

THE CRYSTAL STRUCTURE OF $\text{O}_2^+\text{RuF}_6^-$ AND THE NATURE OF O_2RhF_6 Philippe Botkovitz^a, George M. Lucier^a, Ramesh P. Rao^b, and Neil Bartlett^{a*}

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Abstract

The 146°K X-ray structure of an $\text{O}_2^+\text{RuF}_6^-$ single crystal {cubic: $a = 9.9125(15)$ Å, $V = 974.0(4)$ Å³ $Z = 8$, space group Ia3} obtained from a liquid anhydrous HF (aHF) solution has proved the previously conjectured three-fold disorder of the O_2^+ species and gives interatomic distances O-O = 1.125(17) and RuF = 1.851(2) Å. Interaction of RhF_6 with O_2 in aHF at ≤ 20 °C, gives a red-brown cubic solid having a similar X-ray powder pattern (XRDP) to that of $\text{O}_2^+\text{RuF}_6^-$ but, contrary to expectation for $\text{O}_2^+\text{RhF}_6^-$, it has a larger cell, with $a = 10.17(1)$ Å, $V = 1052(3)$ Å³, $Z = 8$. $\text{NO}^+\text{RhF}_6^-$ is rhombohedral with $a = 5.046(5)$ Å, $\alpha = 97.8(5)$ °, $V = 124.6(4)$ Å³ and isostructural with $\text{NO}^+\text{AuF}_6^-$, and $\text{O}_2^+\text{AuF}_6^-$, the latter having smaller formula unit volume than the former. This suggests that the charge transfer in O_2RhF_6 is less complete than in $\text{O}_2^+\text{RuF}_6^-$ and that the electron affinity of RhF_6 may be less than that of RuF_6 .

Introduction

X-ray powder diffraction data provided powerful structural evidence to support the formulation for the first O_2^+ salt [1], $\text{O}_2^+\text{PtF}_6^-$. The light-atom placement was not sufficiently precise to settle this formulation by itself, however, and it was only the combination of this structural information with the magnetic and chemical properties of $\text{O}_2^+\text{PtF}_6^-$ that established it. N.K. Jha prepared a sample of O_2PtF_6 for the neutron diffraction structure which was carried out by Ibers and Hamilton [2]. They had to

assume that the O_2^+ were tilted off the three-fold axes to avoid an absurdly short O-O distance. This required that there be a three-fold disordering of the O_2^+ .

Subsequently, other O_2^+ salts were prepared and characterized by vibrational spectroscopy and X-ray powder diffraction (XRDP) by Falconer and his coworkers [3]. These included $O_2^+RuF_6^-$, which appeared to be a close structural relative of $O_2^+PtF_6^-$. Because Ru has a lower scattering factor and a lower absorption coefficient than Pt, this new salt promised to give more accurate light atom placement, from a single crystal, even with X-ray data. Although single crystal structural work of Graudejus and Müller, has been described [4] for a variety of $O_2^+MF_6^-$ salts (M = Sb, Ru, Pt, Au) the authors unfortunately did not adopt the postulated cation disorder of Ibers and Hamilton in their refinements of the Ia3 structures. With the recent discovery [5], in these laboratories, of efficient room temperature syntheses for the platinum metal hexafluorides, and the finding [6] that O_2^+ salts can be recovered from aHF solution without significant loss, single crystals of $O_2^+RuF_6^-$ were prepared for a higher-precision structural analysis for O_2^+ . Concurrently a reinvestigation of O_2RhF_6 was undertaken to clarify the structure type, since, Falconer and his coworkers had not succeeded in obtaining useful XRDP.

O_2RhF_6 is cubic and its XRDP shows a close similarity with those of O_2RuF_6 and O_2PtF_6 . Since $NORhF_6$ is rhombohedral, like $NOAuF_6$, and the latter [7] is isomorphous with O_2AuF_6 (which has a slightly smaller unit cell) it was expected that the O_2RhF_6 would also be rhombohedral and of small formula-unit volume. It is not. Reasons for this discrepancy are discussed.

Experimental

Materials, Apparatus and Techniques. The sources of aHF, F_2 , platinum metals, translucent fluorocarbon polymer tubing (FEP), Teflon Swagelock fittings, and Teflon valves, were as previously described [6] as were the fluorine handling and vacuum lines [8]. O_2RuF_6 was made [5] by addition of O_2 to RuF_6 prepared by oxidation of RuF_6^- in aHF at 20 °C with cationic Ag(III). O_2RhF_6 was prepared as follows: With [9] $KRhF_6$ (86.6 mg, 0.338 mmol), $KAgF_4$ purified [10] (139.5 mg, 0.626 mmol) and BiF_5 (828.4 mg, 2.725 mmol) in one arm of a FEP T-reactor, aHF (2.2 ml) was added and the

mixture warmed to $\sim 20^\circ\text{C}$. The aHF became blood red (**RhF₆**). No F₂ was detected when the mixture was cooled to 77 °K. O₂ (~ 200 torr and > 1 mmol) was admitted to the reactor and as the aHF melted a red-brown solid was formed in an orange solution. Removal of aHF in a dynamic vacuum (~ 2 h) left a red-brown solid (15.5 mg, 0.062 mmol O₂RhF₆, an 18% yield). An XRDP showed a cubic pattern akin to those [1,3] of O₂MF₆ (M = Pt, Ru) (see Table 1). **NORhF₆** was made as a red solid by warming (~ 100 °C) RhF₅ (prepared as previously described [9]) in an atmosphere of ONF in a nickel Teflon-gasketed can. An XRDP of this solid showed a sharp rhombohedral pattern, very similar to that [7,11] of NO⁺AuF₆⁻ and was fully indexed on such a cell (see Table 2).

Structure Determination of O₂⁺RuF₆⁻. Dark red crystals were obtained by slow distillation of aHF from a 20 °C solution of the salt, (contained in one arm of a FEP T apparatus) to the other limb, which was cooled slightly below 20°C by controlled evaporation of water in a Dewar flask surrounding that limb. The vacuum dried crystals were manipulated into drawn-down quartz capillaries in the dry argon atmosphere of a Vacuum Atmospheres Corp. Drilab. Each capillary was closed with Kel-F grease and sealed by drawing down in a small flame. After a primary microscopic sorting (with polarized light) suitable crystals were examined on the Enraf-Nonius CAD-4 diffractometer [12] used for the data collection and the best in size and shape was used for data collection. Two data sets were recorded, the first at 20°C and the second at -127°C. Automatic peak search and indexing procedures gave a rhombohedral reduced cell. Inspection of the Niggli values [13] revealed the cubic body-centered cell. The final cell parameters and specific data collection parameters for the two data sets are given in Table 3.

The raw intensity data (1880 at 20°C, 1559 at -127°C) were converted to structure factor amplitudes and their esds by correction for scan speed, background and

Table 1. X-ray powder data* (Cu K α radiation, Ni filter) for O₂RhF₆, cubic cell (probable space group, Ia $\bar{3}$, No. 206) with $a = 10.17(1)$ Å, $V = 1051(4)$ Å³, $Z = 8$.

I/I_0	$1/d^2 \times 10^4$			I/I_0	$1/d^2 \times 10^4$		
	obs	calc	hkl		obs	calc	hkl
s	388	387	200	ms	2329	2319	422
vs	776	773	220	w	3103	3092	440
w	1159	1160	222	m	3489	3479	600
vw	1541	1546	400	w	3862	3865	620
mw	1925	1933	420	vw	5428	5411	642
vwv [†]	2142	2126	332				

* The poor crystallinity of the material rendered lines beyond no. 8 rather broad, nevertheless the simple cubic progression of the strong lines was clearly discernable to a much higher angle.

[†] This line indicates the need for the $z = 8$ unit cell, Rh does not contribute to this line intensity.

Table 2. X-ray powder data (Cu K α , Ni filter) for NO⁺RhF₆⁻, with a rhombohedral cell (possible space group, R $\bar{3}$) $a = 5.046(5)$ Å; $\alpha = 97.8(5)^\circ$; $V = 124.6(4)$ Å³; $Z = 1$

I/I_0	$1/d^2 \times 10^4$			I/I_0	$1/d^2 \times 10^4$		
	obs	calc	hkl		obs	calc	hkl
10	410	410	100	1	3123	3100	211
9	694	692	10 $\bar{1}$	3	3183	3178	21 $\bar{2}$
7	948	948	101	5	3712	3690	300
5	1105	1102	11 $\bar{1}$	"	"	3716	30 $\bar{1}$
3	1645	1640	200	1	3795	3792	202
		1714	111			3870	$\bar{3}11$
1	1794	1794	20 $\bar{1}$	1	4398	4382	31 $\bar{1}$
2	2078	2076	$\bar{2}11$	"	"	4408	22 $\bar{2}$
9, <i>br</i>	2327	2306	201	2	4496	4484	301
"	"	2332	21 $\bar{1}$	<1	4559	4562	30 $\bar{2}$
2	2772	2768	20 $\bar{2}$				

br: broad

Table 3. Crystal and data parameters for O₂RuF₆
Empirical formula: RuF₆O₂

<p>A) Crystal Parameters at T = -127°C [a,b] a = 9.9126(15) Å Space Group: Ia3- b = 9.9126(15) Å c = 9.9126(15) Å Z = 8 α = 90.0° d(calc) = 3.37 g cm⁻³ β = 90.0° d(obs) = γ = 90.0° μ(calc) = 32.4 cm⁻¹ V = 974.0(4) Å³ Size: 0.20x0.20x0.15 mm Formula weight = 247.1 amu</p> <p>B) Data Measurement Parameters [12] Radiation : Mo Kα (λ = 0.71073 Å) Monochromator : Detector : Reflections measured : +/-H, + K, + L 2θ range: 3 -> 60 deg Scan Type: omega Scan width: Scan speed: Background:</p> <p>Vert. Aperture = 4.0 mm Horiz. aperture = 2.0 + 1.0 tan θ mm No. of reflections collected: 1559 No. of unique reflections: 241</p>	<p>A) Crystal Parameters at T = 25 °C [a,b] a = 9.9998(15) Å Space Group: Ia3- b = 9.9998(15) Å c = 9.9998(15) Å Z = 8 α = 90.0° d(calc) = 3.28 g cm⁻³ β = 90.0° d(obs) = γ = 90.0° μ(calc) = 31.5 cm⁻¹ V = 999.9(4) Å³ Size: 0.20x0.20x0.15 mm</p> <p>B) Data Measurement Parameters [12] Radiation : Mo Kα (λ = 0.71073 Å) Highly-oriented graphite (2θ = 12.2) Crystal scintillation counter, with PHA. Reflections measured : +/-H, +/-K, + L 2θ range: 3 -> 50°C Scan Type: theta-2theta Δω = 0.90 + 0.35 tanθ 8.24 (θ, deg/min) Measured over 0.25*(Δω) added to each end of the scan. Vert. aperture = 4.0 mm Horiz. aperture = 2.0 + 1.0 tanθ mm No. of reflections collected: 1880 No. of unique reflections: 149</p>
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Intensity standards: (008),(660),(-6 6 0); measured every 1 hour of x-ray exposure time. Over the data collection period no net decrease in intensity was observed.

Orientation: Three reflections were checked after every 250 measurements. Crystal orientation was redetermined if any of the reflections were offset by more than 0.10 degree from their predicted positions. Reorientation was once during data collection.

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo K α components of 22 reflections with 2θ between 28° and 36°.

[b] In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) of the reported value.

Lorentz and polarization effects [14,15]. No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data [16] showed a variation which was not symmetric around 180° in ϕ , probably due to a mis-centering of the crystal. For this reason an empirical correction was made to the data based on the combined differences of F_{obs} and F_{calc} following refinement of all atoms with isotropic thermal parameters ($T_{max} = 1.16$, $T_{min} = 0.87$, no θ dependence) [17]. Inspection of the systematic absences indicated uniquely space group $Ia\bar{3}$. Removal of systematically absent data and averaging of redundant data yielded the unique data in the final sets, which were 149 for 20°C and 241 for -127°C . For the former, $R(I) = 5.1\%$ for observed data and 5.4% for all data, and for the latter $R(I) = 3.9\%$ for the observed data and 4.3% for all data.

The structure was solved first with the 20°C data, by substitution of the Ru and F positions from the known structure of $\text{O}_2^+\text{PtF}_6^-$ [2] and refined via standard least-squares and Fourier techniques. Following isotropic refinement of the Ru and F, there was only one peak (at $1/4, 1/4, 1/4$) found in the difference Fourier map. This peak was very elongated, however, and was satisfactorily modeled to a first approximation by a unique O atom on the threefold axis $\sim 0.5 \text{ \AA}$ from the inversion center at $(1/4, 1/4, 1/4)$. (It was at this point that the absorption correction was made and the data were averaged.) Inspection of both the Fourier and difference Fourier maps following anisotropic refinement of the F atom showed clearly that the electron density was distorted in a pattern consistent with a small offset of the O atom from the threefold axis. Attempts to refine a partially-occupied O atom in such a position with isotropic thermal parameters failed to converge. However, when the O atom was constrained to have an anisotropic thermal ellipsoid parallel to the threefold axis, refinement of the positional parameters converged smoothly. Figure 1 shows the contour maps of the Fourier and difference Fourier (after refinement) for the low temperature structure.

For the 20°C data set the final residuals for the 16 variables refined against the 92 data for which $F^2 > 3\sigma(F^2)$ were $R = 1.98\%$, $wR = 2.77\%$ and $\text{GOF} = 1.117$. The R value for all 149 data was 4.01% . In the case of the -127°C data set the results of the refinement were much more clear cut, because of the higher resolution that was

attained. The final residuals for the 16 variables against the 130 data for which $F^2 > 3\sigma$ (F^2) were $R = 1.72\%$, $wR = 2.17\%$ and $GOF = 0.865$. The R value for all 241 data was 3.93% .

The quantity minimized by the least squares program was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p -factor, used to reduce the weight of intense reflections, was set to 0.03 throughout each of the refinements. The analytical forms of the scattering factor tables for the neutral atoms were used [18] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion [18].

Inspection of the residuals ordered in ranges of $\sin\theta/\lambda$, $|F_o|$, and parity value of the individual indexes showed that reflections with indexes all even had an average intensity 20 to 50 times that of the other parity groups. All trends in the residuals could be traced to that feature. For the two refinements, 20°C , (-127°C) the largest peak in the final difference Fourier map had an electron density of $0.59 \text{ e}^-/\text{\AA}^3$ ($0.38 \text{ e}^-/\text{\AA}^3$) and the lowest excursion $-0.51 \text{ e}^-/\text{\AA}^3$ ($-0.58 \text{ e}^-/\text{\AA}^3$). Both were located near the Ru atom at the origin. There was no indication of secondary extinction in the high intensity low angle data.

The positional and thermal parameters of the atoms are given in Tables 4 and 5. A listing of the values of F_o and F_c are available as supplemental material.

Table 4. Positional parameters and their estimated standard deviations

-127 °C data				
Atom	x	y	z	B(Å ²)
Ru	0.000	0.000	0.000	1.638(9)*
F	0.107(2)	0.1407(2)	-0.0593(2)	2.39(4)
O	0.2742(8)	0.2660(7)	0.2988(7)	2.11(4)
20 °C data				
Atom	x	y	z	B(Å ²)
Ru	0.000	0.000	0.000	1.70(2)*
F	0.1077(4)	0.1378(4)	-0.0598(4)	3.14(7)
O	0.272(1)	0.265(1)	0.299(1)	3.41(8)

Starred atoms were included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as: $(4/3) [a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$ where a,b,c are real cell parameters, and $\beta(i,j)$ are anisotropic betas.

Table 5. Anisotropic Thermal Parameters - B's

-127 °C data							
Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	b(2,3)	Beqv
F	2.29(7)	2.12(8)	2.77(8)	-0.19(8)	0.47(9)	0.45(8)	2.39(4)
O	2.1(1)	B(1,1)	B(1,1)	0.7(1)	B(1,2)	B(1,2)	2.11(4)
20 °C data							
Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
F	2.9(1)	2.5(1)	4.0(2)	-0.4(1)	1.0(2)	0.8(2)	3.14(7)
O	3.4(3)	B(1,1)	B(1,1)	1.5(3)	B(1,2)	B(1,2)	3.41(8)

The form of the anisotropic temperature factor is: $\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$ where a,b, and c are reciprocal lattice constants.

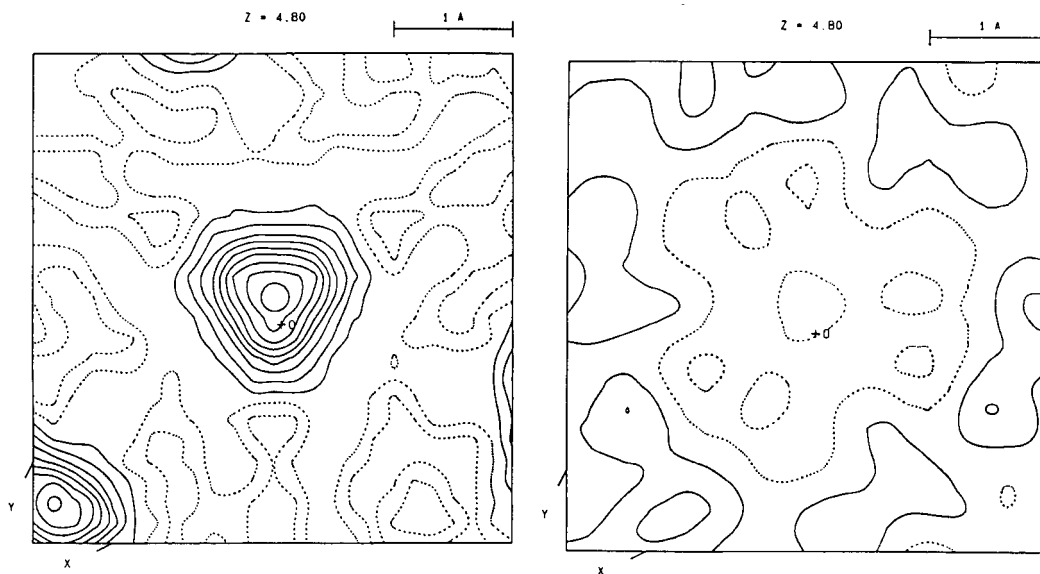


Figure 1. The low temperature data Fourier (l) and Difference Fourier(r) maps oriented so that [111] is perpendicular to the page at the center of each map; the $z = 4.80$ cut is through the O atom (adjacent contour lines represent differences of $1e^- / \text{\AA}^3$)

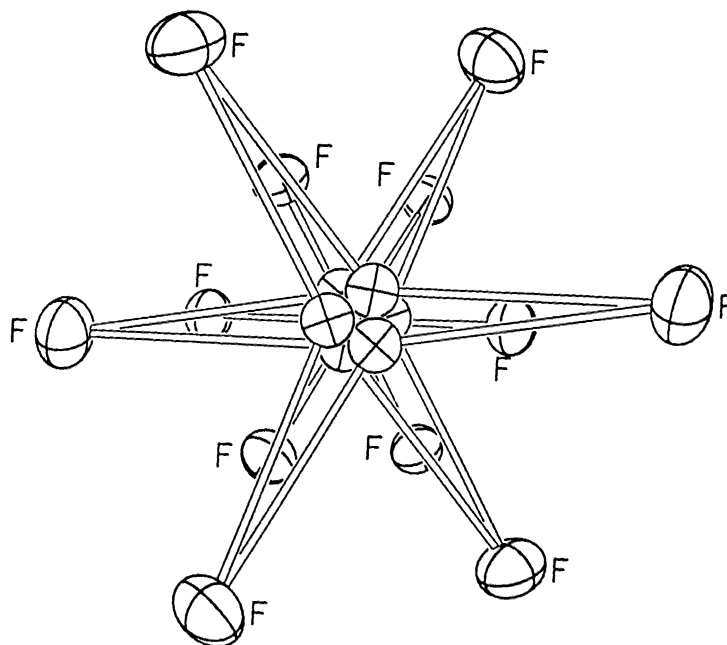


Figure 2. The closest F contacts to the disordered cation in (low temperature) O_2RuF_6 (The ellipsoids are scaled to represent the 50% probability surface)

Results and Discussion

Table 6. Interatomic distances (Å, σ value in parentheses) in O_2RuF_6 (-127 °C and 20 °C data)

-127 °C			20 °C		
Ru	F	1.851(2)	Ru	F	1.848(4)
O	O	1.125(17)	O	O	1.12(4)
F	O	2.359(22)	F	O	2.37(6)
F	O	2.610(13)	F	O	2.63(3)
F	O	2.36(3)	F	O	2.39(7)

Interatomic distances (given in Table 6) for the low temperature structure of $\text{O}_2^+\text{RuF}_6^-$ are not significantly different from those from the room temperature data. The RuF_6^- is slightly elongated along the threefold axis with $\text{F-Ru-F}=90.7(1)^\circ$ and $\text{F-Ru-F} = 89.3(1)^\circ$, and in accord with the site symmetry there is only one $\text{Ru-F} = 1.8514(22)$ Å.

It is the O_2^+ species, however, which is of prime interest in this structure. Herzberg gives [19] the ground state internuclear separation as 1.1227 Å, and the distance observed here of 1.125(17) Å is in harmony with that. Falconer and his coworkers [3] had observed the stretching frequency for the cation in this salt to be 1838 cm^{-1} which is to be compared with their value for $\text{O}_2^+\text{SbF}_6^-$ which is 1861 cm^{-1} . Since Herzberg's value for the gaseous ion, ω_e , is 1876.4 cm^{-1} it is clear that the cation in the antimony salt is more perfectly O_2^+ . {There is probably also a lattice (Coulomb) effect on $\nu(\text{O}_2^+)$, the $\text{O}_2^+\text{SbF}_6^-$ being actually fully ionic.} It is possible that the significant diminution in stretching frequency in the RuF_6^- salt is associated with incomplete electron transfer, at any instant there being a small population of neutral O_2 and RuF_6 in the lattice. The presence of neutral RuF_6 nicely accounts for the red color of the salt, since alkali RuF_6^- salts and O_2^+ salts such as $\text{O}_2^+\text{SbF}_6^-$ have little or no color. Much the same can be said for $\text{O}_2^+\text{PtF}_6^-$ [1] which is dark red, whereas all other PtF_6^- salts are yellow. In $\text{O}_2^+\text{PtF}_6^-$ $\nu(\text{O}_2^+) = 1838 \text{ cm}^{-1}$ also [3]. It is therefore possible, that the interatomic distance in the cation in these last two salts is the same, and slightly

longer than in the gaseous ion. This brings us to an interesting question concerning the nature of $\text{O}_2^+\text{RhF}_6^-$.

Although Falconer and his coworkers [3] gave evidence for the existence of $\text{O}_2^+\text{RhF}_6^-$ they were unable to obtain satisfactory XRDP to support the formulation. They did, however, determine $\nu(\text{O}_2^+) = 1825 \text{ cm}^{-1}$ *i.e.* $\sim 50 \text{ cm}^{-1}$ below $\omega_e(\text{O}_2^+)_{(g)}$. This hints that there are more neutrals in this material than in the Ru and Pt salts. For neutral O_2 , $\omega_e(\text{O}_2) = 1580 \text{ cm}^{-1}$ [19], *i.e.* $\sim 300 \text{ cm}^{-1}$ lower than ω_e for (O_2^+) . Taking the structurally related $\text{O}_2^+\text{SbF}_6^-$, which has $\nu(\text{O}_2^+) = 1861 \text{ cm}^{-1}$, as fully ionic, the decrease of 36 cm^{-1} in the Rh compound could mean that, in it, more than 10% of the O_2 species could be neutral at any instant, the life-time of neutral or cation being short with respect to a vibration.

The availability, from recent work [5], of a convenient room temperature synthesis for the platinum-metal hexafluorides, encouraged a new investigation of O_2RhF_6 . The synthesis of RhF_6 proceeded as smoothly as it had done [5] for PtF_6 and RuF_6 :



Addition of O_2 to the aHF solution produced a red-brown solid at 20°C . This gave a cubic XRDP which bore a close resemblance to that of $\text{O}_2^+\text{RuF}_6^-$, with the usual light-atom super-lattice reflections indicative of the Ia3 space group. A very surprising feature of the pattern, however, was the clear evidence that the unit cell was larger than that of $\text{O}_2^+\text{RuF}_6^-$. Earlier work [9] had shown that RhF_6^- salts were roughly isodimensional with PtF_6^- salts, and recent work in these laboratories [20] has provided the LiMF_6 salts ($M = \text{Ru}, \text{Rh}$) the formula-unit volumes of which are respectively $100.70(3)$ and $98.40(4) \text{ \AA}^3$. The anomalous formula-unit volume of $\text{O}_2^+\text{RuF}_6^-$ is all the more striking when the $\text{NO}^+\text{RhF}_6^-$ salt is considered. The latter has a rhombohedral cell, similar to that adopted by $\text{NO}^+\text{AuF}_6^-$ and $\text{O}_2^+\text{AuF}_6^-$ [7]. It appears, that at a critical effective volume size for the anion, there is a switch from cubic to rhombohedral symmetry, with the latter favored by smaller species. Since the NO^+ cation is effectively

4.4 Å³ larger than O₂⁺ in the gold salts [7] a similar difference was expected for the rhodium pair. Instead, the O₂RhF₆ is cubic, and appears to be 6.5 Å³ larger even than O₂RuF₆. It is possible that this is a consequence of considerably less charge than in the Ru salt case. If so, the electron affinity of RhF₆ must be less than that of RuF₆, since in other salts (*e.g.* Li⁺) the Rh anion, as expected from its greater nuclear charge, is smaller than its Ru relative. If this is so, it stands in marked contrast to the behavior of the third transition series hexafluorides, where the chemical properties of these nearly isodimensional molecules establish [21,22] that IrF₆ has a higher electron affinity than OsF₆. Perhaps in the second transition series, exchange energy effects [23] are more important than in the third. So RuF₆, which has a $d t_{2g}^2$ configuration gains appreciable exchange energy when it takes an electron and attains the highly favorable $d t_{2g}^3$ configuration. In contrast the RhF₆ molecule already has the latter favorable configuration, and in acquiring another electron, (to become $d t_{2g}^4$) it gains no exchange energy. In addition that added electron has to be paired, and this contributes unfavorably to the total energy of the system. It is therefore not so surprising that RhF₆ should be inferior to RuF₆ as an oxidizer. What is surprising is that IrF₆ is superior to OsF₆.

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Povzetek

Kristalna struktura $\text{O}_2^+\text{RuF}_6^-$ in narava O_2RhF_6

Rentgenska kristalna struktura $\text{O}_2^+\text{RuF}_6^-$ {kubična: $a = 9,9125(15)\text{Å}$, $V = 974,0(4)\text{Å}^3$, $Z = 8$, prostorska skupina $Ia3$, določena pri 146 K, je potrdila prejšnjo domnevo o trojnem neredu zvrsti O_2^+ in daje medatomske razdalje $\text{O-O} = 1,125(17)$ in $\text{Ru-F} = 1,851(2)\text{Å}$. Monokristal je bil pripravljen iz raztopine $\text{O}_2^+\text{RuF}_6^-$ v brezvodnem vodikovem fluoridu (aHF). Pri reakciji RhF_6 z O_2 v aHF pri # 20 EC dobimo rdeččrjav kubično trdno snov, ki ima podoben rentgenski praškovni posnetek kot $\text{O}_2^+\text{RuF}_6^-$ toda, v nasprotju s pričakovanji za $\text{O}_2^+\text{RhF}_6^-$, večjo osnovno celico z $a = 10,17(1)\text{Å}$, $V = 1052(3)\text{Å}^3$, $Z = 8$. $\text{NO}^+\text{RhF}_6^-$ je romboedričen z $a = 5,046(3)$, $\alpha = 97,8(5)^\circ$, $V = 124,6(4)\text{Å}^3$ in izostrukturen z $\text{NO}^+\text{AuF}_6^-$ in $\text{O}_2^+\text{AuF}_6^-$. Slednji ima manjši volumen osnovne celice (V/Z) kot prvi. To kaže na to, da je prenos naboja v O_2RhF_6 manjši kot v $\text{O}_2^+\text{RuF}_6^-$ in da naj bi bila elektronska afiniteta RhF_6 manjša kot pri RuF_6^- .