4510 *Inorg. Chem.* **1994,** *33,* 4510−4516

Interaction between Uranium(V) and -(VI) Fluorides and Nitrogen Bases. Characterization and Crystal Structures of the Dimorphic Adduct $UF_5\cdot$bipy (bipy = 2,2′-Bipyridyl)

Lucile Arnaudet, Roland Bougon,* Ban Buu, Monique Lance, Martine Nierlich, and Julien Vigner

SCM-URA 331 CNRS, CEA-Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette, France

Received December 10, 1993®

The interaction between UF_6 or UF_5 and 2-fluoropyridine (F-py) or 2,2′-bipyridyl (bipy) has been investigated in view of obtaining new adducts of these fluorides. In CH_2Cl_2 solution, UF_6 reacts with F-py and bipy to yield $UF_4\cdot$F-py and $U_2F_{12}\cdot$bipy, respectively. However, for the UF_6/bipy system, the reduction of UF_6 by bipy is the dominant process, and the formation of $U_2F_{12}\cdot$bipy might be a preliminary step of this reduction. The reaction of β-UF_5 with F-py does not lead to a crystallized compound, whereas, with bipy, the dimorphic adduct $UF_5\cdot$bipy and the ionic derivative $[(bipy)_2H]^+[UF_6]^-$ are obtained. All these compounds but $UF_4\cdot$F-py are moisture sensitive. The adduct of UF_5 has been characterized by elemental analyses, X-ray powder data, and infrared spectroscopy. Solutions of this adduct in CD_3CN were studied by NMR spectroscopy. The crystal structures of the two forms of $UF_5\cdot$bipy have been determined by X-ray diffraction methods. In both forms the coordination polyhedron of the uranium atom is a distorted monocapped trigonal prism made up of five fluorine atoms and two nitrogen atoms of the bipyridine ligand. The molecular unit, however, has a different local symmetry in the two forms. The space groups, unit cell parameters, and *R* factors are as follows: $UF_5\cdot$bipy (**I**), monoclinic, *C*2/*c* (No. 15), $a = 7.086(3)$ Å, $b = 14.443(3)$ Å, $c = 11.501(3)$ Å, $\beta = 99.79\ (3)°$, $V = 1160.0\ (9)$ Å^3, $Z = 4$, $R = 0.028$; $UF_5\cdot$bipy (**II**), orthorhombic, *Pnma* (No. 62), $a = 9.731(3)$ Å, $b = 6.933(6)$ Å, $c = 17.729(5)$ Å, $V = 1196(2)$ Å^3, $Z = 4$, $R = 0.022$.

Introduction

Nitrogen bases such as pyridine (py), 2-fluoropyridine (F-py), 2,2′-bipyridyl (bipy), or 1,8-naphthyridine (napy) have been found to yield molecular or ionic adducts with the hexafluoride (WF_6), the dioxide difluoride (WO_2F_2), or the oxide tetrafluoride of tungsten (WOF_4) .[1−7] A natural extension of these works was to use uranium hexafluoride, UF_6, instead of WF_6 as coordinating molecule. However, the strong fluorinating agent UF_6 was expected to change dramatically the reaction pathways and to produce at some stage U(V) or U(IV) derivatives. In that connection, it was found that no mentions of a purely molecular adduct of UF_5 appeared in the literature. Uranium pentafluoride is known to be a strong electron-pair acceptor; however, the previous studies were mainly devoted to the preparation and characterization of complexes obtained from F^- ion transfer[8,9] or sharing of F atoms with other metals.[10,11] Few adducts were obtained with organic electron-pair donors,[12−14] and experimental data suggested that they were ionic.[13,15] From these observations, it was considered that a study of the behavior of UF_5 toward the nitrogen bases that had been successfully used with WF_6 and WOF_4[3−6] could lead to genuine molecular adducts of UF_5.

Experimental Section

Apparatus. Volatile fluorides were manipulated in an all-metal vacuum line, which was passivated with chlorine trifluoride prior to its use. Other volatile materials were purified and transferred in a glass vacuum line designed to handle moisture-sensitive materials. Solid products were handled in the dry argon atmosphere of a glovebox (Braun). Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using small crystals pressed between AgBr windows in an Econo press (Barnes Engineering Co.). The spectral region 5000−25 000 cm^{-1} was examined using a Cary Model 2300 spectrophotometer. The samples were ground into mulls with Nujol and placed between CaF_2 disks. Raman spectra of polycrystalline materials contained in 5 mm o.d. glass tubes were recorded on a Coderg Model T 800 spectrophotometer using the 514.5-nm exciting line of an Ar ion Model 2016 Spectra Physics laser filtered with a Coderg premonochromator. Low-temperature Raman spectra were recorded at −196 °C with the sample mounted in an unsilvered Pyrex dewar filled with liquid nitrogen. The NMR spectra were recorded on a Bruker Model AC 200 spectrometer at 200.13, 188.3, and 50.32 MHz for ^{1}H, ^{19}F, and ^{13}C, respectively. Samples were referenced externally with respect to $Si(CH_3)_4$ or $CFCl_3$ with positive shifts being downfield from the standards. Elemental analyses were performed by Mikroanalytische Laboratories, Elbach, Germany.

X-ray Diffraction. X-ray powder diffraction patterns of the samples sealed in 0.5 mm o.d. glass capillaries were obtained by using a Philips

---

® Abstract published in *Advance ACS Abstracts,* August 1, 1994.

(1) Tebbe, F. N.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 172.

(2) Arnaudet, L.; Bougon, R.; Buu, B.; Charpin, P.; Isabey, J.; Lance, M. *Inorg. Chem.* **1989**, *28*, 257.

(3) Arnaudet, L.; Bougon, R.; Buu, B.; Lance, M.; Nierlich, M.; Vigner J. *Inorg. Chem.* **1993**, *32*, 1142.

(4) Arnaudet, L.; Bougon, R.; Buu, B.; Charpin, P.; Isabey, J.; Lance, M.; Nierlich, M.; Vigner, J. *Can. J. Chem.* **1990**, *68*, 507.

(5) Arnaudet, L.; Bougon, R.; Buu, B.; Lance, M.; Navaza, A.; Nierlich, M.; Vigner, J. *J. Fluorine Chem.* **1992**, *59*, 141.

(6) Arnaudet, L.; Bougon, R.; Buu, B.; Lance, M.; Navaza, A.; Nierlich, M.; Vigner, J. *J. Fluorine Chem.* **1994**, *67*, 17.

(7) Arnaudet, L.; Bougon, R.; Buu, B.; Lance, M.; Kaska, W. C. *J. Fluorine Chem.* **1991**, *53*, 171.

(8) Penneman, R. A.; Sturgeon, G. D.; Asprey, L. B. *Inorg. Chem.* **1964**, *3*, 126.

(9) Sturgeon, G. D.; Penneman, R. A.; Kruse, F. H.; Asprey, L. B. *Inorg. Chem.* **1965**, *4*, 748.

(10) Bougon, R.; Charpin, P. *J. Fluorine Chem.* **1979**, *14*, 235.

(11) Sawodny, W.; Rediess, K.; Thewalt, U. *Z. Anorg. Allg. Chem.* **1980**, *469*, 81.

(12) Berry, J. A.; Prescott, A.; Sharp, D. W. A.; Winfield, J. M. *J. Fluorine Chem.* **1977**, *10*, 247.

(13) Halstead, G. W.; Eller, P. G.; Eastman, M. P. *Inorg. Chem.* **1979**, *18*, 2867.

(14) Holloway, J. H.; Staunton, G. M.; Berry, J. A.; Brown, D. *J. Less-Common Met.* **1986**, *120*, 71.

(15) Akona, S. Y. B.; Fawcett, J.; Holloway, J. H.; Russell, D. R.; Leban, I. *J. Fluorine Chem.* **1989**, *45*, 37.

0020-1669/94/1333-4510$04.50/0

Table 1. Crystallographic Data for the Monoclinic (I) and Orthorhombic (II) Crystal Forms of UF_5·bipy

	UF_5·bipy (**I**) ($C_{10}H_8F_5N_2U$)	UF_5·bipy (**II**) ($C_{10}H_8F_5N_2U$)
fw	489.21	489.21
space group	*C*2/*c* (No. 15)	*Pnma* (No. 62)
a, Å	7.086(3)	9.731(3)
b, Å	14.443(3)	6.933(6)
c, Å	11.501(3)	17.729(5)
β, deg	99.79(3)	
V, Å^3	1160.0(9)	1196(2)
Z	4	4
T, K	295	295
λ, Å	0.710 73	0.710 73
μ, cm^{-1}	133.16	129.153
ϱ_{calc}, g cm^{-3}	2.801	2.717
transm coeff	0.322, 0.999	0.562, 0.999
$R(F)^a$	0.028	0.022
$R_w(F)^b$	0.042	0.027

$^a R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w(F) = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w[|F_o|]^2]^{1/2}$.

camera (diameter 11.46 cm) with Ni-filtered Cu α radiation. Crystals suitable for structure determination were selected in the drybox under a microscope and sealed inside 0.5 mm o.d. glass capillaries. X-ray diffraction was carried out on an Enraf-Nonius CAD 4 automated diffractometer. Cell dimensions were obtained by a least-squares refinement of the setting angles of the 25 reflections with θ between 8 and 12°. Three standard reflections were measured each 1 h to monitor the crystal decay (2% and 3% in 15 h for UF_5·bipy (**I**) and UF_5·bipy (**II**), respectively), with a linear correction being made. Intensities were corrected for Lorentz–polarization effects and absorption.[16] The structures were solved by the heavy-atom method and refined by full-matrix least-squares techniques (F) with anisotropic thermal parameters for the uranium and fluorine atoms. The hydrogen atoms were included in the refinement at calculated positions: they were not refined but constrained to ride on their C atoms. All calculations were performed on a Vax 4000-200 computer using the Enraf-Nonius MolEN system.[17] Analytical scattering factors for neutral atoms [18] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Other experimental details appear with the crystal data in Table 1 and in the supplementary material.

Materials. Uranium hexafluoride from Comurhex was purified by pumping at −78 °C. β-Uranium pentafluoride was prepared by UV photolysis of UF_6 using CO as a scavenger.[19] 2-Fluoropyridine, dichloromethane, acetonitrile (from Prolabo), CD_2Cl_2, and CD_3CN (CEA; 99.3% isotopic enrichment) were dried over P_2O_5. 2,2′-Bipyridyl from Aldrich Chemie was sublimed under vacuum at ca. 50 °C. Propylene carbonate (4-methyl-2-dioxolone, $C_4H_6O_3$), purchased from Koch-Light Laboratories Ltd., was distilled and stored over 5 Å molecular sieves.

Reaction of UF_6 with F-py. A 3.75 mmol amount of F-py was condensed into a glass flask cooled at −196 °C that had been evacuated on the vacuum line. An amount of 3 cm^3 of CH_2Cl_2 was then added by condensation at this temperature. The mixture was warmed to ambient temperature, stirred for a few minutes, and cooled again to −196 °C; then 1.50 mmol of UF_6 was condensed onto it. Warming the solution to ambient temperature resulted in a yellow solid deposit on the walls of the flask. This product instantly turned green by contact with the solution without dissolving. Most of the solvent and excess F-py were removed by decantation at this temperature. The green product was finally dried in vacuo at ambient temperature for a few hours. This compound, which was found to be stable to ca. 100 °C, does not sublime at this temperature, and its solubility in CD_2Cl_2 is negligible. Anal. Calcd for UF_4·F-py: U, 57.90; F, 23.11; C, 14.61; H, 0.98; N, 3.41. Found : U, 57.55; F, 22.85; C, 14.53; H, 1.01; N, 3.47.

Reaction of UF_6 with bipy. Using the method described above except that bipy was loaded in the drybox into the dried glass flask, 7.73 mmol of UF_6 was reacted with 2.58 mmol of bipy in 3 cm^3 of CH_2Cl_2. The mixture still at −196 °C was placed in the freezer at −10 °C and left at this temperature for 3 h. The finely divided yellow precipitate that was obtained was isolated by decantation and pumping at ambient temperature. This product stuck on the walls of the flask, and its rapid decomposition when handled in the drybox (water and oxygen content not exceeding 1 ppm) prevented any physical characterization. This product also decomposed (or reacted) in CD_3CN or in propylene carbonate. Its composition was found to correspond to the empirical formula U_2F_{12}·bipy. Anal. Calcd for U_2F_{12}·bipy: U, 55.34; F, 26.50; C, 13.97; H, 0.94; N, 3.26. Found: U, 55.10; F, 26.21; C, 14.22; H, 1.03; N, 3.31. It must be pointed out that preliminary experiments regarding this reaction had indicated that UF_6 was exothermally reduced by bipy as evidenced by the formation of black and green products. The temperature of the reacting mixture had to be maintained as low as possible to obtain a sufficient amount of U_2F_{12}·bipy. The reaction achieved in CH_3CN or with the reactants in the melt (70 °C) gave an amorphous gel in the first case and a complex mixture in which no more free or bound bipy was recovered in the second case.

Reaction of β-UF_5 with F-py. A solution of 1.841 mmol of F-py in 1 cm^3 of CH_3CN was poured onto a solution of 0.673 mmol of β-UF_5 in 3 cm^3 of CH_3CN at ambient temperature. The green solid product obtained by evaporation of the solvent and excess F-py was found to be amorphous to X-rays, and its elemental analysis indicated that it was not a definite compound. The reaction duplicated without CH_3CN led to the same result.

Preparation of UF_5·bipy. In a first method of preparation, the adduct UF_5·bipy was obtained from the reaction of a frozen solution of 0.50 mmol of β-UF_5 in 2 cm^3 of CH_3CN kept at −196 °C into which a solution of 1.16 mmol of bipy in 1 cm^3 of CH_3CN was poured under vacuum. The light green, almost colorless, needle-shaped crystals that were formed upon warming to ambient temperature were decanted and pumped to dryness at this temperature. Anal. Calcd for UF_5·bipy: U, 48.66; F, 19.42; C, 24.55; H, 1.65; N, 5.73. Found: U, 48.50; F, 19.14; C, 24.63; H, 1.75; N, 5.88. The X-ray diffraction study indicated that the compound had crystallized in the orthorhombic system.

In the second method of preparation, UF_5·bipy was obtained from the reaction of a solution of 0.40 mmol of β-UF_5 in 3 cm^3 of CH_3CN onto which a solution of 0.70 mmol of bipy in 1 cm^3 of CH_3CN was poured under vacuum. Both solutions were at 50 °C when they were mixed. The temperature of the resulting solution was slowly decreased from +50 to −18 °C over a period of 48 h. Decantation and pumping of the solid product yielded a block of green powder and pale green crystals with a few needle-shaped crystals. The powder and the pale green crystals were found to have the same X-ray powder pattern, and that of the needle-shaped crystals corresponded to the orthorhombic form of UF_5·bipy. This phase was easily separated in the drybox from the major product, which proved to be also UF_5·bipy but crystallized in the monoclinic system. Anal. Calcd for UF_5·bipy: U, 48.66; F, 19.42; C, 24.55; H, 1.65; N, 5.73. Found: U, 48.30; F, 19.20; C, 24.43; H, 1.74; N, 5.75.

Preparation of $[(bipy)_2H]^+[UF_6]^-$. The ionic derivative $[(bipy)_2H]^+[UF_6]^-$ was obtained from the mother liquor of the preparation of UF_5·bipy (monoclinic form). The evaporation of the volatiles at ambient temperature resulted in a solid residue made up of a block of brown yellow material and a small amount of green powder. The green powder was identified by its X-ray powder pattern as UF_5·bipy (monoclinic form), and on the basis of the elemental analyses, the brown-yellow solid was first thought to be UF_5·2bipy. Calcd for UF_5·2bipy: U, 36.88; F, 14.72; C, 37.22; H, 2.50; N, 8.68. Found (samples from two different preparations): U, 36.55/37.15; F, 14.70/14.65; C, 36.97/36.96; H, 2.38/2.38; N, 8.53/8.51. However, a single-crystal X-ray diffraction study later showed[20] that the only uranium-containing species in this compound was the $[UF_6]^-$ anion and that the

---

(16) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A 24*, 351.

(17) *MolEN: An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

(18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(19) Halstead, G. W.; Eller, P. G.; Asprey, L. B.; Salazar, K. V. *Inorg. Chem.* **1978**, *17*, 2967.

(20) To be submitted for publication.

Table 2. X-ray Powder Diffraction Data for $UF_4 \cdot$F-py, $UF_5 \cdot$bipy (Monoclinic (I) and Orthorhombic (II) Crystal Forms), and $[(bipy)_2H]^+[UF_6]^-$ [a]

$UF_4 \cdot$F-Py		$UF_5 \cdot$bipy (I)				$UF_5 \cdot$bipy (II)				$[(bipy)_2H]^+[UF_6]^-$	
		d, Å				*d*, Å					
d, Å	intens	obsd	calcd	intens	*hkl*	obsd	calcd	intens	*hkl*	*d*, Å	intens
7.07	s	7.22	7.221	m	020	8.84	8.864	w	002	10.40	s
5.62	ms	6.255	6.287	vs	110	6.50	6.457	vs	101	8.22	vvw
4.98	vs	5.622	5.667	w	002	5.37	5.380	s	111	7.25	vw
4.57	w	5.151	5.172	vw	111	4.84	4.865	w	020	6.80	m
4.00	ms	4.491	4.571	s, dble	$\bar{1}12$, 022	4.73	4.762	vw	112	6.10	s
3.847	m		4.458			4.446	4.432	m, br	004	5.693	ms
3.573	s,br	3.914	3.921	s	112	4.073	4.082	mw	113	5.336	s
3.360	w	3.616	3.610	vw	040	3.847	3.886	vvw	121	4.897	ms
2.966	vvw	3.456	3.440	s	041	3.735	3.734	vw	104	4.595	ms
2.820	m	3.212	3.228	vvw	$\bar{2}02$	3.457	3.466	mw	200	4.392	ms
2.740	vw	3.129	3.143	vvw	220	3.280	3.276	m	024	4.111	vvw, br
2.520	vvw	2.928	2.916	mw	221	3.162	3.157	vvw	105	3.798	mw
2.384	w	2.822	2.833	vvw	004	3.035	3.003	vvw	115	3.616	w
2.285	vvw	2.732	2.745	vvw	$\bar{1}14$	2.986	2.990	w	203	3.504	vw
2.225	w	2.623	2.637	m, br	024, $\bar{2}23$	2.794	2.789	w, dble	132	3.386	m
2.187	vvw		2.622				2.788		221	3.30	ms
2.106	w	2.562	2.561	vvw	151	2.720	2.718	w	106	2.905	w
2.034	vvw	2.440	2.447	w	114	2.634	2.631	w	133	2.846	w
1.932	mw	2.412	2.407	vvw	060	2.378	2.381	mw	224	2.569	m
		2.342	2.354	mw	061	2.293	2.291	w	301	2.473	vvw
		2.274	2.286	vvw	$\bar{2}24$	2.184	2.179	mw	312	2.366	m
		2.255	2.253	w	223	2.130	2.132	mw	044		
		2.205	2.206	vvw	134	2.081	2.083	w	136		
		2.108	2.116	ms	153, 330	2.034	2.032	mw	322		
			2.095			1.967	1.968	w	323		
		1.961	1.960	m, br	224						
		1.918	1.919	vvw	045						
		1.886	1.889	vvw	006						
		1.823	1.827	mw	026						
		1.781	1.783	mw	081						
		1.738	1.737	vw	116						
		1.720	1.720	vw	082						

[a] Abbreviations used: br, broad; dble, double; v, very; s, strong; m, medium; w, weak.

bipyridyls were not bound to the uranium atom. In the absence of any X-ray-detectable cationic species, the charge balance implied the presence of a proton H^+ probably bound to the nitrogen atom of a bipy. The presence of the NH^+ species was confirmed by the ^1H NMR spectra. The X-ray powder pattern calculated[20] from the single-crystal X-ray diffraction data was found to match that of the samples that had been analyzed, and this pattern was also obtained with ground single crystals. Consequently, the samples analyzed and the single crystal corresponded to the same product, and the compound had to be formulated as $[(bipy)_2H]^+[UF_6]^-$ and not $UF_5 \cdot$2bipy. The easy formation and escape of an HF molecule from $[(bipy)_2H]^+[UF_6]^-$ most likely account for the analytical discrepancy. This compound was also prepared by using a 2-fold excess of bipy at 50 °C and removing this excess by sublimation at ambient temperature. The quite distinct color of this compound permitted its easy separation from the small amount of $UF_5 \cdot$bipy (monoclinic and orthorhombic forms) which had also been formed. The X-ray powder patterns of $UF_4 \cdot$F-py, $UF_5 \cdot$bipy (monoclinic and orthorhombic crystal forms), and $[(bipy)_2H]^+[UF_6]^-$ are given in Table 2.

Results and Discussion

Reactions of UF_6 with F-py and bipy. As attested by the composition of the solid residue and its insensivity to moisture, the reaction that takes place between UF_6 and F-py in CD_2Cl_2 solution leads to reduction of U(VI) to U(IV). The reaction probably proceeds through the formation of an unstable intermediate compound, possibly [$UF_6 \cdot$F-py] which could not be isolated. The formation of the U(IV) complex UF_4F-py most likely arises from reduction of UF_6 by protons of part of the F-py and not by the solvent, since solutions of UF_6 in CD_2Cl_2 were found to be stable for periods of time exceeding that required by the experiment. However, the experimental data were not sufficient to ascertain the reduction mechanism. The reduction of UF_6 by F-py is not in agreement with Muetterties's observations, who claimed the synthesis of a one-to-one and a one-to-two adduct of UF_6 with F-py.[21] As pointed out, however, by this author in a subsequent paper,[1] some of his previous erroneous conclusions regarding complexes of WF_6, could be explained by traces of water in his reaction media. It may then be assumed that the products he had obtained from the UF_6/F-py system resulted from both hydrolysis and reduction of UF_6.

The reaction of UF_6 with bipy in CD_2Cl_2 leads to the U(VI) derivative $U_2F_{12} \cdot$bipy. The formation of this product may be considered as a preliminary step of the reduction of UF_6. The arrangement of the atoms in the inorganic part of this compound was not determined because it could not be handled at room temperature without decomposing. However, by analogy with the adduct $W_2F_{12} \cdot$bipy, previously prepared and shown to be $[WF_4(bipy)_2]^{2+}([WF_7]^-)_2 \cdot WF_6$,[6] it can be speculated that $U_2F_{12} \cdot$bipy has to be formulated $[UF_4(bipy)_2]^{2+}([UF_7]^-)_2 \cdot UF_6$. The presence of the solvate molecule UF_6 in the compound would then account for its easy decomposition (or reactivity).

Reaction of UF_5 with F-py and bipy. The reaction of β-UF_5 with F-py leads to a solid amorphous to X-rays. A mixture, probably containing reduction products, is obtained.

UF_5/bipy System. The U(V) derivatives $UF_5 \cdot$bipy (monoclinic and orthorhombic crystal forms) and $[(bipy)_2H]^+[UF_6]^-$ were obtained by the reaction of β-UF_5 with bipy in CH_3CN. The solvent CH_3CN yields depolymerization of β-UF_5 and its

---

(21) Muetterties, E. L. *Advances in the Chemistry of the Coordination Compounds*; Macmillan: New York, 1961; p 509.

Table 3. ^1H and ^{13}C NMR Data[a] for Solutions of $[(bipy)_2H]^+[UF_6]^-$ and UF_5·bipy in CD_3CN and Comparison with Those for bipy

	^1H										
	δ_3	δ_4	δ_5	δ_6	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	spectrum
bipy	8.41	7.87	7.37	8.65	7.96	1.20	1.00	7.62	1.83	4.38	1st order
$[(bipy)_2H]^+[UF_6]^-$	8.43	8.14	7.62	8.73	8.02	1.22	0.73	7.64	1.93	4.82	ABXY
UF_5·bipy	8.48	8.29	7.76	8.77	8.14	1.13	0.85	7.64	1.65	5.19	ABXY

	^{13}C								
	δ_2	δ_3	δ_4	δ_5	δ_6	J_{C3H3}	J_{C4H4}	J_{C5H5}	J_{C6H6}
bipy	156.88	138.01	124.90	121.54	150.19	163	163	165	180
$[(bipy)_2H]^+[UF_6]^-$	152.07	122.91	141.29	126.70	148.56	172	169	172	181
UF_5·bipy	149.70	123.59	142.95	127.61	147.77	167	167	167	183

[a] Chemical shifts δ in ppm from TMS, and coupling constants J in Hz; subscripts 3–6 refer to hydrogen and carbon atom positions, with 3 indicating position adjacent to the C—C bond of the two pyridyl ring, and 6, 5, and 4 the *ortho*, *meta*, and *para* position to the nitrogen atom, respectively; subscript 2 refers to the carbon atoms bonding the two pyridyl rings. The $^{13}C-^1H$ coupling constants were determined by the 2-D sequence "HETJRES" provide by Bruker.

Table 4. Infrared Data[a] for UF_5·bipy (Monoclinic (I) and Orthorhombic (II) Crystal Forms), $[(bipy)_2H]^+[UF_6]^-$, and Comparison with Those for bipy

bipy	UF_5·bipy (**I**)	UF_5·bipy (**II**)	$[(bipy)_2H]^+[UF_6]^-$ [b]	main assgnt	bipy	UF_5·bipy (**I**)	UF_5·bipy (**II**)	$[(bipy)_2H]^+[UF_6]^-$	main assgnt
	3120 mw	3110 mw	3110 ms,br		1215 mw	1215 mw	1220 mw	1225 mw	ν ring
3090 mw	3080 w	3080 mw			1170 w	1176 m	1180 ms	1183 w	
3060 mw		3050 sh		ν(C−H)			1162 ms	1165 mw	α(C−H)
3010 w					1142 m	1153 m		1155 mw	
2295 w							1105 m	1124 vw	
1990 w	2000 w	2010 vw	2005 w		1090 ms	1100 mw	1090 vw	1095 m	γ(C−H)
	1975 w	1987 w			1065 m	1070 m	1070 ms	1067 m	
1965 mw	1950 w	1967 vw	1950 vw		1043 ms	1045 mw	1040 vw	1045 m	α(C−H)
		1925 vw					1050 vw		
1895 mw	1895 w	1890 vw			996 m	1017 ms	1017 s	1021 mw	ring breathing
1870 mw	1865 w	1847 vw				1007 ms	1007 s	1002 m	ν ring
1803 mw	1810 w	1812 vw		comb			985 mw		
	1785 w	1793 vw			975 sh	977 w	965 m	962 mw	
		1770 vw			918 vw	920 ms	920 ms	925 w	
		1752 vw			895 m	900 sh	910 ms	903 vw	
1715 mw	1730 w	1730 vw			876 vw		885 w	892 vw	γ(C−H)
1695 mw	1700 w	1713 vw	1716 vw			842 vw	845 vw		
1665 mw		1675 vw	1660 vw			810 sh	807 m	807 sh	
	1635 w	1637 vw	1634 m		755 vs	770 s	765 s	770 s	γ ring + ν ring
	1623 w	1623 vw	1622 m		740 m		740 m	743 mw	γ(C−H)
	1600 ms	1605 sh	1605 ms			732 ms	730 s	725 mw	
		1597 s	1590 ms			675 sh			
1580 s	1570 mw	1577 ms	1575 vw		652 ms	646 m	646 ms	647 w	
1557 ms		1570 ms	1563 ms					635 w	ν ring
1529 vw	1533 w	1535 m	1530 ms			625 m	626 m	621 mw	
1503 w	1500 mw	1500 s	1502 w	ν ring	616 m			612 w	
	1476 m	1482 s	1480 ms			587 ms	592 s	595 vw	
	1462 sh	1460 mw	1463 ms			513 vs, br	515 vs, br	520 vs, br	ν(U−F)
1453 s	1438 ms	1445 s	1440 ms			477 ms	480 s	490 sh	
1417 s	1415 sh	1425 sh	1427 ms		462 w	460 m	453 w	450 mw	ring scissors/shear
1397 sh		1405 sh	1363 w		422 w	426 w	425 vw	421 w	
	1323 ms	1327 s	1326 m	ν(ring−ring)		410 m	415 ms		γ ring
		1320 sh	1320 sh		396 s		405 sh	402 mw	
1306 w		1297 vw	1290 sh	α(C−H)		366 w	365 w		comb
1270 w	1280 w	1280 w	1280 m	ν ring		352 m	350 m	335 mw	ν ring
1253 ms	1243 m	1250 ms	1254 m	α(C−H)		287 w	280 sh		comb

[a] Frequencies in cm^{-1}. Abbreviations: sh, shoulder; br, broad; v, very; s, strong; m, medium; w, weak; comb, combination. The main assignments for the bipy ligand are from ref 22 (ν, stretches; α, in-plane deformations; γ, out-of-plane deformations). [b] $\nu(N-H^+)$ was probably too weak to be observed.

subsequent coordination by CH_3CN molecules.[12] The bidentate base bipy, however, is strong enough to replace the coordinated CH_3CN molecules. Depending on the temperature of the reaction, two crystal arrangements are obtained for the resulting adduct UF_5·bipy. In the presence of an excess of bipy the ionic derivative $[(bipy)_2H]^+[UF_6]^-$ may also be formed. The presence of the proton in this compound is explained by its abstraction from the solvent by the fluoride on standing in hot solution. This compound easily decomposes and releases an HF molecule. The orthorhombic crystal form of UF_5·bipy (**II**) is obtained by mixing of solutions of UF_5 and bipy in CH_3CN at low temperature. The monoclinic form of UF_5·bipy(**I**) is prepared from the same solutions but mixed at 50 °C. It should be pointed out, however, that this form is not obtained without a small amount of the orthorhombic form. The two crystal forms of UF_5·bipy and $[(bipy)_2H]^+[UF_6]^-$ are very moisture sensitive.

Nuclear Magnetic Spectra. Owing to large line widths,[13] attributable to lifetime broadening originating from the paramagnetic f^1 ion, no ^{19}F NMR spectra were obtained. The ^1H and ^{13}C NMR data for UF_5·bipy and $[(bipy)_2H]^+[UF_6]^-$ in CD_3CN solution are listed in Table 3 together with those for bipy. The spectra clearly indicate that the adduct UF_5·bipy is stable

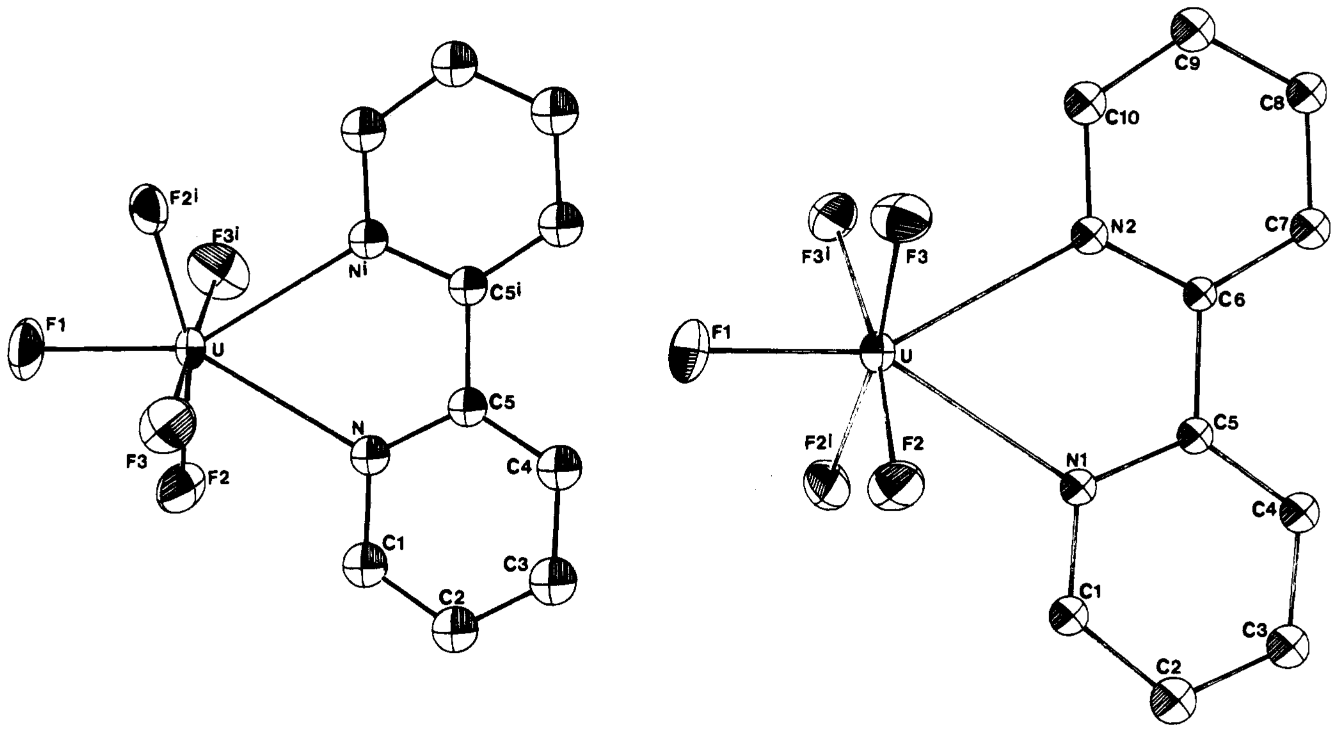

Figure 1. ORTEP[26] drawings and atom labelings of the molecular unit UF_5·bipy in the monoclinic (**I**) (left) and orthorhombic (**II**) (right) forms with the hydrogen atoms omitted. Vibration ellipsoids are drawn at the 30% probability level.

Table 5. Visible and Near-Infrared Bands of UF_5·bipy

freq[a]	assgnt[b]	freq[a]	assgnt[b]
15860 m	$\Gamma_7 \rightarrow \Gamma_6$ (Γ_6)	(6515)	
13072 m	$\Gamma_7 \rightarrow \Gamma_7$ (Γ_8')	6108 sh	
10753 sh		6053 w	$\Gamma_7 \rightarrow \Gamma_7$ (Γ_8)
10310 s	$\Gamma_7 \rightarrow \Gamma_6$ (Γ_8')	(5813)	
7812 w		5405 sh	
7435 sh		5305 m	$\Gamma_7 \rightarrow \Gamma_6$ (Γ_8)
7273 vs	$\Gamma_7 \rightarrow \Gamma_7$ (Γ_7')		

[a] Frequencies in cm^{-1}. Intensity in the abbreviated form: m, medium; s, strong; sh, shoulder; v, very; w, weak. Spurious bands in parentheses. [b] See text.

Table 6. Positional Parameters and *B* Values and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2 [a]
		UF_5·bipy (**I**) (Monoclinic Form)		
U	0.000	0.04083(4)	0.250	2.62(1)*
F(1)	0.000	−0.1018(7)	0.250	6.2(3)*
F(2)	−0.156(1)	0.0194(5)	0.0850(6)	4.4(2)*
F(3)	0.261(1)	0.0432(5)	0.1965(8)	5.4(2)*
N	−0.005(1)	0.1947(6)	0.1343(7)	2.7(2)
C(1)	−0.000(1)	0.1905(8)	0.0177(8)	3.3(2)
C(2)	0.007(2)	0.2672(8)	−0.050(1)	3.7(2)
C(3)	0.017(1)	0.3539(8)	0.0010(9)	3.7(2)
C(4)	0.012(1)	0.3599(8)	0.1220(9)	3.2(2)
C(5)	0.005(1)	0.2800(7)	0.1857(8)	2.5(2)
		UF_5·bipy (**II**) (Orthorhombic Form)		
U	0.20537(8)	0.250	0.11519(4)	3.49(2)*
F(1)	0.055(1)	0.250	0.1956(7)	8.5(5)*
F(2)	0.0951(8)	0.034(1)	0.0654(4)	5.9(2)*
F(3)	0.2971(9)	0.036(1)	0.1769(4)	6.0(2)*
N(1)	0.267(1)	0.250	−0.0263(8)	2.8(3)
N(2)	0.461(2)	0.250	0.0758(8)	3.0(3)
C(1)	0.170(2)	0.250	−0.077(1)	3.8(5)
C(2)	0.185(2)	0.250	−0.153(1)	4.5(5)
C(3)	0.314(2)	0.250	−0.180(1)	4.4(5)
C(4)	0.419(2)	0.250	−0.129(1)	3.6(4)
C(5)	0.400(2)	0.250	−0.0533(9)	2.6(4)
C(6)	0.504(2)	0.250	0.004(1)	2.2(4)
C(7)	0.642(2)	0.250	−0.011(1)	3.5(4)
C(8)	0.734(2)	0.250	0.045(1)	4.3(5)
C(9)	0.694(2)	0.250	0.117(1)	3.8(4)
C(10)	0.557(2)	0.250	0.131(1)	4.0(5)

[a] Asterisk denotes B_{eq} value, equal to $^4/_3\sum_i\sum_j\beta_{ij}\vec{a}_i\vec{a}_j$.

in CD_3CN solution at ambient temperature. As far as $[(bipy)_2H]^+[UF_6]^-$ is concerned, the proton H^+ is probably in rapid exchange at ambient temperature since the solutions had to be cooled down to observe the NH^+ signal (12.1 ppm at 243 K). The deshielding of the protons decreases in the order UF_5·bipy > $[(bipy)_2H]^+[UF_6]^-$ > bipy.

Vibrational Spectra. The UF_5 derivatives, even cooled at liquid nitrogen temperature, decomposed in the beam of the laser, and Raman lines of free bipy were observed. Only a few Raman lines located at frequencies different from those of free bipy could be confidently assigned to the compounds, so only infrared data are given in Table 4.

As far as the vibrations of the organic ligand are concerned, their modifications were found to be similar to those previously observed and discussed for the adducts WOF_4·bipy and WO_2F_2·bipy.[4] A strong band, missing in the infrared spectrum of free bipy appeared at 1323, 1327, and 1326 cm^{-1} for UF_5·bipy (**I**), UF_5·bipy (**II**), and $[(bipy)_2H]^+[UF_6]^-$, respectively. This band corresponds to the strong Raman line found at 1300 cm^{-1} for free bipy [4], and at 1320 cm^{-1} for UF_5·bipy (**II**). It probably originates from the inter-ring stretching mode.[22] Also characteristic of the bonding of the organic ligand is the shift of the strong band, assigned to an out-of-plane ring deformation mode, observed at 755 cm^{-1} for free bipy and at 770, 765, and 770 cm^{-1} for UF_5·bipy (**I**), UF_5·bipy (**II**), and $[(bipy)_2H]^+[UF_6]^-$, respectively. The ring breathing mode located at 995 cm^{-1} for free bipy, and best observed in the Raman spectrum, is also shifted to higher frequencies (e.g., 1014 cm^{-1} (Raman) and 1017 cm^{-1} (IR) for UF_5·bipy (**II**)). The three infrared bands located around 515 cm^{-1} were assigned to U−F vibration modes by comparison with infrared data for UF_5.[23] Only one corresponding Raman line could be observed for UF_5·bipy (**II**) at 595 cm^{-1}.

---

[22] Thornton, D. A.; Watkins, G. M. *Bull. Soc. Chim. Belg.* **1991**, *100*, 221.

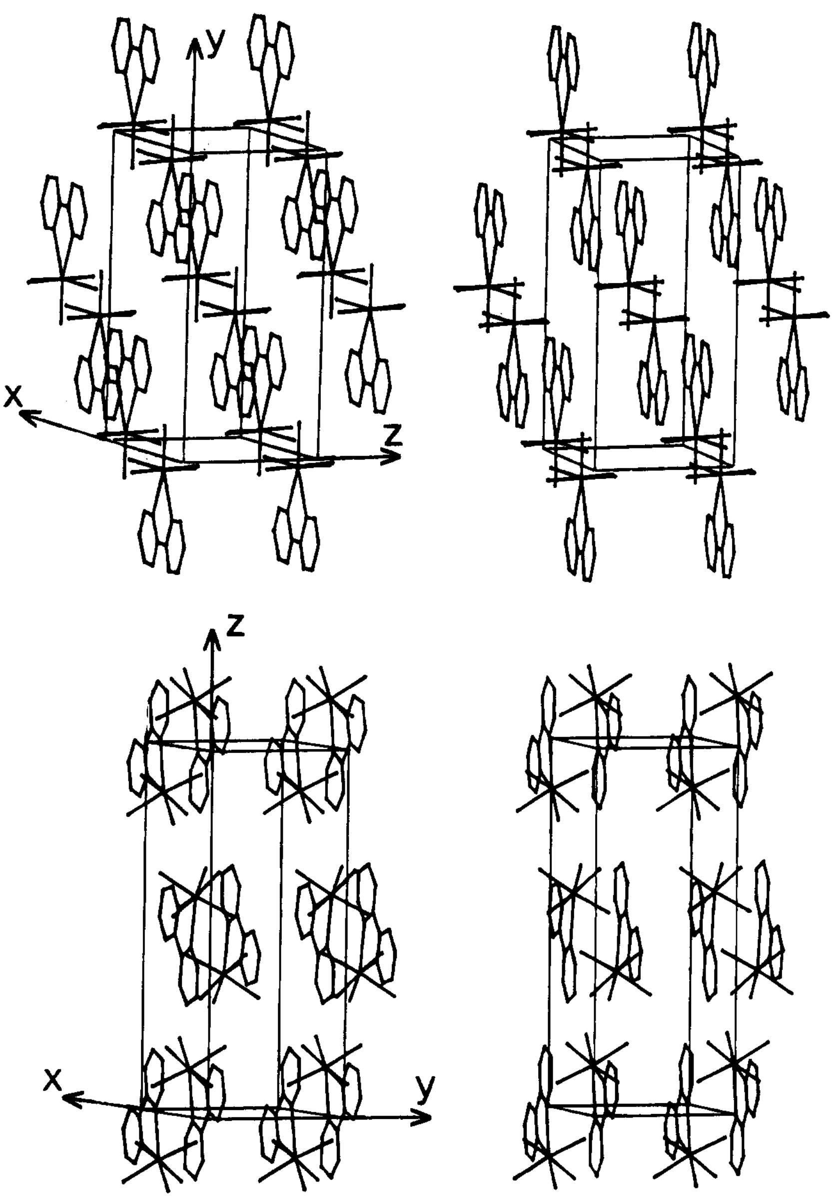

Figure 2. Stereoscopic views of the structure in the unit cell of UF_5. bipy in the monoclinic (**I**) (top) and orthorhombic (**II**) (bottom) forms.

From the observed relative intensities of the infrared and Raman bands, the highest U—F frequency in the three U(V) derivatives may be assigned to the most symmetric U—F stretching mode.

Visible and Near-Infrared Spectra. The electronic absorption spectrum of UF_5·bipy (**I** and **II**) was observed. Such a spectrum may be assigned to the crystal field splitting and vibronic coupling effects on the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ [Rn] $5f^1$ system[24] and thus confirms the +5 oxidation state of uranium found by elemental analysis. The data corresponding to the observed spectrum are given in Table 5. No theoretical model that corresponded to the symmetry of the ligand field of the U^{5+} ion in UF_5·bipy could be referred to. Consequently, the crude approximation was made that the relative ordering of energy levels was the same as that calculated for distorted hexacoordinated U^{5+} species.[25] Thus the assignment given in Table 5 corresponds to a perturbation of the $5f^1$-orbital energy levels by a D_4 field plus spin—orbit coupling.[25] The symbols in parentheses in the table refer to the corresponding levels in O_h symmetry. A few extra bands due to vibronic transitions are observed on the high-energy side of the 0—0 bands.

Crystal Structures. The molecular stereochemistry of the two forms of UF_5·bipy was established by single-crystal studies. Crystal data are given in Table 1. Final positional and thermal parameters are given in Table 6 with their standard deviations. The relevant distances and angles are given in Table 7. Figure 1 shows the molecular unit and atomic labeling schemes, and Figure 2 gives stereoscopic views of the molecular packing. The coordination of the uranium atom in both forms is a distorted monocapped trigonal prism with one fluorine atom (F(1)) occupying the capping site. The two triangles formed by [F(2), F(3), N] and [F(2^i), F(3^i), (N^i)] in **I** , and [F(2^i), (F2), N(1)] and [F(3), F(3^i), N(2)] in **II**, are parallel (the angles between the corresponding least-squares planes are 4.7 ± 1 and 4.1 ± 5°, respectively). In **I**, the distances from the U and F(1) atoms to these planes are 1.362(8) and 1.447(7) Å, respectively; in **II**, the mean values of these distances are 1.387(1) and 1.461(9) Å. The molecular unit has a different local symmetry in the two forms. In the monoclinic form (**I**), the atoms U and F(1) lie on a diad axis, whereas, in the orthorhombic form (**II**), U, F(1), and the pyridine lie on a mirror plane. The main

---

(23) Jacob, E. *Z. Anorg. Allg. Chem.* **1973**, *400*, 45.

(24) Reisfeld, M.; Grosby, G. A. *Inorg. Chem.* **1965**, *4*, 65.

(25) Selbin, J.; Ballhausen, C. J.; Durrett, D. G. *Inorg. Chem.* **1972**, *11*, 510.

(26) Johnson, C. K. *ORTEP II*; Report No. ORNL 5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 7. Selected Bond Lengths (Å) and Angles (deg)

UF$_5$·bipy (I)[a]		UF$_5$·bipy (II)[b]	
U−F(1)	2.060(8)	U−F(1)	2.04(1)
U−F(2)	2.052(7)	U−F(2)	2.043(9)
U−F(3)	2.043(9)	U−F(3)	2.047(9)
U−N	2.588(9)	U−N(1)	2.58(2)
		U−N(2)	2.58(2)
F(1)−U−F(2)	81.3(2)	F(1)−U−F(2)	85.7(4)
F(1)−U−F(3)	91.0(3)	F(1)−U−F(3)	86.5(4)
F(1)−U−N	149.2(2)	F(1)−U−N(1)	147.7(6)
F(2)−U−F(2$^{\mathrm{i}}$)	162.7(4)	F(1)−U−N(2)	151.4(6)
F(2)−U−F(3)	95.6(2)	F(2)−U−F(2$^{\mathrm{i}}$)	94.3(6)
F(2)−U−F(3$^{\mathrm{i}}$)	84.7(2)	F(2)−U−F(3)	85.9(4)
F(2)−U−N	72.3(3)	F(2)−U−F(3$^{\mathrm{i}}$)	172.2(4)
F(2)−U−N$^{(\mathrm{i})}$	124.3(3)	F(2)−U−N(1)	72.6(3)
F(3)−U−F(^{3}i)	178.1(6)	F(2)−U−N(2)	112.9(3)
F(3)−U−N	76.5(3)	F(3)−U−F(3$^{\mathrm{i}}$)	92.8(5)
F(3)−U−N$^{(\mathrm{i})}$	101.8(3)	F(3)−U−N(1)	114.8(3)
N−U−N$^{(\mathrm{i})}$	61.6(4)	F(3)−U−N(2)	74.0(4)

[a] Symmetry code for i: $-x, y, \frac{1}{2} - z$. [b] Symmetry code for i: $x, \frac{1}{2} - y, z$.

difference is found in the packing of the molecular unit UF$_5$·bipy since in **I** all the molecular units are in the same orientation and form successive layers of UF$_5$ and bipy, whereas, in **II**, the molecules pack head to tail (see Figure 2).

The stereochemistry of metal complexes containing bidentate ligands has been predicted by the minimization of the total repulsion energy between individual donor atoms.[27] The normalized bite (here N—N/N—U distances) determined for UF$_5$·bipy (**I** and **II**) from the crystal data is 1.02. The molecular structure is in agreement with one of the two close minima on the potential-energy surface predicted by the authors[27] for a normalized bite of 1.0 (in their paper minimum *A* that corresponds to an idealized monocapped trigonal prism).

Conclusion. This study has illustrated the high reactivity of uranium hexafluoride since nitrogen bases, usually inert toward other hexafluorides such as WF$_6$, were found to react with UF$_6$. The first molecular adduct of UF$_5$ has been obtained with the nitrogen base 2,2′-bipyridyl. This adduct is dimorphic, and in both crystal forms the coordination polyhedron of the uranium atom is a monocapped trigonal prism.

Acknowledgment. We are indebted to Mrs. G. Derost for her help with the electronic spectra.

Supplementary Material Available: Tables of crystal data, bond distances, bond angles, complete atomic positional parameters, anisotropic thermal parameters, and least-squares planes (11 pages). Ordering information is given on any current masthead page.

---

[27] Dewan, J. C.; Henrick, K.; Kepert, D. L.; Trigwell, K. R.; White, A. H.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1975**, 546.