with a relatively labile complex having a symmetrical planar ligand $[Co(tetraMeen)(NO_2)_2]^+$ were studied in detail (Table IX). The rate constant is essentially pH and NO_2^- independent and unaffected by laboratory light or ionic atmosphere. Using either ^{15}N or ^{18}O as the tracer gives identical results. The major differences between this complex and $[Co(PnAO\text{-}H)(NO_2)_2]^0$ are the large $[OH^-]$ dependence and the kinetically different nitro groups in the latter. Since the tetraMeen and AO do not show similar behavior to PnAO complexes, some very novel bonding characteristics appear to be present with the latter. We ascribe this novel character to a tendency toward distortion toward a square-pyramidal geometry which may occur when the equatorial ligand has a great tendency to stabilize the planar configuration. Some similarities in properties seem to be found with vitamin B_{12}, cyano complexes of Co(III), and, to a lesser extent, complexes of DMG.

A feature of the NO_2^- replacement studies is whether the oxygen of complexed NO_2^- is retained in the released NO_2^- and whether the formation of the nitro complex retains the nitrite ion oxygens. Tables X and XI answer these questions. First, free NO_2^- in base does not show any exchange with the solvent in 1 hr at 60°. When NO_2^- is released from any of the three CoPnAO complexes by N_3^- in basic media essentially all the ^{18}O is retained in the NO_2^-. The formation of the nitro complex (neutral conditions) incorporates both NO_2^- oxygens into the complex ion.

Unsuccessful attempts have been made to prepare the isomer pair of a mixed complex, *i.e.*, $R(NO_2)_F(N_3)_S{}^0$ and $R(NO_2)_S(N_3)_F{}^0$, where F and S refer to the fast and slow positions. Attempts are continuing in search of these unusual isomers.

Summary

It has been shown that *trans*-$[Co(PnAO\text{-}H)X_2]^0$ has kinetically nonequivalent Co–X bonds ($X^- = NO_2^-, N_3^-, Cl^-$). Kinetic studies show an abnormal lability for the X^- groups. The mechanism of X^- group replacement resembles other systems presently thought to be primarily dissociative. An unexpected $[OH^-]$ dependency is observed for anion replacement, anation of the aquo complex, and isotopic anion exchange but not for the water exchange on the aquo complex. *trans*-$[Co(tetraMeen)_2(NO_2)_2]^+$, although similar to the PnAO complex with respect to being relatively labile, shows entirely different pH behavior in the exchange reaction and is kinetically symmetrical with respect to the NO_2^- groups.

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Registry No. *trans*-$[Co(PnAO\text{-}H)(NO_2)_2]$, 41371-79-3; *trans*-$[Co(PnAO\text{-}H)(N_3)_2]$, 41371-80-6; *trans*-$[Co(PnAO\text{-}H)(NO_2)(N_3)]$, 41371-81-7; *trans*-$[Co(PnAO\text{-}H)(NO_2)(OH_2)]ClO_4$, 41371-82-8; *trans*-$[Co(PnAO\text{-}H)(Cl_2)]$, 41371-83-9; *trans*-$[Co(PnAO\text{-}H)(Br_2)]$, 41371-84-0; *trans*-$[Co(PnAO\text{-}H)(I_2)]$, 41371-85-1; *trans*-$[Co(tetraMeen)_2(NO_2)_2]ClO_4$, 41371-86-2; *trans*-$NH_4[Co(DMG\text{-}2H)(NO_2)_2]$, 24256-61-9; *trans*-$[Co((AO)_2\text{-}H)(NO_2)_2]$, 41371-87-3; *trans*-$[Co(en)_2(NO_2)_2]NO_3$, 14240-12-1.

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Crystal Structure of Rhodium Pentafluoride

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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; $\beta = 100.42\ (2)°$; $V = 663.85$ Å^3; $Z = 8$; $d_c = 3.95$ g cm^{-3}. A final conventional R factor of 0.029 was obtained using 1207 nonzero 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 ± 1° and the Rh–F interatomic distance ~2.01 ± 0.01 Å. For the other F atoms in the RhF_6 group the Rh–F interatomic distances are within the range 1.796 (4)–1.820 (4) with an average distance of 1.808 (8) 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 far.[6] The crystal structures of RuF_5 and OsF_5 have been reported,[7,8] and X-ray powder photography has shown[3,4] all of the platinum-metal pentafluorides to be isomorphous. Evidently these pentafluorides constituted a class which was structurally distinct[4] 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

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Table I. RhF_5 Positional and Thermal Parameters and Standard Deviations

Atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
RH(1)	0.50371 (3)[b]	0.24806 (3)	−0.00432 (9)	1.50 (2)	1.29 (2)	1.64 (2)	0.02 (2)	0.06 (1)	0.06 (2)
RH(2)	0.29951 (3)	0.49850 (5)	−0.30200 (6)	1.32 (2)	1.56 (2)	1.56 (2)	0.01 (1)	−0.03 (1)	0.05 (2)
F(1)	0.6375 (3)	0.1685 (5)	0.0919 (7)	1.7 (1)	2.5 (2)	2.9 (2)	0.7 (1)	−0.2 (1)	−0.1 (1)
F(2)	0.4549 (3)	0.1010 (5)	−0.1861 (7)	3.6 (2)	1.9 (2)	2.9 (2)	−0.1 (1)	−0.5 (2)	−0.8 (1)
F(3)	0.5470 (3)	0.3296 (5)	−0.2629 (7)	2.1 (1)	2.9 (2)	2.1 (1)	−0.0 (1)	0.6 (1)	0.3 (1)
F(4)	0.4533 (3)	0.1869 (4)	0.2608 (7)	2.6 (1)	3.0 (2)	2.1 (1)	−0.4 (1)	0.5 (1)	0.5 (1)
F(5)	0.3560 (2)	0.3350 (4)	−0.1097 (6)	1.4 (1)	1.6 (1)	2.7 (2)	0.1 (1)	−0.1 (1)	0.6 (1)
F(6)	0.5543 (3)	0.4127 (4)	0.1933 (6)	1.7 (1)	1.9 (1)	2.1 (2)	−0.3 (1)	0.1 (1)	−0.6 (1)
F(7)	1.2477 (3)	0.6475 (5)	−0.4769 (7)	2.5 (2)	2.2 (2)	3.1 (2)	0.5 (1)	−0.3 (1)	1.1 (1)
F(8)	0.3547 (3)	0.4313 (5)	−0.5580 (7)	3.3 (2)	3.0 (2)	1.7 (1)	0.0 (1)	0.5 (1)	−0.6 (1)
F(9)	0.1679 (3)	0.4160 (5)	−0.3992 (7)	1.7 (1)	3.4 (2)	2.8 (2)	−0.8 (1)	−0.5 (1)	−0.1 (1)
F(10)	0.2604 (3)	0.5619 (5)	−0.0240 (6)	2.4 (1)	2.8 (2)	2.0 (1)	0.1 (1)	0.5 (1)	−0.4 (1)

[a] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hj - 2\beta_{13}hl - 2\beta_{23}kl)$. The B_{ij} in the table $= 4\beta_{ij}/a_i{}^*a_j{}^*$, where $a_j{}^*$ and $a_j{}^*$ are the ith and jth reciprocal cell lengths. [b] Number in parentheses is the estimated standard deviation in the least significant digit.

Rh, Ir, and Pt (see forthcoming paper[14]) 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 a forthcoming paper.[14] 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 × 0.11 × 0.07 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), and $c = 5.5173$ (6) Å and $\beta = 100.42$ (2)°, $V = 663.85$ Å^3, $Z = 8$, $d_c = 3.95$ g cm^{-3}. As usual with dense, reactive fluorides, the number of fluorine atoms in the unit cell was estimated by applying Zachariason's criterion[15] of ~18 Å^3 per F atom. This indicated $Z = 8$. Single-crystal precession photographs indicated the systematic absences $h0l$ when $h = 2n + 1$ and $0k0$ 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 Mo Kα_1 ($\lambda = 0.709261$ Å) radiation, at a take-off angle of ~2°] were used for a least-squares refinement of the cell parameters. Data were collected and treated as described in a recent article.[16] 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 $\pm hkl$ 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 ω scan of the crystal showed a peak width at half-height of ~0.1°. Although, for RhF_5, the absorption coefficient $\mu = 50.02$, the small size ($\mu r \simeq 0.5$) and regular shape of the chosen crystal permitted us to ignore an absorption correction. The only other difference from the previously described data treatment[16] was in the choice of the value of q, 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 described.[16] Scattering factors for neutral fluorine were taken from Turner and Doyle[17] and those for neutral Rh from the tables of Cromer and Waber.[18]

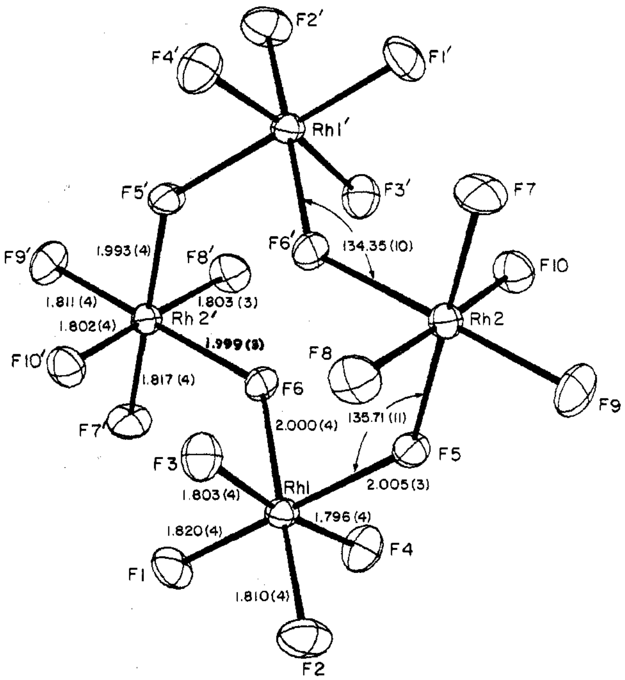

Figure 1. The RhF_5 tetramer.

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, in which isotropic thermal parameters were used for the Rh atoms, resulted in a conventional R factor[16] 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 ten peaks were assigned as F atoms and refinement, employing isotropic thermal parameters, yielded a final conventional $R = 0.067$. Three cycles of least-squares refinement, in which anisotropic thermal parameters were permitted 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 the least-squares refinement with all atoms anisotropic 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 nonzero 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 weighted[16]

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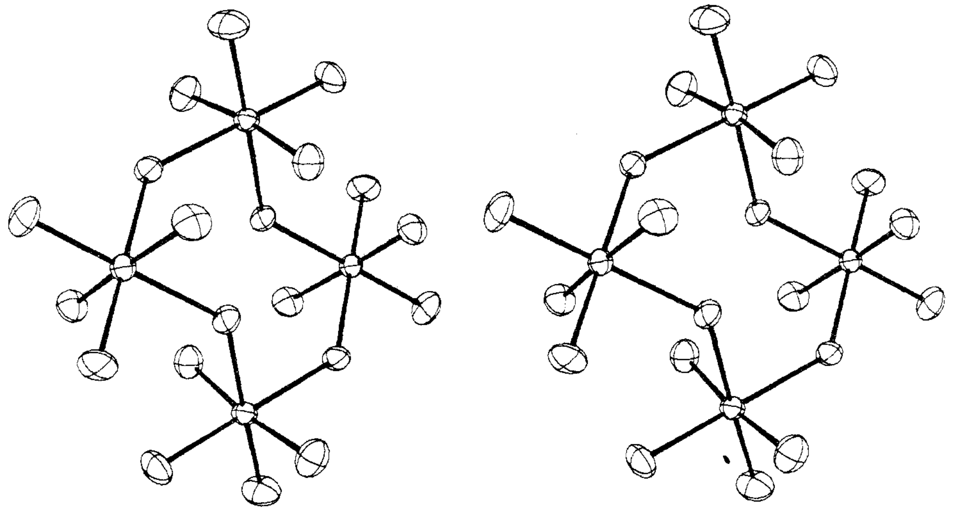

Figure 2. Stereoscopic view of the RhF_5 tetramer.

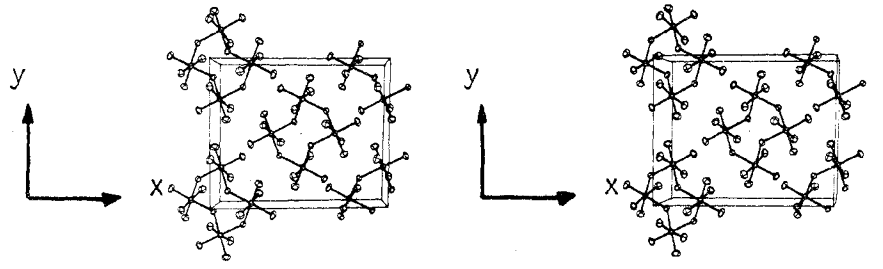

Figure 3. The packing of RhF_5 tetramers and the unit cell.

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 Figures 1 and 2 and documented in Table III. The packing of the tetramers is shown in Figure 3. The F-atom arrangement in the structure approximates to a hexagonal close-packed arrangement as described[8] 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 4. 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 (Figures 1 and 2). 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 nonequivalent 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 nonbridging atoms, the averaged interatomic distances being 1.999 (4) and 1.808 (8) 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 less for the bridging F atoms than for the nonbridging. This is no doubt why, in each RhF_6 group, the nonbridging F ligands, above and below the plane containing the bridging F ligands, are displaced toward the bridging-F edge of the octahedron.

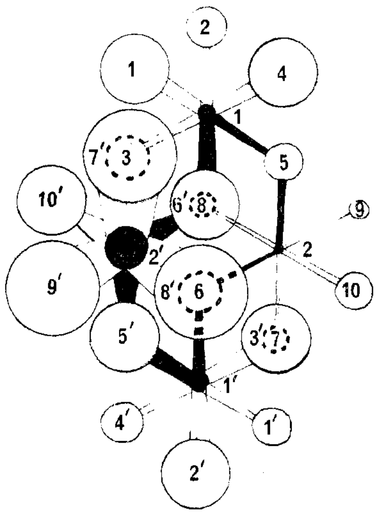

Figure 4. Idealized hexagonally close-packed RhF_5 tetramer. (The atoms are numbered to correspond with Figure 1 and the fluorine-bridge bonds of the tetramer are heavily shaded. The closest F-atom layer is represented by the biggest open circles and the farthest by the smallest.)

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 Figures 1 and 2, but the closeness of the Rh(1)-Rh(2) distances of 3.704

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[19] See paragraph at end of paper regarding supplementary material.

Table III. Bond Distances (A) and Angles (deg) within the RhF$_5$ Tetramer

	Distances		
	M-F		
Rh(1)-F(1)	1.820 (4)	Rh(2)-F(7)	1.817 (4)
Rh(1)-F(2)	1.810 (4)	Rh(2)-F(8)	1.803 (3)
Rh(1)-F(3)	1.803 (4)	Rh(2)-F(9)	1.811 (4)
Rh(1)-F(4)	1.796 (4)	Rh(2)-F(10)	1.817 (4)
Rh(1)-F(5)	2.005 (3)	Rh(2)-F(5)	1.993 (4)
Rh(1)-F(6)	2.000 (4)	Rh(2)-F(6′)	1.999 (3)
	M-M		
Rh(1)-Rh(1′)	4.998 (2)	Rh(2)-Rh(2′)	5.965 (2)
Rh(1)-Rh(2)	3.686 (2)	Rh(1)-Rh(2′)	3.704 (2)
	F-F (Cis)		
F(1)-F(2)	2.575 (5)	F(9)-F(7)	2.565 (7)
F(1)-F(3)	2.616 (6)	F(9)-F(8)	2.615 (5)
F(1)-F(4)	2.614 (5)	F(9)-F(10)	2.613 (6)
F(2)-F(3)	2.605 (7)	F(7)-F(8)	2.599 (6)
F(2)-F(4)	2.612 (5)	F(7)-F(10)	2.617 (5)
F(5)-F(2)	2.690 (7)	F(6)-F(1)	2.728 (7)
F(5)-F(3)	2.644 (4)	F(6)-F(3)	2.634 (5)
F(5)-F(4)	2.625 (5)	F(6)-F(4)	2.623 (6)
F(5)-F(8)	2.649 (5)	F(6)-F(7′)	2.718 (5)
F(5)-F(9)	2.691 (5)	F(6)-F(10′)	2.633 (5)
F(5)-F(10)	2.623 (6)	F(6)-F(8′)	2.624 (5)
F(5)-F(6)	2.810 (4)	F(6)-F(5′)	2.808 (6)
	F-F (Other)		
F(6)-F(6′)	2.882 (8)	F(3)-F(10′)	2.820 (5)
F(1′)-F(7)	2.960 (7)	F(3)-F(8)	2.810 (5)
	Angles		
F(1)-Rh(1)-F(2)	90.33 (23)	F(5)-Rh(2)-F(6)	89.38 (18)
F(1)-Rh(1)-F(3)	92.45 (20)	F(5)-Rh(2)-F(7)	179.84 (23)
F(1)-Rh(1)-F(4)	92.61 (21)	F(5)-Rh(2)-F(8)	88.34 (20)
F(1)-Rh(1)-F(5)	179.73 (34)	F(5)-Rh(2)-F(9)	89.90 (21)
F(1)-Rh(1)-F(6)	91.02 (19)	F(5)-Rh(2)-F(10)	87.26 (20)
F(2)-Rh(1)-F(3)	92.27 (23)	F(6)-Rh(2)-F(7)	98.74 (22)
F(2)-Rh(1)-F(4)	92.83 (25)	F(6)-Rh(2)-F(8)	87.12 (18)
F(2)-Rh(1)-F(5)	89.52 (21)	F(6)-Rh(2)-F(9)	179.26 (23)
F(2)-Rh(1)-F(6)	178.64 (28)	F(6)-Rh(2)-F(10)	87.52 (19)
F(3)-Rh(1)-F(4)	172.79 (35)	F(7)-Rh(2)-F(8)	91.78 (23)
F(3)-Rh(1)-F(5)	87.78 (19)	F(7)-Rh(2)-F(9)	89.98 (23)
F(3)-Rh(1)-F(6)	87.54 (19)	F(7)-Rh(2)-F(10)	92.63 (25)
F(4)-Rh(1)-F(5)	87.18 (18)	F(8)-Rh(2)-F(9)	92.68 (22)
F(4)-Rh(1)-F(6)	87.24 (19)	F(8)-Rh(2)-F(10)	173.10 (28)
F(5)-Rh(1)-F(6)	89.14 (19)	F(9)-Rh(2)-F(10)	92.63 (20)
Rh(1)-F(5)-Rh(2)	135.71 (11)	Rh(1)-F(6)-Rh(2′)	134.35 (10)

(2) and 3.686 (2) Å alone demonstrates this similarity. Each bridging F ligand is (within two 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 134.4 (1) and 135.7 (1)°.

There are no statistically significant variations in the nonbridging fluorine Rh-F interatomic distances. The mean value of the Rh-F (nonbridging) interatomic distance (using the data from both RhF$_6$) is 1.808 (8) 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 nonbridging 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 [RhF$_5$]$_4$ probably pertains in them, too.

Table IV. Structure Type and Formula Unit Volume (*V*) of the First, Second, and Third Transition Series Pentafluorides[k]

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

[a] Reference 10. [b] Reference 20. [c] Reference 11. [d] Reference 12. [e] Reference 7. [f] Reference 7. [g] Reference 8. [h] Present work. [i] Reference 13. [j] Reference 14. [k] An asterisk indicates a complete structural analysis has been reported; O, orthorhombic VF$_5$ type; M1, monoclinic NbF$_5$ type; M2, monoclinic RhF$_5$ type.

Although single crystals of IrF$_5$ have been obtained,[14] none were 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 have established the space group *P*2$_1$/*a* and indicate 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 Figures 1 and 2 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[11-13] 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 angles[10] of ~150°. In the platinum-metal pentafluoride group, the M-F-M angle in the tetrameric unit is ~135°. Edwards and Jones have stated[10] that all of the structures exhibit close packing of the fluorine atoms. In the MoF$_5$ type structure[12] 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 4.) As may be seen from the effective formula unit volumes listed in Table IV, however, TcF$_5$ 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 [RhF$_5$]$_4$ is similar to units seen in the other pentafluoride structures. Since the averaged nonbridging M-F interatomic distances in (RhF$_5$)$_4$ are 1.808 (8) Å whereas the averaged bridging M-F distances are 1.999 (4) Å, we can safely assume that the former bonds are appreciably stronger than the latter.

The bonding of the bridging F atoms in (RhF$_5$)$_4$ appears to be similar to that of the bridging F atom in the Sb$_2$F$_{11}^-$ ion. In XeF$_3^+$Sb$_2$F$_{11}^-$ (ref 21) the Sb-F-Sb angle is somewhat greater than here, but the bridging Sb-F interatomic distance (2.03 Å) is 0.18 Å greater than the nonbridging (1.85 Å). This recalls the equation for the empirical relationship between bond order and bond length given by Pauling,[22] which

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predicts a bond of order unity to be 0.18 Å shorter than one of order 0.5. If we represent nonbridging bonds in $(RhF_5)_4$ as electron-pair bonds, then, if the Pauling equation is valid, the bridging M-F bonds must be single electron bonds. Now, this F-bridging situation is reminiscent of the Cl bridging in Al_2Cl_6 and the CH_3 bridging in $Al_2(CH_3)_6$. The geometries of Al_2Cl_6 and $Al_2(CH_3)_6$ are similar[23,24] and in each case the bridging ligand-Al interatomic distance is greater than the nonbridging, the actual values being: Al-Cl, bridging = 2.21 Å, nonbridging = 2.06 Å; Al-CH_3, bridging = 2.24 Å, nonbridging = 2.00 Å. The bridge bonding in $Al_2(CH_3)_6$ is usually discussed[24] in terms of three-center two-electron bonding. A similar bonding model appears to be appropriate for the halogen-bridging cases discussed here. As has already been pointed out, however, the M-F-M bridging is not the same for all of the transition metal pentafluorides.

The near-hexagonal close packing of the fluorine atoms in RhF_5 indicates that the M-F-M angle of ~135° 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 nonbridging. It is notable that in AuF_3 polymer,[25] 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 Nb → Rh and Ta → Pt is not screened by the formally nonbonding d electrons (which occupy the dt_{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 $(MF_4^+F^-)_4$. 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 Edwards[26] has already presented evidence for the salt $NbF_4^+SbF_6^-$.

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.

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Supplementary Material Available. Table II, which gives a listing of observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2640.

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Thermal Rearrangements of Icosahedral Carboranes. Molecular and Crystal Structure of 5,12-Dichloro-1,7-dimethyl-1,7-dicarba-*closo*-dodecaborane(12)

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Thermal rearrangement of 9,12-dichloro-*C,C'*-dimethyl-*o*-carborane at 420° yields 5,12-dichloro-*C,C'*-dimethyl-*m*-carborane as the major product, in addition to a large number of the possible 15 other meta isomers. This major product is the only one expected from the cuboctahedral intermediate mechanism. Other products may result from triangle rotations in this intermediate and possibly from other less important mechanisms. This major product is orthorhombic, in the space group $Pmn2_1$, and has two molecules in a unit cell having dimensions of $a = 7.725$, $b = 10.181$, and $c = 8.079$ Å. The value of $R_F = \Sigma|k|F_o| - |F_c||/\Sigma k|F_o|$ is 0.078 for 460 observed diffraction maxima.

Earlier studies[1,2] of thermal rearrangements of monohalocarboranes $(B_{10}H_9XC_2H_2)$ have supported the original proposal[3] that the major transformation proceeds through a cuboctahedral intermediate (Figure 1). Products in addition to those produced by this mechanism are believed[1,2] to arise principally from triangle rotations occurring only during the lifetime of this intermediate. It is not yet known whether apparent preference for rotation of triangles which are furthest from C atoms occurs because of electronic or steric effects. Nevertheless, electronic effects are known[2] in the final equilibria for different halogens, and preferred collisional effects have been proposed[2] for triangles in which one B atom is attached to Cl. Also, further study is required in order to decide whether rotation of a pentagonal cap,[4,5] or of a

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