

## Nitrosyl Hexafluoroplatinate(V), $\text{NO}^+[\text{PtF}_6]^-$ : Preparation and Magnetic Susceptibility. The Magnetic Susceptibility of $\text{O}_2^+$

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ALTHOUGH the magnetic susceptibility of dioxygenyl hexafluoroplatinate(V) has been measured<sup>1</sup> over the temperature range 77—298°K and has been shown<sup>1</sup> to be consistent with the combination of a paramagnetic (nitric oxide-like)  $\text{O}_2^+$  and a paramagnetic  $[\text{PtF}_6]^-$  species, the susceptibility of neither of these ions has been separately determined hitherto. On the basis of its anticipated structural similarity to  $\text{O}_2^+[\text{PtF}_6]^-$  the nitrosyl salt,  $\text{NO}^+[\text{PtF}_6]^-$ , appeared to be the most suitable for this purpose.

Nitric oxide is readily oxidized by platinum hexafluoride but it has not proved possible to control the reaction to produce a pure product. A mixture of  $\text{NOPtF}_6$  and  $(\text{NO})_2\text{PtF}_6$  is always produced.<sup>2</sup> Platinum hexafluoride is, however, able to oxidize nitrosyl fluoride with the elimination of fluorine\*:  $\text{ONF} + \text{PtF}_6 \rightarrow \text{ON}^+[\text{PtF}_6]^- + \frac{1}{2}\text{F}_2$ . In a typical experiment, platinum hexafluoride (5.20 mmoles), prepared by Weinstock, Malm, and Weaver's method,<sup>3</sup> was warmed to room temperature, in a closed nickel vessel, with

data being, for the cubic form:  $a_0$ ,  $10.118 \pm 0.003 \text{ \AA}$ ;  $U_{\text{calc}}$ ,  $1036 \text{ \AA}^3$ ;  $Z$ , 8; space group probably  $Ia\bar{3}$  ( $T_h^h$ , No. 206).<sup>4</sup>

The infrared spectrum, in the range 800—400  $\text{cm}^{-1}$ , of a thin film of the salt, formed on the silver chloride windows of a nickel cell, shows a very strong absorption centred on  $632 \text{ cm}^{-1}$ , assumed to be the pseudo- $\nu_3$  of "octahedral"  $[\text{PtF}_6]^-$ . The spectrum is very similar to that of dioxygenyl hexafluoroplatinate(V),<sup>1,5</sup> but different from that of  $[\text{PtF}_6]^{2-}$  salts which show<sup>6</sup> their strongest absorption at  $583 \text{ cm}^{-1}$ .

The magnetic susceptibility of  $\text{NO}^+[\text{PtF}_6]^-$  (cub.) has been measured over the temperature range 77—303°K. As in the case of the dioxygenyl salt,<sup>1</sup> the susceptibility obeys the Curie-Weiss law ( $\theta$  being:  $\text{NOPtF}_6$ , 32;  $\text{O}_2\text{PtF}_6$ , 45°). This simple behaviour shows that there are no strong interactions of the molecular magnets and in view of the isomorphism and near isodimensionality of the two salts, the susceptibility of the  $[\text{PtF}_6]^-$  ion has been taken to be the same in both. The molar

TABLE

Molar susceptibility data (in c.g.s. units) for  $\text{O}_2^+[\text{PtF}_6]^-$ ,  $\text{NO}^+[\text{PtF}_6]^-$  and  $\text{O}_2^+$

Temp. (°K)	$10^6 \chi_M(\text{O}_2^+[\text{PtF}_6]^-)$	$10^6 \chi_M([\text{PtF}_6]^-)$	$\chi_M(\text{O}_2^+)$	$\mu_{\text{eff}}(\text{O}_2^+)$	$\mu(\text{NO})(8)$
80	6490	3590	2900	1.36	—
100	5500	2900	2600	1.42	—
140	4150	2160	1990	1.50	1.64
180	3400	1740	1660	1.55	1.71
220	2860	1470	1390	1.57	1.77
260	2490	1290	1200	1.58	1.82
300	2170	1140	1030	1.57	1.86

$\chi_M$ -Values from plots of  $\chi_M$  against  $T^\circ\text{K}$

an excess of nitrosyl fluoride (8.46 mmoles). The mildly exothermic reaction produced fluorine (2.67 mmoles) which was identified by, (1) its vapour pressure at  $-196^\circ$ , (2) absence of infrared absorption, and (3) its complete reaction with liquid mercury. The mustard yellow solid product was characterized by (1) analysis, (2) X-ray powder-photography, (3) infrared spectroscopy, and (4) magnetic-susceptibility measurement, as nitrosyl hexafluoroplatinate(V). The salt is isomorphous with its dioxygenyl analogue and with the other third-transition-series salts, the crystal

susceptibility of the  $[\text{PtF}_6]^-$  ion was evaluated by making a diamagnetic correction of  $10 \times 10^{-6}$  c.g.s. units for the  $\text{NO}^+$  ion. The susceptibility of the  $\text{O}_2^+$  ion was obtained by difference from the  $\text{O}_2^+[\text{PtF}_6]^-$  data. The results are given in the Table. The results quoted for  $\text{O}_2^+[\text{PtF}_6]^-$  are new values obtained from a sample prepared by the reaction  $\text{O}_2 + \text{PtF}_6 \rightarrow \text{O}_2\text{PtF}_6$ . They are similar to the data given previously.<sup>1b</sup>

As anticipated<sup>1,7</sup> for the "non-bonding" valence electron configuration  $d_{t(2g)}^5$ , in an octahedral field, the (temperature-independent) magnetic

\* Some  $\text{ONF}_3$  has been detected in the gaseous product, by infrared spectroscopy.

moment of the  $[\text{PtF}_6]^-$  ion,  $\mu'_{\text{eff}} = 1.74$  B.M., is very close to the spin-only value, for one unpaired electron, of 1.73 B.M. The susceptibility derived for the  $\text{O}_2^+$  ion is smaller than that of NO at the same temperature, but the marked diminution in moment with reduction in temperature is similar to the behaviour of NO.<sup>8</sup> Like the latter, the  $\text{O}_2^+$  ion is therefore assigned a  ${}^2\Pi$  ground state, the reduced moment at lower temperatures being due to spin-orbit coupling. A greater splitting of the  $J = \frac{3}{2}, \frac{1}{2}$  levels in  ${}^2\Pi \text{O}_2^+$  compared with  ${}^2\Pi \text{NO}$  would account for the lower value of the moment in  $\text{O}_2^+$ .

Since the formula-unit volume of  $\text{NO}^+[\text{PtF}_6]^-$  ( $U/Z = 129.5\text{\AA}^3$ ) is  $\sim 3\text{\AA}^3$  greater than for  $\text{O}_2^+[\text{PtF}_6]^-$  ( $U/Z = 126.3\text{\AA}^3$ ) and since the interionic forces must be similar for the two cases, it is probable that the  $\text{NO}^+_{(\text{c})}$  is  $\sim 3\text{\AA}^3$  larger than  $\text{O}_2_{(\text{c})}$ . Evidently the greater total nuclear charge of the  $\text{O}_2^+$  outweighs the effect of the antibonding  $\pi$ -electron, which is usually visualized as adding to the effective size of such a species. A similar effect is seen in a comparison of the molecular volume of solid fluorine<sup>9</sup> ( $\beta$ -form  $37.1\text{\AA}^3$ ) with its solid oxygen isomorph ( $\gamma$ -form  $39.8\text{\AA}^3$ ).

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