The behavior contrasts strongly with that of the bipyridine complexes, $M(bipy)_3^{2+}$. The corresponding ratios are 6.0^{12} (M = Fe), 40 (M = Co), and 4.0^{12} (M = Ni). However the limiting values which we equate to k_1 are quite similar for the highest bipyridine and terpyridine complex of a particular metal, *e.g.*, $Fe(bipy)_3^{2+}$ dissociates[12a] in 1.5 *M* HCl with a first-order rate constant 3.5×10^{-3} sec^{-1} at 35°, remarkably close to that for $Fe(terpy)_2^{2+}$, 9.0×10^{-3} sec^{-1}. For $Co(bipy)_3^{2+}$, $k_1 =$ 32 sec^{-1} and, for $Co(terpy)_2^{2+}$, $k_1 \sim 125$ sec^{-1}, both at 18°. Finally for $Ni(bipy)_3^{2+}$, $k_1 = 3.8 \times 10^{-4}$ sec^{-1} [12b] and, for $Ni(terpy)_2^{2+}$, $k_1 \sim 5.8 \times 10^{-3}$ sec^{-1} at 1.0°. It thus appears that the rate constant for rupture of a pyridine nitrogen–metal bond is only slightly smaller when it is part of a single ring (bipyridine) than when it forms part of a double ring (terpyridine) system. Both are, of course, much smaller than in the metal–pyridine complex itself. The order of kinetic stability of the metal–nitrogen bond measured by k_1 is Fe > Ni > Co.

Burgess and Prince[7] have shown that the dissociation of $Fe(terpy)_2^{2+}$ is strongly base catalyzed and our own work is in agreement with this. There is no indication that a limiting rate is reached in strong base, but, for example, at 35° and in 0.12 *M* OH^-, the first-order rate constant[7] is 4.4×10^{-3} sec^{-1}, of the same order as the corresponding value in 0.1 *M* H^+. It appears that both OH^- and H^+ can prevent rejoining of severed M–N bonds in terpyridine complexes by attaching themselves to vacated positions of the metal ion or the basic nitrogen.[2]

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(12) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 3807 (1954); **75**, 5102 (1953).

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Further Evidence of Stereochemical Nonrigidity in Five- and Seven-Coordinate Structures

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We present evidence of stereochemical nonrigidity[1] in five- and seven-coordinate molecules.[2] The seven-coordinate species were derived from complexes of molybdenum and tungsten hexafluorides, and the five-coordinate molecule is $(C_6H_5)_2NPF_4$ kindly furnished us by Dr. R. Schmutzler.

The acceptor activity of metal hexafluorides has been established relative to fluoride ion[3] and organic donor molecules;[4] however, the structures of the resulting complexes have not been determined although in Na_2UF_8 preliminary analysis of X-ray data indicates the uranium atom is coordinated to eight fluorine atoms.[3b] We have reexamined the F^{19} spectra of tungsten and molybdenum hexafluoride complexes with organic bases and find a fairly rigorous demonstration of seven-coordination in $WF_6 \cdot P(CH_3)_3$.

The F^{19} spectrum (56.4 and 94 Mc) of $WF_6 \cdot P(CH_3)_3$ dissolved in acetonitrile or in sulfur dioxide consists of a major doublet due to PF coupling with W^{183}–F^{19} satellite doublets. The doublet resonance was unperturbed down to the lowest temperatures (∼−85°) possible with these solutions. These data are nearly conclusive[5] for a monomolecular complex with the phosphine and six fluorine atoms bound to the tungsten atom. Strict equivalence of fluorine atoms in $WF_6 \cdot P(CH_3)_3$ is not possible in any of the idealized seven-coordinate geometries.[2] Spectroscopic equivalence may be a reflection of a very small fluorine chemical shift or a rapid intramolecular rearrangement through which fluorine atom environments are averaged. We favor the latter alternative.[2,6] This observation of nmr spectroscopic equivalence of ligand atoms is characteristic of many seven-coordinate structures.[2,6]

Tungsten hexafluoride complexes with nitrogen bases were prepared, *e.g.*, $WF_6N(CH_3)_3$, and solution spectroscopic equivalence of fluorine atoms was observed; however, the possibility of equivalence having genesis in a fast base dissociation

$$WF_6N(CH_3)_3 \rightleftharpoons WF_6 + N(CH_3)_3$$

could not be eliminated because, unlike the nmr spectrum of the phosphine adduct, there was no observable spin–spin coupling between fluorine atoms and magnetic nuclei associated with the amine ligand. Interestingly the less sterically hindered amine, pyridine, yielded with WF_6 the complex $WF_6(NC_5H_5)_2$ in addition to a 1:1 adduct. The single-line F^{19} resonance of $WF_6NC_5H_5$ (−164 ppm) is shifted slightly to high field of WF_6 (−166 ppm) and the single line of $WF_6(NC_5H_5)_2$ appears at still higher field (−136 ppm, 25°). The chemical shift of the 1:2 adduct is temperature dependent (−122 ppm, −30°) and the change in chemical shift with temperature is consistent with the equilibrium

$$WF_6(NC_5H_5)_2 \overset{\Delta}{\rightleftharpoons} WF_6(NC_5H_5) + NC_5H_5$$

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[1] E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

[2] References pertinent to rearrangements are given in reviews by E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966), for five-coordination and by E. L. Muetterties and C. M. Wright, *ibid.*, **21**, 109 (1967), for seven-coordination.

[3] (a) B. Cox, D. W. A. Sharp, and A. G. Sharpe, *J. Chem. Soc.*, 1242 (1956); (b) J. G. Malm, H. Selig, and S. Siegel, *Inorg. Chem.*, **5**, 130 (1966).

[4] E. L. Muetterties, "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 509.

[5] We found no other F^{19} resonance that could be attributed to a fluoride ion; and, in any case, a species such as $WF_5P(CH_3)_3{}^+F^-$ should exhibit fluorine atom nonequivalence for the octahedral cation. The P^{31} nmr spectrum would unequivocally establish the number of fluorine atoms bound to tungsten. However, we have not the spectrometer sensitivity to obtain the detailed fine structure with these dilute (with respect to number of phosphorus atoms) solutions.

[6] E. L. Muetterties and K. J. Packer, *J. Am. Chem. Soc.*, **86**, 293 (1964).

In WF_6NCCH_3, there was a main resonance at −15° as well as $W^{183}F^{19}$ satellites but the satellites were not detected at room temperature where the main resonance is significantly broadened presumably owing to some exchange process.

The tungsten fluoride complexes are exceedingly reactive. Illustrative of this is the behavior of $WF_6 \cdot P(CH_3)_3$ in sulfur dioxide solution. Above about −20° an irreversible reaction occurs to give initially a mixture of at least two compounds. Slowly, as discerned by following the F^{19} nmr spectrum, the spectrum of the WOF_5^- ion appears (quintet–doublet).[7] The identity of the WF and FF coupling constants for WOF_5^- and those reported originally by Muetterties[4] for WF_6 complexes indicates that reaction with solvent or hydrolysis due to trace moisture vitiates the original[4] structural characterization of these metal hexafluoride complexes.

The F^{19} nmr spectral behavior of $(C_6H_5)_2NPF_4$[8] precisely parallels that of $(C_2H_5)_2NPF_4$ with spectroscopic equivalence at 25° and a pattern at $\sim -70°$ consistent with trigonal-bipyramidal geometry with an equatorial diphenylamino group. The intramolecular averaging process is similarly assayed in terms of a PF_4 bending mode[9] probably associated with a PN rotational process with a barrier of the order of magnitude of 6 kcal.

Experimental Section

Reagents and Procedures.—Commercial tungsten hexafluoride was stored over sodium fluoride in a stainless steel cylinder and then distilled into a vacuum system or used directly in the solution preparation of complexes. Reagent grade acetonitrile was stored over phosphorus(V) oxide and distilled in a vacuum system prior to use. Sulfur dioxide was fractionally distilled and stored in a stainless steel cylinder. The donor molecules were commercial samples or were prepared by conventional procedures and then fractionally distilled prior to use, usually with prestorage over molecular sieve.

Tungsten hexafluoride and its complexes are very reactive with air. The materials were handled in a vacuum system (approximately 10^{-5} mm), the Vacuum/Atmospheres Corp. drybox system, or in glass equipment from which air was carefully excluded.

Preparation of Complexes. $F_6WP(CH_3)_3$.—Tungsten hexafluoride, 22.7 g (0.076 mole), was condensed under vacuum into a flask containing a frozen solution of 5.8 g (0.076 mole) of $P(CH_3)_3$ dissolved in 100 ml of dichloromethane. The mixture was warmed to about −60° and stirred for several minutes to produce a deeply colored red solution. The solution was allowed to warm over a 0.5-hr period to room temperature. Formation of the final product, an orange solid of low solubility in the medium, commenced at about −30 to −40°. The yield was 26.2 g (92%), mp 144–146° dec. *Anal.* Calcd for $WF_6PC_3H_9$: W, 49.2; F, 30.5; P, 8.3; C, 9.6; H, 2.4. Found: W, 49.3; F, 30.6; P, 7.8; C, 9.8; H, 2.2. The F^{19} nmr spectrum of an acetonitrile solution of this material showed small peaks at −144.6, −54.4, and −53.4 ppm attributed to impurities. These impurities were effectively removed by recrystallization of the material from acetonitrile solution at −15°. The solution was not heated above room temperature. *Anal.* (recrystallized material). Found: W, 49.9; F, 30.7; P, 8.1; C, 9.9; H, 2.6; N, 0.0.

The complex decomposed under vacuum at 80°; volatile yellow-to-red solids with variable compositions were collected which in general contained considerably more carbon and hydrogen (presumably as CH_3 groups) than required for the simple 1:1 adduct. *Anal.* Found for the first portion of the sublimate, a yellow solid: W, 46.7; F, 27.4; P, 8.2; C, 14.6; H, 3.8; corresponding to the approximate formulation $W_{1.0}F_{5.7}(CH_{3.1})_{1.8}P_{1.0}(CH_{3.1})_3$.

Solutions of the 1:1 adduct for spectral observations were prepared using acetonitrile, sulfur dioxide, or sulfur dioxide–dichloromethane mixtures as solvents. Decomposition of the saturated acetonitrile solutions occurred sufficiently slowly to allow spectral examination at room temperature. The half-life of such a solution at 25° was about 1 day.

In sulfur dioxide solution below −20° the complex was stable for a matter of hours. At 0° in this solvent, reaction was fairly rapid to produce a sample with major peaks at −147.4 and −64.3 ppm (doublet; $J = 63$ cps, $J_{WF} = 74$ cps) and peaks of small intensity at +128.6 (multiplet, with a minimum of four lines, $J = 12$ cps) and +145.4 ppm (multiplet, with a minimum of five lines, $J = 13$ cps), in addition to lines at the characteristic WOF_5^- positions. At room temperature, the intensity of the resonances attributed to WOF_5^- slowly increased as the intensity of the doublet at −64.3 ppm diminished.

The F^{19} nmr spectrum of the unreacted complex in either of the solvents consisted of a doublet over the temperature range examined, from ambient temperature to the freezing points of the solutions. Additional structure appearing on each member of the doublet arising from W–F coupling was observed at −20° in the sulfur dioxide solution. The spectrum was unchanged to −85°.

$F_6WN(CH_3)_3$.—A three-neck flask containing 50 ml of dichloromethane was fitted with a condenser vented to a hood and two gas inlet tubes extending below the surface of the solvent. Trimethylamine and WF_6, each diluted with phosphorus pentoxide dried nitrogen, were passed at approximately equal rates for 1 hr through the respective inlet tubes as the solvent was stirred. The mixture was maintained at or below room temperature. Unreacted gases were purged from the system using a stream of nitrogen, and, in a nitrogen-filled drybox, the insoluble solids were collected, crystallized from acetonitrile, and dried under vacuum. *Anal.* Calcd for $WF_6NC_3H_9$: W, 51.5; F, 31.9; N, 3.9; C, 10.1; H, 2.5. Found: W, 51.8; F, 31.3; N, 3.9; C, 10.4; H, 2.7.

No decomposition of the complex in acetonitrile or in sulfur dioxide solutions was apparent. Single-line F^{19} nmr spectra were obtained between the ambient temperature and the freezing points of the solutions. Peak widths were relatively broad throughout the temperature range examined (30 cps at half-height at room temperature) and no WF satellites were detected.

Reaction of WF_6 with Pyridine.—In a vacuum system, 20 g (0.067 mole) of WF_6 was condensed with liquid nitrogen into a flask containing a solution of 5.3 g (0.067 mole) of pyridine in 100 ml of dichloromethane. The mixture was warmed to the melting point, stirred, and further warmed over a 1-hr period to room temperature. A trace of insoluble material was separated from the solution by filtration. By stepwise removal of solvent, two distinctly different white crystalline materials were isolated. Elemental analyses of the first crop, 1.5 g, mp 146° dec, suggested the composition $F_6W(NC_5H_5)_2$. *Anal.* Calcd for $WF_6N_2C_{10}H_{10}$: W, 40.3; F, 25.0; N, 6.1; C, 26.3; H, 2.2. Found: W, 38.1; F, 25.6; N, 6.7; C, 27.7; H, 2.5.

Two succeeding crops (3.6 and 7.7 g) were lower melting (110 and 104°, respectively) and elemental analyses indicated a 1:1 adduct. *Anal.* Calcd for $WF_6NC_5H_5$: W, 48.8; F, 30.2; N, 3.7; C, 15.9; H, 1.3. Found for the sample melting at 104°: W, 46.2; F, 29.6; N, 3.8; C, 18.8; H, 1.6.

Repetition of the preparative procedure with twice the amount of pyridine yielded the pure, higher melting 1:2 adduct (softening point 139°, mp 144° dec). *Anal.* Found: W, 40.5; F, 25.3; N, 6.1; C, 26.5; H, 2.3. Fluorine nmr spectra of both the 1:1 and 1:2 complexes consisted of a single line. No W–F coupling was observed. The chemical shift of the 1:2 adduct in SO_2 or

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[7] The WOF_5^- ion was independently synthesized from WOF_4 and $(C_3H_7)_4NF$ in dichloromethane solution.

[8] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).

[9] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

TABLE I

FLUORINE NMR SPECTRA

Compound	Solvent	Temp,[a] °C	δ,[b] ppm	J_{WF}, cps	Additional information
WF_6	$CFCl_3$		−165.2	44	
WF_6	Cyclohexane		−165.4	41	
WF_6	Mesitylene		−166.0	39	
WF_6	SO_2		−166.4	44	
WF_6	CH_3CN		−165.9	. . .	
WF_6	CH_3CN	−15	−165.2	48	
$F_6WP(CH_3)_3$	CH_3CN		−135.5	. . .	J_{PF} = 73 cps
$F_6WP(CH_3)_3$	SO_2	−20	−137.4	38	J_{PF} = 73 cps
$F_6WN(CH_3)_3$	SO_2		−144.8	. . .	
$F_6WNC_5H_5$	SO_2		−163.9	. . .	
$F_6WNC_5H_5$	CH_2Cl_2		−162.5	. . .	
$F_6W(NC_5H_5)_2$	SO_2	25	−135.9	. . .	
WOF_4	SO_2		−73.9	64	
$(n\text{-}C_3H_7)_4N^+WOF_5^-$	CH_3CN		Doublet −49.4 Quintuplet +82.8	70	J_{FF} = 53 cps
$(n\text{-}C_3H_7)_4N^+WOF_5^-$	SO_2		Doublet −54.3 Quintuplet +71.9	71	J_{FF} = 52 cps
$(C_6H_5)_2NPF_4$	Toluene	−72	+46.4 (F_a) +73.0 (F_e)		J_{PF_a} = 788 cps; J_{FF} = 81 cps J_{PF_e} = 941 cps
$(C_6H_5)_2NPF_4$	Toluene		+59.8		J_{PF} = 865

[a] Unless otherwise specified the temperature was about 28° without external temperature control. [b] Reference: internal $CFCl_3$.

acetonitrile solutions was markedly temperature dependent. In sulfur dioxide solution, the shift varied from −137.9 ppm at +31° to −121.7 ppm at −30°. No comparable temperature dependence of chemical shift was found in any of the other complexes studied.

The WF_6–CH_3CN System.—A white solid, soluble in acetonitrile, was formed on reaction of WF_6 and CH_3CN but was not isolated in this study. The nmr spectrum of a solution of 0.1 ml of WF_6 dissolved in a mixture of 0.4 ml of CH_3CN and 0.1 ml of $CFCl_3$ consisted of a broad line (70 cps at half-height) at room temperature and of a relatively sharp (9 cps) line at −15° with visible WF satellites.

Preparation of WOF_4 and WOF_5^-.—Tungsten hexafluoride, 14 g (0.047 mole), was condensed into an evacuated Hastelloy-C bomb containing 5.0 g (0.022 mole) of tungsten trioxide. The vessel was sealed and shaken at 400° for 6 hr, cooled to room temperature, vented to a hood, and purged several times with nitrogen at 100 psi. The product was transferred under nitrogen and sublimed in glass equipment at 100° under vacuum. The yield was 5.6 g or 31% based on the equation $WO_3 + 2WF_6 \rightarrow 3WOF_4$. Resublimation yielded 4.3 g (mp 97–102°; lit.,[10] 110°). *Anal.* Calcd for WOF_4: W, 66.7; F, 27.5. Found: W, 67.6; F, 27.6. This material was used without further purification for the preparation of WOF_5^-.

Tetra-*n*-propylammonium fluoride was prepared by neutralization of a 10% solution of tetra-*n*-propylammonium hydroxide in water with an aqueous solution of 48% hydrofluoric acid. The bulk of the water was removed at approximately 3 mm and the resulting semisolid was further dried under vacuum (10^{-5} mm) at 100° for 6 hr. A solution of 2.5 g of this solid dissolved in 10 ml dichloromethane was added under a nitrogen atmosphere to 2.2 g of WOF_4 suspended in 5 ml of dichloromethane. The mixture was filtered and solvent was removed from the filtrate to the point of crystallization of the product $(n\text{-}C_3H_7)_4NWOF_5$. The first crop of product isolated in this manner weighed ~0.6 g and was recrystallized from dichloromethane. *Anal.* Calcd for $C_{12}H_{28}NWOF_5$: C, 30.0; H, 5.9; N, 2.9; F, 19.7; W, 38.2. Found: C, 29.5; H, 5.7; N, 3.3; F, 19.3; W, 38.2.

Nmr Procedures.—Fluorine-19 nmr spectra were obtained at 56.4 and 94 Mc using Varian HR-60 and HA-100 instruments. Samples were maintained in sealed evacuated tubes at liquid nitrogen temperatures prior to examination. Chemical shifts are reported with reference to internal $CFCl_3$.

Acknowledgment.—We are indebted to Dr. R. Schmutzler for the sample of $(C_6H_5)_2NPF_4$.

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[10] O. Ruff, F. Eisner, and W. Heller, *Z. Anorg. Allgem. Chem.*, **52**, 256 (1907).

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Base Hydrolysis of $[Co(NH_3)_5X]^{2+}$ Ions

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The rate law for base hydrolysis of cobalt(III) complexes has been established for a wide variety of complexes[1] as

$$-\frac{d[\text{complex}]}{dt} = k[\text{complex}][OH^-]$$

but mostly for low base concentrations. However, a recent article[2] on the base hydrolysis of the chloropentaamminecobalt(III) ion has described a rate law which deviates substantially from a first-order dependence on $[OH^-]$ at higher OH^- concentrations, Figure 1. This deviation was interpreted on the basis of an ion-pair mechanism, but the possibility of the result arising from the production of an appreciable concentration of the deprotonated intermediate was not excluded.

This note questions the validity of the rate data ob-

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[1] For collected references see F. Basolo and R. G. Pearson "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967.

[2] S. C. Chan, *J. Chem. Soc., Sect. A*, 1124 (1966).