show that the reactions of equimolar quantities of platinum hexafluoride with nitric oxide, nitrosyl fluoride, nitryl fluoride, and dinitrogen tetroxide can be represented by the equations

$$NO + PtF_6 \longrightarrow NOPtF_6 \quad (1)$$

$$NOF + PtF_6 \longrightarrow NOPtF_6 + {}^1/_2F_2 \quad (2)$$

$$NO_2F + PtF_6 \longrightarrow NO_2PtF_6 + {}^1/_2F_2 \quad (3)$$

$$N_2O_4 + PtF_6 \longrightarrow N_2O_3PtF_6 + {}^1/_2O_2 \quad (4)$$

The yields of the solid products were essentially quantitative for each reaction at room temperature. Confirmation of the molecular formulas for the solid products was obtained by elemental analyses.

When an excess of nitryl fluoride or dinitrogen tetroxide was employed, the solid products were those described by eq 3 and 4, although minor deviations in the gas yields were observed. For the nitrosyl fluoride–platinum hexafluoride system, however, the reaction could proceed beyond the 1:1 stage and gave the compound $(NO)_2PtF_6$. This compound could also be prepared in stepwise fashion by the reaction of dinitrogen tetroxide with nitrosonium hexafluoroplatinate.

Treatment of nitrosonium hexafluoroplatinate with nitric oxide gave no reaction at 25°. In contrast, it was found that nitronium hexafluoroplatinate would take up nitric oxide to give nitrosonium nitronium hexafluoroplatinate at room temperature. This same compound could be prepared by the reaction of nitronium hexafluoroplatinate with dinitrogen tetroxide.

The relationships between the various compounds are summarized by the equations

$$2NOF + PtF_6 \longrightarrow (NO)_2PtF_6 + F_2 \quad (5)$$

$${}^1/_2N_2O_4 + NOPtF_6 \longrightarrow (NO)_2PtF_6 + {}^1/_2O_2 \quad (6)$$

$$NO + NO_2PtF_6 \longrightarrow N_2O_3PtF_6 \quad (7)$$

$${}^1/_2N_2O_4 + NO_2PtF_6 \longrightarrow N_2O_3PtF_6 + {}^1/_2O_2 \quad (8)$$

Four distinct compounds defined by analytical and stoichiometric data have been obtained from these investigations. Additional properties characterizing these materials are presented below.

Nitrosonium Hexafluoroplatinate.—This compound is a bright yellow solid. When heated it appeared to decompose with little gas evolution up to 300°. When observed in a quartz tube, the solid became orange at 130°, brown at 170°, and at 250° appeared to fuse and wet the tube. At higher temperatures the material turned black.

The density of nitrosonium hexafluoroplatinate determined pycnometrically is 4.10 ± 0.02 g/cc. X-Ray diffraction data (Table II) for the compound were indexed on the basis of a cubic cell with $a_0 = 10.135 \pm 0.014$ A. The visually estimated relative intensities were the same as those found for dioxygenyl hexafluoroplatinate; therefore, it appears that the two compounds are isostructural. The infrared spectra of the solid consisted of strong bands at 2327 ± 2, 2316 ± 2, and 567 ± 4 cm^{-1} (Figure 1). Epr spectra showed the material to be paramagnetic with $g = 2.0$.

TABLE II
X-RAY DIFFRACTION DATA

Compd	ρ, g/cc		a_0, A	V (unit cell), A^3
	Exptl	Calcd		
$N_2O_3PtF_6$	4.10 ± 0.03	4.27	10.605 ± 0.018	1198
NO_2PtF_6	4.16 ± 0.03	4.26	10.344 ± 0.027	1107
$NOPtF_6$	4.10 ± 0.02	4.32	10.135 ± 0.014	1041
$(NO)_2PtF_6$	4.08 ± 0.02	4.27	10.468 ± 0.010	1147
$NOOsF_6$[a]		4.27	10.126	1038
O_2PtF_6[a]	4.20	4.48	10.032	1010

[a] Data from ref 2.

Nitrosonium hexafluoroplatinate is hygroscopic but can be stored indefinitely in dry nitrogen. The compound reacts violently with water with liberation of nitrogen dioxide and formation of a strongly acid yellow solution. The ultraviolet absorption spectrum of the solution showed the presence of the hexafluoroplatinate(IV) ion. Qualitative tests[17] on this solution indicated the presence of nitrite but not nitrate ions. These observations are in accord with the known hydrolytic behavior of the nitrosonium ion.[18]

Nitrosonium hexafluoroplatinate was not affected by contact with fluorine at a pressure of 6.6 atm for 20 hr. When the reaction of equimolar quantities of platinum hexafluoride and nitrosyl fluoride was carried out in a reactor containing a large excess of fluorine, only nitrosonium hexafluoroplatinate was formed. However, in

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[17] P. E. Wenger and R. Duckert, "Reagents for Qualitative Analysis," Elsevier Publishing Co., Inc., New York, N. Y., 1948, pp 291, 294.

[18] C. C. Addison and J. Lewis, *Quart. Rev.* (London), **9**, 115 (1955).

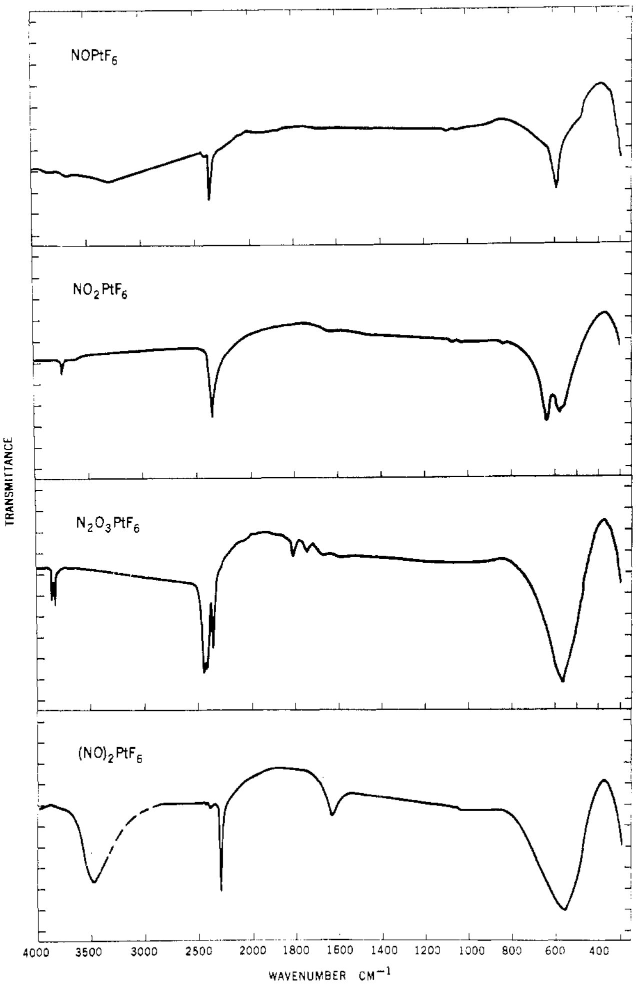

Figure 1.—Infrared spectra of nitrosonium and nitronium hexafluoroplatinate compounds in Nujol mulls. The band shape for $(NO)_2PtF_6$ at 3500 cm^{-1} is not known owing to interference of Nujol.

this case some unreacted platinum hexafluoride was present (estimated at 10.4 mole %).

Nitronium Hexafluoroplatinate.—This material is a yellow solid which reacts violently with water to give an acid solution containing the nitrate but not the nitrite ion. The X-ray diffraction data of the compound were indexed on the basis of a cubic cell with a_0 = 10.344 ± 0.027 A, giving a theoretical crystal density of 4.26 g/cc. The experimentally determined value of 4.16 ± 0.03 g/cc is in good agreement with the calculated value (Table II). Infrared spectra of the compound in Nujol mulls showed strong bands at 2362 ± 3, 642 ± 2, 595 ± 1, 583 ± 3, 567 ± 1 and a moderately intense band at 3750 ± 6 cm^{-1}. The epr measurement on the solid at −196° showed the compound to be paramagnetic with $g = 1.75$.

Nitrosonium Nitronium Hexafluoroplatinate.—The X-ray diffraction powder data from the pale yellow solid were indexed on the basis of a cubic cell with a_0 = 10.605 ± 0.018 A. The calculated X-ray crystal density of 4.27 g/cc agrees favorably with the experimentally determined value of 4.10 ± 0.03 g/cc. The infrared spectra of the compound showed strong bands at 2391 ± 3, 2364 ± 8, 2319 ± 5, 2310 ± 3, and 573 ± 5 cm^{-1} and weak bands at 3790 ± 5, 3770 ± 6, 1800 ± 5, 1690 ± 3, and 1590 ± 5 cm^{-1}. The epr measurements showed the compound to be diamagnetic.

Tests on solutions of the hydrolyzed product showed the presence of both nitrate and nitrite ions. This result is expected for the hydrolytic behavior of a solid containing both the NO^+ and NO_2^+ ions.

The compound decomposed at approximately 140° with evolution of a small amount of dinitrogen tetroxide. When heated slowly to 400°, the sample changed color from pale yellow to black. The experimentally determined density of the pyrolysis product, 4.88 g/cc, was considerably greater than that of the starting material. The X-ray diffraction pattern of this material was identical with that of the starting compound. Infrared spectra of the material in a Nujol mull showed the presence of a strong NO^+ band at 2310 cm^{-1} and strong, broad anion absorption at 570 cm^{-1}. In a similar experiment in which a sample of $N_2O_3PtF_6$ was heated to 475°, the X-ray diffraction pattern of the product was blank, indicating an amorphous solid. Chemical analysis of the black product gave the empirical formula $NOPtF_4$.

Dinitrosonium Hexafluoroplatinate.—X-Ray diffraction data from this yellow compound were indexed in the cubic system with a_0 = 10.468 ± 0.010 A. The calculated crystal density of 4.27 g/cc is in satisfactory agreement with the experimentally determined value of 4.08 g/cc. Aqueous solutions of the compound contained nitrite ion, but tests for nitrate were negative. The infrared spectrum showed a very sharp, strong band at 2309 ± 1 cm^{-1}, which was considerably greater in intensity than the 2316-cm^{-1} band of $NOPtF_6$. A strong, broad absorption at 569 ± 3 cm^{-1} and medium to weak bands at 1805, 1740, and 1643 cm^{-1} were also observed. Since the intensities of the bands at 1805 and 1740 cm^{-1} decreased markedly when the solid was heated at 70° under vacuum, they were thought to be due to adsorbed gases. Dinitrosonium hexafluoroplatinate which was prepared by reaction 6 exhibited a broad infrared band at 3500 cm^{-1} which did not change in intensity when the compound was heated under vacuum at 70°.

The epr measurements on the solid at −196° showed that the material prepared by either reaction 5 or 6 was diamagnetic.

Discussion

Salts containing the nitrosonium or nitronium ion undergo hydrolytic reactions leading to formation of nitrite or nitrate ions, respectively.[5,18,19] Qualitative tests of this kind on the four new compounds described here indicate that they should be formulated as nitrosonium hexafluoroplatinate(V), dinitrosonium hexafluoroplatinate(IV), nitronium hexafluoroplatinate(V), and nitrosonium nitronium hexafluoroplatinate(IV). The diamagnetism of $(NO)_2PtF_6$ and $N_2O_3PtF_6$ offers additional evidence for platinum in these compounds being present in the +4 oxidation state. The para-

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(19) A. Hantzsch, *Z. Physik. Chem.*, **65**, 41 (1909).

magnetism of $NOPtF_6$ and NO_2PtF_6 is consistent with a Pt(V) ion. The infrared spectra and X-ray crystal data of the compounds are in agreement with these structural interpretations.

Platinum hexafluoride appears to exhibit unique behavior toward nitrosyl fluoride and nitryl fluoride. Geichman, Smith, and Ogle have reported that WF_6, MoF_6, and UF_6 react with nitrosyl and nitryl fluorides to form the compounds $NOMF_7$ and NO_2MF_7, respectively (M = W, Mo, or U). No evidence has been found to indicate formation of the PtF_7^- ion in analogous reactions with platinum hexafluoride. Even when the reactions were carried out in the presence of excess fluorine, the Pt(VI) ion was not formed.

Although the ionization potentials of nitrosyl fluoride and nitryl fluoride are not known, an electron-transfer reaction analogous to that employed for the preparation of O_2PtF_6[2] might have been anticipated. If such an electron-transfer mechanism has any importance in these reactions, it would follow that the ions NOF^+ and NO_2F^+ are unstable with respect to loss of fluorine and formation of NO^+ and NO_2^+. On the other hand, if nitrosyl and nitryl fluoride function in the normal manner as fluoride ion donors, instability of the PtF_7^- ion with respect to loss of fluorine and formation of PtF_6^- would be implied.

The ionization potential of nitrous oxide (12.9 ev)[4] is only 6% larger than that of oxygen, but no reaction was observed between platinum hexafluoride and nitrous oxide at temperatures to 100°. Although the implications of this observation are unclear, it must be borne in mind that crystal energies of the resultant products play an important, if not dominant, role in the over-all energetics of the process.

The electron-transfer mechanism obviously plays a dominant role in the reaction of platinum hexafluoride with nitric oxide. This reaction may be rationalized in terms of Bartlett's energy scheme[2] since the ionization potential of nitric oxide is only 9.5 ev.[4] The fact that $NOPtF_6$ is isostructural with O_2PtF_6 suggests that the reactions of platinum hexafluoride with nitric oxide and oxygen are perfectly analogous.

Although oxygen is a product of the platinum hexafluoride–dinitrogen tetroxide reaction, no O_2PtF_6 was detected by visual examination or in the X-ray diffraction pattern of the solid product. Hence, it appears that platinum hexafluoride reacts much faster with dinitrogen tetroxide than with oxygen or that dinitrogen tetroxide can displace O_2^+ from O_2PtF_6 to form oxygen and $N_2O_3PtF_6$.

Infrared Spectra.—The investigation by Sharp and Thorley[20] shows that nitrosonium compounds exhibit a characteristic strong absorption in the region between 2150 and 2400 cm^{-1}. The intense absorption at 2321 cm^{-1} (center of band) observed for $NOPtF_6$ is therefore ascribed to the NO^+ stretching mode. This assignment applies also to the strong, sharp bands at 2310 and 2309 cm^{-1} of $N_2O_3PtF_6$ and $(NO)_2PtF_6$, respectively.

For NO_2PtF_6, the ν_3 band of the linear NO_2^+ ion was found at 2362 ± 3 cm^{-1}, in close agreement with the frequencies reported for other NO_2^+ compounds.[11,21] The sharp, lower intensity band at 3750 ± 6 cm^{-1} is assigned to the infrared-allowed $\nu_1 + \nu_3$ combination band. If ν_1 is taken as 1396 cm^{-1} from the Raman data of $NO_2^+ClO_4^-$,[21] then $\nu_1 + \nu_3 = 3758$ cm^{-1}, in good agreement with the observed value for the combination band. Osberg and Hornig[22] have accounted fully for similar bands in the case of the isoelectronic linear CO_2 molecule. This combination band has also been reported for the nitronium ion in nitric acid–sulfuric acid mixtures[23] and for the compounds $NO_2^+BF_4^-$ and $NO_2^+SbF_6^-$.[24]

Both the ν_3 band and the combination band $\nu_1 + \nu_3$ are observed for $N_2O_3PtF_6$ and provide sound evidence for the presence of the nitronium ion in this compound. Since the spectra show that both NO^+ and NO_2^+ ions exist in solid $N_2O_3PtF_6$, the presence of the nitrosonium–nitrogen dioxide ion,[25] $N_2O_3^+$, appears unlikely.

The ν_2 bending mode of the nitronium ion has been reported at 570 cm^{-1} in $NO_2^+ClO_4^-$ [21] and at 538 cm^{-1} in $NO_2^+NO_3^-$.[26] For carbon dioxide this absorption is found at 660 cm^{-1}.[22] Of the compounds reported here, only NO_2PtF_6 exhibited an absorption at 642 cm^{-1} which may be due to the ν_2 mode of the NO_2^+ ion. Although no corresponding band was found for $N_2O_3PtF_6$, the very strong absorption at 574 cm^{-1} could well have obscured the weaker band near 650 cm^{-1}. The assignment of the ν_2 band for NO_2^+, although reasonable, must be considered as tentative since similar absorption near 650 cm^{-1} has been reported as due to vibrational modes of the anions in the compounds O_2PtF_6[2] and $KPtF_6$.[27]

All of the compounds showed strong, broad absorption near 570 cm^{-1} which is attributed to the anions. For NO_2PtF_6, the band was moderately well resolved into a triplet, but for the other compounds no structure was observed. The 570-cm^{-1} absorption band lies well within the range observed for other hexafluoroplatinate ions, *e.g.*, PtF_6^- at 570 to 575 cm^{-1},[2,27,28] and PtF_6^{2-} at 565 cm^{-1}.[28] Although some features might have been expected which would have distinguished between PtF_6^- and PtF_6^{2-} in the four compounds, none were observed.

Some of the weaker bands found in the spectra of $N_2O_3PtF_6$ and $(NO)_2PtF_6$ appeared to arise from impurities. For example, the intensities of the bands between 1600 and 1800 cm^{-1} were variable and decreased markedly when the compounds were heated under vacuum at 70°. These weaker bands may be due

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[28] We have found the following bands for these compounds in Nujol mulls and KBr pellets (cm^{-1})

	KBr pellet	Nujol	
O_2PtF_6	570	570	631
K_2PtF_6	565	565	
$KPtF_6$	570	575	

to the presence of small amounts of adsorbed gases such as nitrosyl fluoride or dinitrogen tetroxide. The bands near 3500 and 1640 cm^{-1} in the spectrum of $(NO)_2PtF_6$ may be due to lattice water absorbed during the preparation of the mulls.

Other features of the spectra of these compounds were of lesser importance to the gross structural implications. That the stretching mode of the NO^+ ion appeared as a doublet in $NOPtF_6$ and $N_2O_3PtF_6$ should probably be interpreted as being due to coupling with lattice modes. A similar interpretation is reasonable for the splitting of the ν_3 and $\nu_1 + \nu_3$ bands of the NO_2^+ ion in $N_2O_3PtF_6$. However, in this case the splitting might be due to different interactions between randomly oriented NO^+ and NO_2^+ ions in the crystal. For example, if the NO^+ and NO_2^+ ions lie on the major threefold axis of a structure similar to that of O_2PtF_6,[2] then the three possible orientations of the ions NO^+—NO^+, NO_2^+—NO_2^+, and NO^+—NO_2^+ would result in two different crystal environments for both NO^+ and NO_2^+.

X-Ray Diffraction Results.—The crystal data indicate that $NOPtF_6$ is isostructural with O_2PtF_6[2] and $KSbF_6$.[29] These three compounds have nearly identical cell dimensions, and since the visually estimated relative intensities of $NOPtF_6$ are very nearly the same as those found for O_2PtF_6, the space groups for these two compounds are assumed to be identical, *i.e.*, T_h^4-$Ia3$. This similarity is to be expected since the NO^+ and O_2^+ ions are close in size.

It has been estimated that the NO^+ group, when rotating and acting as a sphere, has an effective radius of 1.40 A,[20] which is close to the radius of potassium ion (1.33 A). Since the molecular volume of SbF_6^- is nearly the same as that of the ions OsF_6^-, RuF_6^-, and PtF_6^-,[27] the isostructural relationship of $NOPtF_6$ and $KSbF_6$ is expected.

When the larger linear NO_2^+ ion is substituted for NO^+ in the crystal, the lattice expands a small amount (2.06%); this expansion is still more pronounced for $N_2O_3^{2+}PtF_6^{2-}$ (4.64%). Although $NOPtF_6$ and O_2PtF_6 are believed to be isostructural, it cannot be determined at present whether NO_2PtF_6 and $N_2O_3PtF_6$ are also isostructural to O_2PtF_6, since the corresponding relative intensities for some reflections differ considerably. However, since these compounds are cubic, and nearly isodimensional, they probably possess closely related packing features.

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CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
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The Sodium Fluoride–Lanthanide Trifluoride Systems[1]

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Phase diagrams are reported for the $NaF-LnF_3$ binary systems. Hexagonal phases of the formula $NaF \cdot LnF_3$ are formed in all $NaF-LnF_3$ systems. Above 700° the hexagonal phases $NaF \cdot PrF_3$ to $NaF \cdot LuF_3$ become converted to disordered fluorite-like cubic phases of variable composition. The composition limits of the cubic phase region are extended in proportion to the difference in ion size between Na^+ and Ln^{3+} and vary in breadth ranging from 9 mole % ($NaF-PrF_3$) to 25 mole % ($NaF-LuF_3$). In each case, the LnF_3-rich phase boundary was found empirically to be $5NaF \cdot 9LnF_3$ as the interstitial positions for anions become filled. Values of the fluorite unit-cell constants were calculated from ionic radii and found to be in good agreement with measured values. Unit-cube dimensions, a_0, range from a maximum value of 5.720 A for the LnF_3-rich phase in the system $NaF-PrF_3$ to 5.425 A for the NaF-rich phase in the system $NaF-LuF_3$. Lattice constants for the hexagonal phases $NaF \cdot LaF_3$ to $NaF \cdot LuF_3$ vary for a_0 from 6.157 to 5.967 A and for c_0 from 3.822 to 3.523 A. At high temperatures the $5NaF \cdot 9LnF_3$ phase displays disordering characteristic of the fluorite-like solid solutions; at lower temperatures cationic ordering takes place in the $5NaF \cdot 9LnF_3$ phases where Ln = Dy to Lu, transforming the cubic phase to an orthorhombic phase. Hexagonal $NaF \cdot LnF_3$ and orthorhombic $5NaF \cdot 9LnF_3$ compounds are partially miscible in the solid state. In the series Dy to Lu, the hexagonal phase is increasingly soluble in $5NaF \cdot 9LnF_3$, stabilizing the 5:9 phase to the extent that the lutetium compound is stable at temperatures below 300°, the lower temperature limit of this study. Optical properties and refractive indices of the intermediate crystalline phases in the $NaF-LnF_3$ systems were determined as part of this investigation. Minimum liquidus temperatures in the $NaF-LnF_3$ systems are associated with an $NaF-NaF \cdot LnF_3$ eutectic which varies in composition only from 25 to 29 mole % LnF_3 and in temperature from 733 to 595°.

Introduction

We proposed some time ago[2] that the system $NaF-YF_3$ would serve as a model for the binary systems $NaF-SmF_3$, $-EuF_3$, $-GdF_3$, $-TbF_3$, $-DyF_3$, $-HoF_3$, $-ErF_3$, $-TmF_3$, $-YbF_3$, and $-LuF_3$. This hypothesis was based

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