# Crystal and Molecular Structures of Rhenium Heptafluoride

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**Rhenium heptafluoride, $ReF_7$, is one of only two stable binary compounds $MX_7$ with a heptacoordinated metal atom M and halide atom X. Its low-temperature crystal structure, as determined by high-resolution powder neutron diffraction, reveals the molecular structure, which has been the subject of speculation and debate for many years. Here it is shown within experimental error that at 1.5 kelvin the lowest energy configuration of $ReF_7$ has symmetry $C_s$ (*m*) and is a distorted pentagonal bipyramid. The deviation of the two axial Re–F bonds from collinear and the puckering of the ring of equatorial fluorine atoms are similar to what has been postulated as one of the conformations of the pseudorotational motion observed at higher temperatures.**

$ReF_7$ and $IF_7$ are the only two stable binary compounds of the type $MX_7$. $OsF_7$ can also occur, but decomposes above 170 K (*1*). The molecular structures of these compounds pose several questions (*2*) and are subject to steric crowding and fluxionality. Up to hexacoordination, the valence-shell electron-pair-repulsion theory (VSEPR) developed by Gillespie and Nyholm (*3*) correctly predicts the molecular structure. Furthermore, an extension of this approach, the "principle of repelling points on a sphere," works independently of the repulsive force law invoked for $MX_n$ with $n \leq 9$ with the exception of $n = 7$ (*4*). For heptacoordination compounds, the latter predicts structures whose symmetry ranges from $D_{5h}$ for soft repulsions that distort to lower symmetries such as a monocapped trigonal prism or a monocapped octahedron as the repulsions harden, with $C_{2v}$ and $C_{3v}$ symmetry (*5*), respectively. Gas-phase and solution spectroscopic studies of $IF_7$ and $ReF_7$ indicate that the favored arrangement is based on the pentagonal bipyramid (*6*). The presence of five ligands in the equatorial ring of a pentagonal bipyramid results in steric crowding. Puckering of the ring may relieve the strain, but the odd number of ligands is thought to cause fluxionality and pseudorotation of the ligands (*5*). A determination of the crystal structure of a heptafluoride at low temperature presents an opportunity to investigate the arrangement of this unusual coordination number without the problems posed by fluxionality. Although $IF_7$ is the most studied heptafluoride compound (*6*), the determination of its crystal structure at low temperature has so far proved intractable because of the effects of two phase transitions (*7*). Little is known about the solid-state behavior of $ReF_7$ below the phase transition that occurs below 183 K. Thus, the arrangement of seven nonchelated ligands around a central atom has remained an outstanding problem in chemistry.

In common with many other binary fluorides with high coordination number, $ReF_7$ solidifies to form an orientationally disordered, body-centered-cubic phase, which transforms to a lower symmetry structure, between 183 K and 163 K (*8*). The presence of a phase transition in $ReF_7$ has prevented the growth of a single crystal of the low-temperature phase. In this work we have used powder neutron diffraction to determine the structure of $ReF_7$ at 1.5 K. Neutron diffraction was used because the scattering process is not dominated by the heavy rhenium atom as would be the case for x-rays. Hence, neutron diffraction is more sensitive to the arrangement of the fluorine atoms.

The structural phase transitions of solid $ReF_7$ were first investigated with the diffractometer D1B at the Institut Laue Langevin, Grenoble, France. This instrument is equipped with a position-sensitive detector that spans 80° in scattering angle. The diffraction pattern was monitored as the temperature was cycled between 1.5 K and 200 K (Fig. 1). On warming, a phase transition to the cubic phase is seen at 153 K. Below 153 K a steady increase in the splitting in the diffraction peaks can be seen with decreasing temperature. We have solved the crystal structure of $ReF_7$ at 1.5 K from high-resolution data collected on the neutron diffractometers D1A and D2B (*9*). From data collected at 151 K, just 2 K below the transition to the cubic phase, the structure was initially solved as monoclinic, space group $C2/c$ (*10*). Subsequently, the diffraction patterns of $ReF_7$ at 1.5 K were indexed as a triclinic distortion, with space group $C\bar{1}$. During careful analysis of both data sets it became apparent that the structure at 151 K is really triclinic, though the distortion of the unit cell angles from 90° is too small to give resolvable splittings in the diffraction pattern. Structure solution was by autoindexing (*11*), pattern decomposition (*12*), and use of direct methods (*13*). The solution of crystal structures from powder data has recently been reviewed (*14*).

The structure of $ReF_7$ at 1.5 K was refined by the method of Rietveld (*15*), with initial coordinates derived from the solution at 151 K. The best parameters for $ReF_7$ at 1.5 K, obtained from the data shown in Fig. 2, are presented in Table 1. Even at 1.5 K, anisotropic displacement factors were required to describe the scattering density of the fluorine atoms. Independent anisotropic thermal parameters for each fluorine atom results in overparameterization and slightly non–positive-definite thermal ellipsoids of vibration for some atoms. The most satisfactory refinement uses TLS constraints to simulate rigid body translational (T) and librational (L) motion for the molecules, with T constrained as isotropic and S (the cross term between translation and libration) set to zero. The mean amplitude of vibration of the fluorine atoms is 0.12 Å. A view of the crystal structure is shown in Fig. 3.

Examination of the molecular structure (Fig. 4) shows that $ReF_7$ is a distorted pentagonal bipyramid. The equatorial ring is puckered with a mean displacement of 0.17 Å from the ideal plane formed by the rhenium and equatorial fluorine atoms. The mean deviation from perpendicular of the angle between axial and equatorial Re–F bonds is 6.2°. In addition to the puckering, the axial Re–F bonds are bent from collinear by 5.4°, which is smaller than the value of 7.44 to 7.65° determined by gas phase electron diffraction. The average Re–F dis-

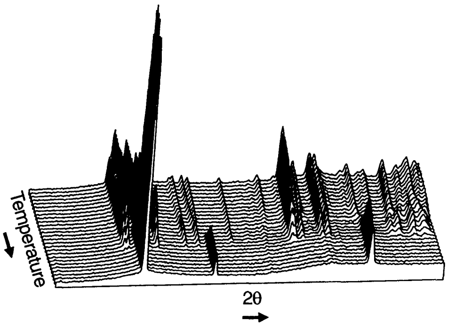

**Fig. 1.** Variation of the diffraction pattern of $ReF_7$ with temperature. On warming, a transition is observed to a body-centered-cubic phase at 153 K. The data were collected with nominal $\lambda$ = 2.52 Å on the diffractometer D1B with the multidetector covering the 2θ range 15 to 95°.

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tance of 1.843 Å agrees well with the latter study's value of 1.835(5) Å.

Although formally the crystallographic point symmetry of the molecule is $C_1$ (1), the molecule has a mirror plane within experimental error that passes through Re, F(1), F(2), and F(6), so that the molecular symmetry is $C_s$ ($m$). The mean distance and angular deviations from $C_s$ symmetry are 0.0014 Å and 0.4°, respectively. Deviations from mirror symmetry are to be expected because the molecules are packed in a lattice lacking mirror planes. The average axial bond length of 1.823 Å is shorter than the mean equatorial value of 1.851 Å, a result similar to that observed in $IF_7$ (5). The mean equatorial to equatorial F···F distance is 2.201 Å, which is comparable to that observed in hexacoordinated fluorine compounds such as $SF_6$ (16), whereas the axial to equatorial fluorine distance is at least 0.22 Å longer. Axial bending and puckering of the equatorial ring are invoked in the pseudorotational motion of $ReF_7$ in the gas phase, where the molecule transforms from one $C_2$ conformation to an equivalent one via a $C_s$ intermediate (5). Thus, the molecular structure at 1.5 K can be viewed as a frozen-in state of the pseudorotational motion.

At 151 K the crystal structure of $ReF_7$ is actually triclinic with a pseudo–twofold axis present in the molecule in addition to the mirror plane. As the transition to the cubic phase is approached, the triclinic distortion decreases, but whether a true monoclinic phase exists just before the cubic transition is reached could not be determined from the current study. At 151 K the thermal motion resulting from librations of the fluorine atoms about the central rhenium atom are much larger than the distortions from $D_{5h}$ symmetry.

Above 153 K the crystal structure of $ReF_7$ is body-centered-cubic, space group $Im3m$ with a lattice parameter $a$ = 6.2027(7) Å at 200 K. The molecules are orientationally disordered and perform large-amplitude librations, rotations, or pseudorotations. A crystal structure represents a mean structure averaged over time and the sample volume. Because of the orientational disorder, the fluorine atom density is distributed over the surface of a sphere and can be described with the use of symmetry-adapted spherical harmonic functions, as has been done for the high-temperature crystal structure of $SF_6$ (16). Although the molecular symmetry of $ReF_7$ is lower than that of $SF_6$, the crystal structures are very similar, with the Re atoms at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and the fluorine atom density located preferentially on the six fourfold axes about each Re. For $ReF_7$ at 165 K, the average Re–F bond length refined from D2B data is 1.836(5) Å, in excellent agreement with the low-temperature value.

In the cubic phase each molecule is coordinated by eight others. At low temperature the $ReF_7$ molecules adopt a hexagonal close-packed arrangement. The mole-

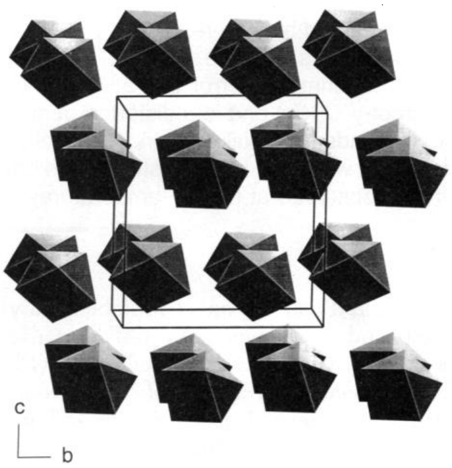

**Fig. 3.** View of the crystal structure of $ReF_7$ at 1.5 K.

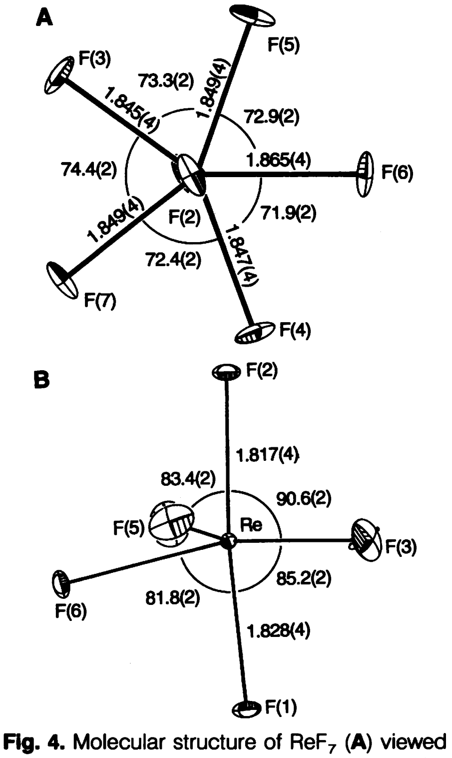

**Fig. 4.** Molecular structure of $ReF_7$ (**A**) viewed down the axis of the pentagonal bipyramid [Re and F(1) are eclipsed by F(2)] and (**B**) viewed perpendicular to the mirror plane of the molecule [F(4) and F(7) are eclipsed by F(5) and F(3), respectively]. The thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å) and angles (°) are shown. Bond angles not illustrated are F(1)–Re–F(7) = 85.8(2)°, F(2)–Re–F(7) = 89.8(2)°, F(1)–Re–F(4) = 97.8(2)°, F(1)–Re–F(5) = 98.6(2)°, F(2)–Re–F(4) = 83.8(2)°, F(2)–Re–F(6) = 103.6(2)°, and F(1)–Re–F(2) = 174.6(2)°.

**Fig. 2.** Observed, calculated, and difference powder neutron diffraction patterns of $ReF_7$ at 1.5 K measured on D2B with nominal $\lambda$ = 1.594 Å. Vertical ticks indicate calculated reflection positions. $R$ factors for the fit are $R_{wp}$ = 13.4%, $R_I$ = 8.3%, and $R_{exp}$ = 5.6%.

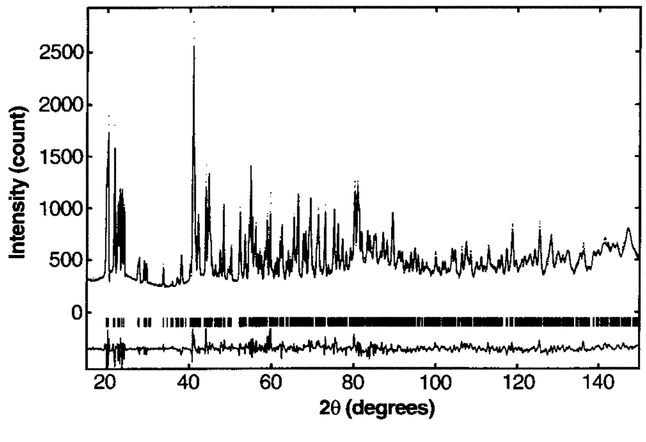

**Table 1.** Refined parameters of $ReF_7$ at 1.5 K in space group $C\bar{1}$ from D2B data with nominal $\lambda$ = 1.594 Å. Lattice parameters: $a$ = 5.5039(1) Å, $b$ = 8.5026(2) Å, $c$ = 9.0916(2) Å, $\alpha$ = 88.513(2)°, $\beta$ = 93.843(2)°, and $\gamma$ = 89.496(2)°. $V$/molecule = 106.086(4) Å$^3$ with $Z$ = 4. Equivalent isotropic displacement factors are calculated from refined TLS matrices. Number in parentheses denotes estimated standard deviation in last digit.

| Atom | $x$ | $y$ | $z$ | $B_{equiv}$ (Å$^2$) |
|---|---|---|---|---|
| Re | −0.0039(4) | 0.1347(2) | 0.2476(2) | 0.23 |
| F(1) | 0.2945(6) | 0.1204(4) | 0.3485(3) | 0.89 |
| F(2) | −0.2907(6) | 0.1343(3) | 0.1363(4) | 0.89 |
| F(3) | 0.1659(6) | 0.1066(4) | 0.0819(4) | 1.30 |
| F(4) | −0.1836(6) | 0.0404(4) | 0.3892(3) | 1.34 |
| F(5) | 0.0277(6) | 0.3315(3) | 0.1601(4) | 1.18 |
| F(6) | −0.0562(6) | 0.2823(4) | 0.3907(4) | 1.01 |
| F(7) | 0.0229(6) | −0.0806(3) | 0.2286(4) | 0.88 |

cules in subsequent layers are rotated by 180° with respect to each other. This leads to an efficient packing of the molecules. The dipole moment of $ReF_7$ is small (*17*), and antiferroelectric ordering is likely to play only a minor role.

## REFERENCES AND NOTES

1. O. Glemser, H. W. Roesky, K.-H. Hellberg, H.-U. Werther, *Chem. Ber.* **99**, 2652 (1966).
2. A.-R. Hahjoub, T. Drews, K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **31**, 1036 (1992).
3. R. J. Gillespie and R. S. Nyholm, *Q. Rev. Chem. Soc.* **11**, 339 (1957).
4. T. A. Claxton and C. G. Benson, *Can. J. Chem.* **44**, 157 (1966).
5. E. J. Jacob and E. S. Bartell, *J. Chem. Phys.* **53**, 2235 (1970).
6. K. O. Christie, E. C. Curtis, D. A. Dixon, *J. Am. Chem. Soc.* **115**, 1520 (1993).
7. T. Vogt, A. N. Fitch, J. K. Cockcroft, *J. Solid State Chem.* **103**, 275 (1993).
8. S. Stanley and D. A. Northrop, *Inorg. Chem.* **5**, 2187 (1966).
9. Twenty-four grams of $ReF_7$ (nominal purity 98%), supplied by Fluorochem Ltd. (Glossop, United Kingdom), was sublimed in vacuo into a 15-mm diameter quartz glass ampoule and sealed. The vacuum line was flamed out and pretreated with $ReF_7$ vapor to avoid decomposition of the $ReF_7$ during sublimation. Catalytic traces of water on the surface of the glass result in the formation of impurities such as $ReOF_5$ and $SiF_4$ (*7*). Ideally the sample should have been checked for soluble solid-state impurities such as $ReOF_5$, for example, by Raman spectroscopy where the Re–O bond gives rise to a strong band at 992 $cm^{-1}$. However, the absence of other by-products such as $SF_4$ indicated a pure sample. $ReF_7$ is a deep yellow solid. The ampoule, held in a thin-walled vanadium tube, was transferred to a liquid-helium flow cryostat, and powder neutron diffraction patterns were collected as a function of temperature on the position-sensitive multidetector diffractometer D1B at the Institut Laue Langevin, Grenoble. High-resolution powder neutron diffraction patterns were subsequently collected of $ReF_7$ at both 1.5 K and 151 K with $\lambda$ = 2.99 Å and $\lambda$ = 1.594 Å (both nominal) on the diffractometers D1A and D2B, respectively. On warming slowly, a transition to the cubic high-temperature phase was observed at 153 K.
10. The D1A diffraction pattern of $ReF_7$ at 151 K taken with nominal $\lambda$ = 2.99 Å was indexed using the $2\theta$ positions of 21 reflections with the program FZON (*11*) as C-centered monoclinic with $a$ = 5.619 Å, $b$ = 8.608 Å, $c$ = 9.228 Å, $\beta$ = 93.90°, and $M_{20}$ = 19.0. Integrated $F^2$ values were extracted from the shorter wavelength data measured on D2B with the program PAWHKL (*12*). The values of $F^2$ were used as input to direct methods program SHELXS (*13*), which found the five atoms required to define a complete $ReF_7$ molecule in space group *C2/c*. The structure was refined by the method of Rietveld with the program PROFIL (*18*).
11. J. W. Visser, *J. Appl. Crystallogr.* **2**, 89 (1969).
12. G. S. Pawley, *ibid.* **14**, 357 (1981).
13. SHELXS86; G. M. Sheldrick, University of Göttingen (1986). See also G. M. Sheldrick, C. Krüger, R. Goddard, Eds., *Crystallographic Computing* (Oxford Univ. Press, London, 1985), vol. 3, pp. 175–189.
14. A. K. Cheetham and A. P. Wilkinson, *J. Phys. Chem. Solids* **52**, 1199 (1991).
15. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
16. J. K. Cockcroft and A. N. Fitch, *Z. Kristallogr.* **184**, 123 (1988).
17. E. W. Kaiser, J. S. Muenter, W. Klemperer, J. Falconer, *J. Chem. Phys.* **53**, 53 (1970).
18. PROFIL, 4.10; J. K. Cockcroft (1992). A Rietveld refinement program with chemical and thermal constraints and restraints.

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# Encapsulation of Methane and Other Small Molecules in a Self-Assembling Superstructure

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**Physical inclusion of small molecules in larger structural lattices is well known in the crystalline state and is a common feature of the chemistry of zeolites. In the liquid state, a variety of synthetic macrocyclic molecules are available to complex and contain smaller guest species. An alternative strategy for binding is explored: assembly of cavity-forming structures from smaller subunits. Encapsulation of small guest molecules such as methane can be achieved with a synthetic structure that assembles reversibly through hydrogen bonding.**

Studies of molecular recognition phenomena have led to increasingly sophisticated compounds—cryptands (*1*), cryptophanes (*2*), and carcerands (*3*)—for binding ions and small molecules. These covalently bound structures feature macrocyclic shapes with openings of various sizes that permit entrance and exit of the guest. Free and complexed species are separated by energy barriers related to the ease of passage of the guest through the openings. Reversible assembly of the host around the guest is a frequent lesson taught by biological chemistry; weak intermolecular forces are used and viral capsids are the paradigm example. The economic appeal of using multiple copies of a single, self-complementary structure for guest inclusion led us to explore this means for binding small molecules.

We recently introduced the structure **1** (Fig. 1) and gave evidence of its self-association into a dimeric assembly in solution (*4*). The molecule is prepared in a single operation from commonly available materials and is easily isolated. The structure features an array of hydrogen bonding sites along its periphery and a skeletal curvature that positions these sites in a self-complementary manner. The dimer is held together by eight hydrogen bonds along the seam of a roughly spherical structure that resembles a tennis ball.

The inner dimensions, as defined by molecular modeling (*5*), indicate a cavity of 50 to 55 Å$^3$ and suggest that suitable smaller molecules of complementary shape and symmetry can fit within. In solvents such as chloroform-*d* ($CDCl_3$) which compete weakly for hydrogen bonds, two forms of the dimer are present, as evidenced by proton nuclear magnetic resonance (NMR) spectroscopy at 500 MHz. One form is "empty" (*6*), whereas the other is most likely occupied by solvent. The exchange between these two forms is slow on the NMR time scale; separate signals are seen for the resonances of the N–H and one of the benzylic protons. As the temperature is lowered, the occupied form increases in concentration at the expense of the empty one. By using a number of guests in $CDCl_3$, it is possible to probe the dimer's capacity for small molecules of appropriate size with NMR titrations. For example, as $CH_2Cl_2$ is added, signals for a third dimeric species appear in the N–H and benzylic regions of the spectra. In favorable cases using guests such as methane ($CH_4$), ethane ($CH_3CH_3$), and ethylene ($H_2C{=}CH_2$), sig-

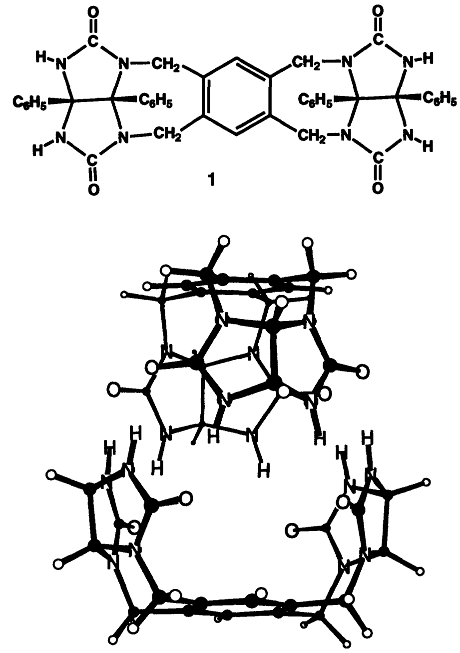

**Fig. 1.** Monomeric **1** and energy-minimized structure of the dimer (MacroModel 3.5x with AMBER* force field and GB/SA chloroform solvation). Phenyl groups have been omitted for clarity.

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