Lawrence Berkeley National Laboratory

Recent Work

Title

THE CRYSTAL STRUCTURE OF RHODIUM PENTAFLUORIDE

Permalink

<https://escholarship.org/uc/item/8rr7v0p0>

Authors

Morrell, Barbara K.

Zalkin, Allan

Tressaud, Alain

et al.

Publication Date

1973

Submitted to
Inorganic Chemistry

RECEIVED
INORGANIC
LABORATORY

LBL-1154 c.1
Preprint

RECEIVED
INORGANIC
LABORATORY

THE CRYSTAL STRUCTURE OF RHODIUM PENTAFLUORIDE

Barbara K. Morrell, Allan Zalkin,
Alain Tressaud and Neil Bartlett

January 8, 1973

Prepared for the U. S. Atomic Energy
Commission under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-1154
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Contribution from the Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Chemistry; University of California, Berkeley, California 94720.

THE CRYSTAL STRUCTURE OF RHODIUM PENTAFLUORIDE

by

Barbara K. Morrell, Allan Zalkin, Alain Tressaud and Neil Bartlett

Received:

ABSTRACT

The crystal structure of rhodium pentafluoride has been determined from three dimensional X-ray data. The compound is monoclinic, $P2_1/a$, with $a = 12.3376(13)$, $b = 9.9173(8)$, $c = 5.5173(6)$ Å, $\beta = 100.42(2)^\circ$, $V = 663.85$ Å³, $z = 8$, $d_c = 3.95$ g cm⁻³. A final conventional R factor of 0.029 was obtained using 1207 non-zero reflections. The structural unit is a fluorine bridged tetramer similar to those reported for $(RuF_5)_4$ and $(OsF_5)_4$. Each Rh atom is coordinated by six fluorine atoms in an approximately octahedral arrangement. Each of a cis pair of F atoms in the RhF_6 group is shared with another Rh atom, the Rh-F-Rh angle being $135 \pm 1^\circ$ and the Rh-F interatomic distance $\sim 2.01 \pm 0.01$ Å. For the other F atoms in the RhF_6 group the Rh-F interatomic distances are within the range 1.81 - 1.83 Å.

INTRODUCTION

Of the Group VIII transition metals, the following pentafluorides are known: RuF_5 ,¹ OsF_5 ,² RhF_5 ,³ IrF_5 ,⁴ and PtF_5 .⁵ Attempts to prepare PdF_5 have failed so far⁶. The crystal structures of RuF_5 and OsF_5 have been reported^{7,8}, and X-ray powder photography has shown^{4,3} all of the platinum-metal pentafluorides to be isomorphous. Evidently these pentafluorides constituted a class which was structurally distinct⁴ from the pentafluorides of Tc ⁹ and Re ¹⁰ on the one hand and those of Nb ¹¹, Mo ¹², Ta ¹¹ and W ¹³ on the other hand. Although the close resemblance of the X-ray powder photographs of the pentafluorides of Rh , Ir and Pt (see accompanying paper¹⁴) suggested close structural similarities, the isostructural relationship to those of Ru and Os remained to be proved. Furthermore, neither the RuF_5 nor the OsF_5 structure has been determined with high precision. Although more difficult to handle than IrF_5 and PtF_5 , RhF_5 offered the possibility of highest precision as a consequence of lower absorption coefficient and the lower ratio of the metal to fluorine scattering factors. Accordingly we undertook the structure determination of RhF_5 .

EXPERIMENTAL SECTION

Crystal Data.- Rhodium pentafluoride was prepared as described in the accompanying paper¹⁴. Crystals were grown by vacuum sublimation in a quartz tube, the parent sample being at -100° . A ruby-red crystal grown in this way, approximately $0.130 \times 0.11 \times 0.07\text{mm}$ was wedged in a drawn 0.3 mm diameter quartz X-ray capillary, which was sealed under dry nitrogen.

RhF_5 (mol wt 197.9) is monoclinic with $a = 12.3376(13)$, $b = 9.9173(8)$, $c = 5.5173(6)$ Å and $\beta = 100.42(2)^\circ$, $V = 663.85$ Å³, $z = 8$, $d_c = 3.95$ g cm⁻³. As usual with dense, reactive fluorides, the number of fluorine atoms in the unit cell was estimated by applying Zachariason's criterion¹⁵ of ~ 18 Å³ per F atom. This indicated $z = 8$. Single-crystal precession photographs indicated the systematic absences $h\ 0\ l$ when $h = 2n + 1$ and $0\ k\ 0$ when $k = 2n + 1$. The structure was successfully refined in the space group $P2_1/a$ indicated by the systematic absences.

X-Ray Measurements.- A Picker automatic four circle diffractometer, equipped with a fine focus Mo anode tube, was used for data collection. Twelve high-angle reflections, using $\text{MoK}\alpha_1$ ($\lambda = 0.709261$ Å) radiation, at a take-off angle of $\sim 2^\circ$ and were used for a least-squares refinement of the cell parameters. Data were collected and treated as described in a recent article¹⁶. Three standard reflections (040), (080), and (600) were monitored every 200 reflections and showed no decay in intensity during the course of data collection. All reflections of the form $\pm\ h\ k\ l$ were measured out to a 2θ angle of 60° . A total of 2124 intensity data were collected and averaged to yield a data set of 1945 unique reflections, 1775 of which were greater than background and 1504 satisfied the criterion $I > \sigma(I)$. An omega scan of the crystal showed a peak width at half height of $\sim 0.1^\circ$. Although, for RhF_5 , the absorption coefficient $\mu = 50.02$, the small size ($\mu r \approx 0.5$) and regular shape of the chosen crystal permitted us to ignore an absorption correction. The only other difference from the previously described data treatment¹⁶ was in the choice of the value of g , the arbitrary factor, employed to prevent relative error for large counts becoming unrealistically small. This factor was originally set at

0.04 but was increased to 0.05 in the final refinement to improve weighting.

Structure Refinement.- Programs used in the structure solution and refinement were as previously described¹⁶. Scattering factors for neutral fluorine were taken from Turner and Doyle¹⁷ and those for neutral Rh from the tables of Cromer and Waber¹⁸.

A three-dimensional Patterson synthesis provided for a ready location of the two rhodium atoms of the asymmetric unit. Three cycles of full-matrix least-squares refinement, employing isotropic thermal parameters for the Rh atoms resulted in a conventional R factor¹⁶ of 0.25 for 1504 reflections for which $I > \sigma(I)$. A Fourier synthesis revealed ten major peaks, in addition to the two Rh atom peaks in the asymmetric unit. These 10 peaks were assigned as F atoms and with isotropic thermal parameters refined to a final conventional $R = 0.067$. Three cycles of least-squares refinement, allowing anisotropic thermal parameters for the rhodium atoms resulted in an R factor of 0.049. A difference Fourier at this point showed that all peaks had been taken into account by the structure. The final cycle of least-squares, refining all atoms anisotropically, gave $R = 0.041$. Limiting the refinement to the 1207 data for which $I > 3\sigma(I)$ reduced the R to 0.033. An extinction correction of the form $F_o^1 = F_o[1.0 + \epsilon \times I]$ where $\epsilon = 1.6 \times 10^{-7}$ was applied to correct for discrepancies of high intensity reflections. This correction resulted in a final R value of 0.029 for the non-zero weighted data. Including zero-weighted data, R was 0.054 for 1945 data, and the standard deviation of an observation of unit weight was 1.09. The final weighted¹⁶ R_2 was 0.037. Final positional and thermal parameters given in Table I are from the last refinement. The F_o and F_c data for RhF_5 (Table II) are given in the

microfilm version of this paper.¹⁹

DESCRIPTION OF STRUCTURE

Crystals of rhodium pentafluoride consist of close-packed tetrameric units. The tetramer is illustrated in Figure 1, and documented in Table III. The packing of the tetramers is shown in Figure 2. The F atom arrangement in the structure approximates to a hexagonal close packed arrangement as described⁸ by Mitchell and Holloway for OsF_5 and RuF_5 . The relationship of the tetramer unit to the "hexagonal-close-packing" is shown in Figure 3. The closest interatomic distances between tetramers are consistent with van der Waals interactions.

The tetrameric unit consists of somewhat distorted octahedral RhF_6 groups sharing cis corners (Figure 1). The shared (bridging) fluorine atoms and the rhodium atoms constitute a puckered eight-membered ring. The tetramer is centered on a center of symmetry but contains two crystallographically non-equivalent RhF_6 groups. The structure analysis reveals that these two crystallographically distinct RhF_6 groups are the same size and shape. Each RhF_6 group has been distorted from octahedral symmetry as a consequence of each of a pair of F-ligands (in cis relationship) being involved in bridge bonding to another Rh atom. In each RhF_6 group, the bridging-F atoms are further from the rhodium atom than the non-bridging atoms, the averaged interatomic distances being 2.003 and 1.816 Å, respectively. The bridging F ligands, being further from the Rh atom are also further from the other F ligands of the RhF_6 group. Ligand repulsions in the RhF_6 group must, therefore, be smaller for the bridging F atoms than for the non-bridging.

This is no doubt why, in each RhF_6 group, the non-bridging F ligands, above and below the plane containing the bridging F ligands, are displaced towards the bridging-F edge of the octahedron.

Not only are the two crystallographically distinct RhF_6 groups very similar, so are the two Rh(1)-F-Rh(2) bridge features. The close similarity of the bridges is illustrated by interatomic distances and bond angles given in Figure 1, but the closeness of the Rh(1)-Rh(2) distances of 3.692(2) and 3.709(2) alone demonstrates this similarity. Each bridging F ligand is, within the estimated standard deviations, equidistant from the two Rh atoms to which it is coordinated. Nor are the Rh-F(5) distances significantly different from the Rh-F(6) distances. The two Rh-F-Rh angles are 134.3(1) and 135.7(1).

There are no statistically significant variations in the non-bridging-fluorine Rh-F interatomic distances. The mean value of the Rh-F (non-bridging) interatomic distance (using the data from both RhF_6) is 1.816 Å.

DISCUSSION

The crystal structure of RhF_5 establishes that it is isostructural with RuF_5 ⁷ and OsF_5 ⁸, as the powder data had suggested^{3,4}. Unfortunately, the RuF_5 and OsF_5 structures are not of high precision and the clear differentiation of the non-bridging M-F interatomic distances from the bridging, seen in RhF_5 is not apparent in the OsF_5 and RuF_5 results^{7,8}. The shapes of the tetrameric units of RuF_5 and OsF_5 are, however, essentially the same as found for RhF_5 and the same bond length and bond angle pattern seen in $[\text{RhF}_5]_4$ probably pertains in them too.

Although single crystals of IrF_5 have been obtained¹⁴, none was of suitable size and shape to yield an accurate structure and when it

became clear that the structure would be no more precise than that reported for RuF_5 , the analysis was abandoned. Nevertheless, the precession and Weissenberg photographic data has established the space group $P2_1/a$ and indicates a close structural relationship to the other platinum-metal pentafluorides. We, therefore, believe that these pentafluorides will all show essentially the same tetrameric unit as detailed for RhF_5 in Figure 1 and Table III.

The distribution of known transition metal pentafluoride structure types, is shown in Table IV. The pentafluorides of Nb, Ta, Mo and W have been shown by Edwards and his coworkers^{11, 12, 13} to possess a square tetrameric unit with linear M-F-M bridge angles. The pentafluorides of Tc^9 , Re^{10} , Cr^{20} , and V^{10} have polymeric chain structures with bridging M-F-M angles¹⁰ of $\sim 150^\circ$. In the platinum-metal pentafluoride group, the M-F-M angle in the tetrameric unit is $\sim 135^\circ$. Edwards and Jones have stated¹⁰ that all of the structures exhibit close packing of the fluorine atoms. In the MoF_5 type structure¹² the fluorine atom array is distorted cubic close-packed, with metal atoms occupying one fifth of the octahedral holes, whereas, in the RuF_5 type a related but hexagonal close-packed arrangement pertains. (The hexagonal close packing in RhF_5 may be seen in Figure 3.) As may be seen from the effective formula unit volumes listed in Table IV, however, TeF_5 and ReF_5 are less close packed than their neighbors.

A pseudo-octahedral MF_6 unit is a feature of all of the structures of crystalline metal pentafluorides examined so far. The MF_6 units are usually linked by a sharing of cis related F atoms and the RhF_6 unit seen in $[\text{RhF}_5]_4$ is similar to units seen in the other pentafluoride

structures. Since the non-bonding M-F bonds are in the range 1.7-1.8 Å whereas the bridging M-F are 2.1-2.0 Å, we can safely assume that the former bonds are appreciably stronger than the latter. Indeed, description of the M-F-M bonds as three-center four-electron bonds²¹ and the non-bridging M-F bonds as electron-pair bonds seems appropriate. As has already been pointed out, however, the M-F-M bond is not the same for all of the bridged pentafluorides.

The near-hexagonal close-packing of the fluorine atoms in RhF_5 indicates that the M-F-M angle of $\sim 135^\circ$ seen in this structure must be as acute as any such bridging angle could become, without further lengthening of the bridging bonds relative to the non-bridging. It is notable that in AuF_3 polymer²², the Au-F-Au bridge angle is 116° , but the gold atom coordination, in F atoms, is four in a square, not octahedral.

The adoption of the RhF_5 type structure by those pentafluorides at the right hand end of each transition series suggests that the bridge-bonding in this type has a greater measure of covalency than in the other structure types. This is because the increasing nuclear charge in the series $\text{Nb} \rightarrow \text{Rh}$ and $\text{Ta} \rightarrow \text{Pt}$, is not screened by the formally 'non-bonding' d electrons (which occupy the $d_{t_{2g}}$ orbitals). Evidently in VF_5 and its structural relatives, the covalency constraint on the M-F-M bridging is great enough to render the better packed NbF_5 type structure energetically less desirable, but yet not great enough to produce the RhF_5 type. On the basis of this rationalization, the NbF_5 type structure comes closest to representation as an ionic assembly $(\text{MF}_4^+ \text{F}^-)_4$. Of the transition metal pentafluorides it is,

therefore, more likely that those of the NbF_5 type should form MF_4^+ salts with excellent F^- acceptors such as SbF_5 and Edwards²³ has already presented evidence for the salt $\text{NbF}_4^+ \text{SbF}_6^-$.

It remains to be seen whether AuF_5 , PdF_5 , and MnF_5 can be obtained as crystalline solids. There is no certainty that these pentafluorides would be fluorine bridged polymers and not monomers (like AsF_5 and PF_5) but if bridging does occur, the RhF_5 type structure appears to be the most likely one to be adopted.

ACKNOWLEDGMENTS

This work was sponsored under the auspices of the U. S. Atomic Energy Commission. One of us (A.T.) thanks C.R.N.S. for fellowship support.

REFERENCES

1. O. Ruff and E. Vidic, Z. anorg. Chem. 143, 163 (1925).
2. G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 2618 (1960).
3. J. H. Holloway, P. R. Rao, and N. Bartlett, Chem. Commun., 393 (1965).
4. N. Bartlett and P. R. Rao, Chem. Commun., 252 (1965).
5. N. Bartlett and D. H. Lohmann, Proc. Chem. Soc. 14 (1960); J. Chem. Soc. 619 (1964).
6. N. Bartlett and K. Leary, to be published.
7. J. H. Holloway, R. D. Peacock, and R. W. H. Small, J. Chem. Soc., 644 (1964).
8. S. J. Mitchell and J. H. Holloway, J. Chem. Soc.(A), 2789 (1971).
9. A. J. Edwards, D. Hugill, and R. D. Peacock, Nature, 200, 672 (1963).
10. A. J. Edwards and G. R. Jones, J. Chem. Soc. (A), 1651 (1969).
11. A. J. Edwards, J. Chem. Soc., 3714 (1964).
12. A. J. Edwards, R. D. Peacock, and R. W. H. Small, J. Chem. Soc., 4486 (1962).
13. A. J. Edwards, J. Chem. Soc.(A), 909 (1969).
14. N. Bartlett, P. R. Rao, and M. Akhtar, Inorg. Chem., (accompanying paper).
15. W. H. Zachariason, J. Amer. Chem. Soc., 70, 2147 (1948).
16. D. D. Gibler, C. J. Adams, M. Fischer, A. Zalkin, and N. Bartlett, Inorg. Chem. 11, 2325 (1972).
17. P. A. Doyle and P. S. Turner, Acta Cryst. A24, 390 (1968).
18. D. T. Cromer and J. T. Waber, Acta Cryst. 18, 104 (1965).

19. Table II, which gives a listing of observed and calculated structure factor amplitudes, will appear immediately following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit check or money order for \$----- for photocopy or \$2.00 for microfiche, referring to code number INORG-73-0000.
20. A. J. Edwards, Proc. Chem. Soc., 1963, 205.
21. R. E. Rundle, Rec. Chem. Progress, 23, 195 (1962).
22. F. W. B. Einstein, P. R. Rao, J. Trotter and N. Bartlett, J. Chem. Soc. (A), 478 (1967).
23. A. J. Edwards, Chem. Commun., 820 (1970).

Table I. RhF_5 POSITIONAL AND THERMAL PARAMETERS, AND STANDARD DEVIATIONS

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
Rh(1)	.50371(3)	.24806(3)	-.00430(9)	1.48(2)	1.28(2)	1.71(2)	.02(2)	.07(1)	.05(2)
Rh(2)	.29951(3)	.49850(5)	-.30200(6)	1.31(1)	1.55(2)	1.62(2)	.01(1)	-.03(1)	.05(2)
F(1)	.6375(3)	.1685(5)	.0919(7)	1.7(1)	2.5(2)	3.0(2)	.7(1)	-.2(1)	-.1(1)
F(2)	.4549(3)	.1010(5)	-.1851(7)	3.6(2)	1.9(2)	3.1(2)	-.1(1)	-.5(2)	-.8(1)
F(3)	.5469(3)	.3296(5)	-.2629(6)	2.1(1)	2.9(2)	2.2(1)	-.0(1)	.6(1)	.3(1)
F(4)	.4533(3)	.1869(4)	.2609(7)	2.5(1)	2.9(2)	2.2(1)	-.4(1)	.5(1)	.5(1)
F(5)	.3560(2)	.3350(4)	-.1097(6)	1.4(1)	1.6(1)	2.8(2)	.1(1)	-.1(1)	.6(1)
F(6)	.5543(3)	.4127(4)	.1933(6)	1.7(1)	1.9(1)	2.2(2)	-.3(1)	.1(1)	-.6(1)
F(7)	1.2477(3)	.6475(5)	-.4769(7)	2.5(2)	2.1(2)	3.2(2)	.5(1)	-.3(1)	1.1(1)
F(8)	.3547(3)	.4313(5)	-.5580(7)	3.3(2)	3.0(2)	1.8(1)	.0(1)	.5(1)	-.6(1)
F(9)	.1679(3)	.4160(5)	-.3992(7)	1.7(1)	3.4(2)	3.0(2)	-.8(1)	-.5(1)	-.1(1)
F(10)	.2604(3)	.5619(5)	-.0240(6)	2.4(1)	2.8(2)	2.1(1)	.1(1)	.6(1)	-.4(1)

Table III. BOND DISTANCES (Å) AND ANGLES (Deg.) WITHIN THE RhF₅ TETRAMER

Distances				Angles			
M-F							
Rh(1)-F(1)	1.821(4)	Rh(2)-F(7)	1.822(4)	F(1)-Rh(1)-F(2)	90.46(23)	F(5)-Rh(2)-F(6)	89.25(18)
Rh(1)-F(2)	1.816(4)	Rh(2)-F(8)	1.816(3)	F(1)-Rh(1)-F(3)	92.65(20)	F(5)-Rh(2)-F(7)	179.84(23)
Rh(1)-F(3)	1.816(4)	Rh(2)-F(9)	1.812(4)	F(1)-Rh(1)-F(4)	92.36(21)	F(5)-Rh(2)-F(8)	88.86(21)
Rh(1)-F(4)	1.810(4)	Rh(2)-F(10)	1.817(4)	F(1)-Rh(1)-F(5)	179.73(34)	F(5)-Rh(2)-F(9)	90.04(21)
Rh(1)-F(5)	2.006(3)	Rh(2)-F(5)	1.999(4)	F(1)-Rh(1)-F(6)	90.89(19)	F(5)-Rh(2)-F(10)	86.75(20)
Rh(1)-F(6)	2.005(4)	Rh(2)-F(6)	2.000(3)	F(2)-Rh(1)-F(3)	91.70(23)	F(6)-Rh(2)-F(7)	90.87(22)
				F(2)-Rh(1)-F(4)	93.36(25)	F(6)-Rh(2)-F(8)	87.37(18)
				F(2)-Rh(1)-F(5)	89.39(21)	F(6)-Rh(2)-F(9)	179.26(23)
Ni-M							
Rh(1)-Rh(1')	4.998(2)	Rh(2)-Rh(2')	5.458(2)	F(2)-Rh(1)-F(6)	178.85(28)	F(6)-Rh(2)-F(10)	87.30(19)
Rh(1)-Rh(2)	3.692(2)	Rh(1)-Rh(2')	3.709(2)	F(3)-Rh(1)-F(4)	172.84(35)	F(7)-Rh(2)-F(8)	91.25(23)
				F(3)-Rh(1)-F(5)	87.57(19)	F(7)-Rh(2)-F(9)	89.84(23)
				F(3)-Rh(1)-F(6)	88.10(19)	F(7)-Rh(2)-F(10)	93.15(25)
F-F (cis)							
F(1)-F(2)	2.582(5)	F(9)-F(7)	2.566(7)	F(4)-Rh(1)-F(5)	87.43(18)	F(8)-Rh(2)-F(9)	92.43(22)
F(1)-F(3)	2.630(7)	F(9)-F(8)	2.619(5)	F(4)-Rh(1)-F(6)	86.72(19)	F(8)-Rh(2)-F(10)	173.14(28)
F(1)-F(4)	2.620(5)	F(9)-F(10)	2.629(6)	F(5)-Rh(1)-F(6)	89.72(19)	F(9)-Rh(2)-F(10)	92.85(20)
F(2)-F(3)	2.606(7)	F(7)-F(8)	2.600(6)				
F(2)-F(4)	2.638(5)	F(7)-F(10)	2.643(5)	Rh(1)-F(5)-Rh(2)	135.71(11)	Rh(1)-F(6)-Rh(2)	134.34(10)
F(5)-F(2)	2.691(7)	F(6)-F(1)	2.730(7)				
F(5)-F(3)	2.648(4)	F(6)-F(3)	2.660(5)				
F(5)-F(4)	2.641(5)	F(6)-F(4)	2.623(6)				
F(5)-F(8)	2.674(5)	F(6)-F(7)	2.726(5)				
F(5)-F(9)	2.699(5)	F(6)-F(10)	2.638(5)				
F(5)-F(10)	2.624(6)	F(6)-F(8)	2.639(5)				
F(5)-F(6)	2.818(4)	F(6)-F(5)	2.809(6)				
F-F (other)							
F(6)-F(6')	2.897(8)	F(3)-F(10)	2.827(5)				
F(1)-F(7)	2.974(7)	F(3)-F(8)	2.817(5)				

TABLE IV

Structure Type and Formula Unit Volume (V) of the 1st, 2nd and 3rd
Transition Series Pentafluorides

	V*	Cr				
Type	O ^a	O ^b				
V(Å ³)	85	83				
	Nb*	Mo*	Tc	Ru*	Rh*	
Type	M1 ^c	M1 ^d	O ^e	M2 ^{f,g}	M2 ^h	
V(Å ³)	88	88	95	83	83	
	Ta*	W*	Re	Os*	Ir	Pt
Type	M1 ^c	M1 ⁱ	O ^a	M2 ^g	M2 ^j	M2 ^j
V(Å ³)	89	89	94	85	82	82

* Indicates a complete structural analysis has been reported; O - orthorhombic VF₅ type; M1 - monoclinic NbF₅ type; M2 - monoclinic RhF₅ type.

a-Reference 10

f-Reference 7

b-Reference 20

g-Reference 8

c-Reference 11

h-present work

d-Reference 12

i-Reference 13

e-Reference 7

j-Reference 14

XBL 728-6758

Figure 1a: The RhF₅ Tetramer.

Figure 1b: Stereoscopic View of the RhF₅ Tetramer.

Figure 2: The packing of RhF_5 tetramers and the unit cell.

XBL 7212-7360

Figure 3: Idealized hexagonally-close-packed RhF_5 tetramer. (The atoms are numbered to correspond with Figure 1a and the fluorine-bridge bonds of the tetramer are heavily shaded. The closest F-atom layer is represented by the biggest open circles and the farthest by the smallest.)

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720