

**Figure 7.** Fourier transform spectrum of FeOCl(py)<sub>1/3</sub> at room temperature (upper trace) and of pyridine (lower trace) over the range  $4000 \ge \nu \ge 400 \text{ cm}^{-1}$ . The assignments of some of the fundamental modes and combination bands are given in Table V.

orientations of the intercalant are still possible, viz., with the  $C_{2v}$  axis parallel or perpendicular to the van der Waals plane. The molecular diameter of pyridine is estimated to be 4.92 Å parallel to the  $C_{2v}$  axis and 5.12 Å perpendicular to this axis in the plane of the ring (i.e., the  $H_3-H_5$  diameter). Since the *b*-axis expansion of FeOCl in forming the pyridine intercalate is 5.54 Å, either orientation could be accommodated in the van der Waals layer, and no clearcut distinction between the two orientations can be drawn from the present data alone. However, two additional observations are pertinent in the present context. Palvadeau et al.<sup>4</sup> have carried out a detailed powder pattern analysis on the intercalates  $FeOCl(py)_{1/4}$  and  $FeOCl(py)_{1/3}$ . In the case of the latter, they note that the a unit cell parameter is doubled, indicating the existence of a super structure in the a,b plane. In addition these authors note that ESR data suggest partial transfer of the nitrogen lone-pair electron density into the FeOCl layers. It thus appears clear that a model which is in agreement with these various observations is one in which pyridine molecules form an ordered array within the van der Waals layer, with the lone-pair electrons of the nitrogen aotms of adjacent molecules pointing alternately "up" and "down" toward the iron atoms. It must be emphasized here that these structural inferences apply only to a particular FeOCl intercalate, namely,  $FeOCl(py)_{1/3}$ . Examination of other intercalants (e.g., 4-(dimethylamino)pyridine,<sup>5</sup> inter alia) in which the major and minor dimensions within the molecular plane are significantly different or in which ring substituents impose special steric requirements shows that these appear to assume other orientations with respect to the host matrix and must be considered on an individual basis.

**FeOCl(imid)**<sub>1/4</sub>( $H_2O$ )<sub>1/2</sub>. The infrared data for this intercalant, using the frequencies reported by Garfinkel and Edsall<sup>21</sup> and the assignments of Cordes and Walter,<sup>22</sup> are summarized in Table VI. Most of the normal modes which involve either ring breathing (expansion) or the CH bending modes and which are prominent features of the spectra reported<sup>21</sup> for imidazole in KCl appear to be either weak or absent in the infrared spectrum of the intrercalate. The prominent normal modes which are observed in the latter are the bands at 620  $cm^{-1}$  (B<sub>2</sub>,  $\nu_{21}$ ) due to an NH out-of-plane mode 755 cm<sup>-1</sup> (B<sub>2</sub>,  $v_{18}$ ) due to CH out-of-plane bending motions, the band at 1045 cm<sup>-1</sup> (presumably the A<sub>1</sub>,  $\nu_8$  mode at 1058 cm<sup>-1</sup> in the unintercalated base), and the band at 1092 cm<sup>-1</sup> ( $B_1$ ,  $\nu_{15}$ ) due to in-plane hydrogen atom scissor motions. In particular, it is significant that the very strong ring-torsional mode at 658 cm<sup>-1</sup> and the band at 1264 cm<sup>-1</sup> (A<sub>1</sub>,  $\nu_6$ ), assigned to a symmetric ring breathing motion, are completely absent in the intercalate. These data reflect a significant interaction between the heterocyclic ring base and the chlorine atoms of the matrix such that significant nonbonding (Coulomb) interaction must obtain. This conclusion from the vibrational spectral data is particularly interesting in view of the fact that the FeOCl- $(imid)_{1/4}(H_2O)_{1/2}$  intercalate Mössbauer spectra show the sigmoid behavior of QS(T), detailed above.

It is clear that a more complete understanding of the chemical interactions between the intercalants and the FeOCI host matrix will require a careful and detailed study by Fourier infrared techniques over a temperature range comparable to that of the Mössbauer spectroscopic data. Such temperature-dependent vibrational spectroscopic studies are currently under way in these laboratories.

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**Registry No.** FeOCl(py)<sub>1/3</sub>, 76613-07-5; FeOCl(amm)<sub>3/4</sub>, 76613-08-6; FeOCl(isopropy))<sub>1/3</sub>, 76613-09-7; FeOCl(pic)<sub>1/4</sub>, 76613-10-0; FeOCl(buty)<sub>1/4</sub>, 76613-11-1; FeOCl(octa)<sub>1/6</sub>, 76613-12-2; FeOCl(imid)<sub>1/4</sub>, 76613-13-3; FeOCl(quin)<sub>1/6</sub>, 76613-14-4; FeOCl(lut)<sub>1/6</sub>, 76613-15-5; FeOCl(dodec)<sub>1/6</sub>, 76613-16-6; FeOCl, 13870-10-5; py, 110-86-1.

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## Ligand Basicity in Complexed Uranyls: Oxygen Bases

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The THF adduct of uranyl hexafluoroacetylacetonate undergoes fast reversible displacement reactions with other bases in chloroform solutions. The NMR shift of the  $\alpha$ -CH<sub>2</sub> group is found to be a useful monitor of the equilibrium established and has been used to measure the relative strength of oxygenated bases. The values correlate well with Gutmann's donor number (DN), the heat of reaction of the bases with SbCl<sub>5</sub>.

The THF complex of uranyl hexafluoroacetylacetone (1) has recently been shown to be of sufficient stability to sublime

intact at temperatures up to 100 °C.<sup>1</sup> This is remarkable in view of the fact that the analogous complex with diethyl ether

<sup>(21)</sup> Garfinkel, D.; Edsall, J. T. J. Am. Chem. Soc. 1958, 80, 3807.
(22) Cordes de N. D., M.; Walter, J. L. Spectrochim. Acta, Part A 1968, 24A, 237.

decomposes under similar conditions.<sup>2</sup> The difference in stability is evidently related to the Lewis basicity of the oxygen donors toward UO<sub>2</sub>[(CF<sub>3</sub>CO)<sub>2</sub>CH]<sub>2</sub> (or its oligomers in solution). Hence, the strength of the donor-acceptor interaction is an important criterion when species which retain their integrity in the gas phase are synthesized.<sup>3</sup> This paper deals with measurements of the relative base strength of oxygenated ligands toward the complexed uranyl ion.

Basicities were determined by an NMR method in which a base was added to a chloroform solution of the THF adduct. This causes the displacement of some THF molecules which rapidly exchange with the remaining complexed THF leading to an averaged signal for the  $\alpha$ -CH<sub>2</sub> protons which is shifted relative to that when no base is added. From the magnitude of the shift the equilibrium constant for reaction 1 may be

$$B + UO_2(FAA)_2 \cdot THF \xrightarrow{A} UO_2(FAA)_2B + THF (1)$$
  
$$\delta_{measd} = \delta_{THF}\chi_{THF} + \delta_1\chi_1 = \delta_{THF}\chi_{THF} + \delta_1(1 - \chi_{THF})$$

readily extracted (on the assumption that the measured shift is a linear function of the mole fraction of these components). In this equation,  $\delta$  is the shift measured from internal Me<sub>4</sub>Si,  $\delta_{\text{THF}}$  is the shift of the  $\alpha$ -CH<sub>2</sub> protons of THF, and  $\delta_1$  is the shift of the  $\alpha$ -CH<sub>2</sub> protons of THF in the uranyl complex.

The measured free energy changes may be compared with other measures of ligand basicity such as Gutmann's donor number<sup>5,6</sup> and measured or estimated enthalpies of complexation with use of Drago and Wayland's correlations.<sup>6,7</sup> The correlations provide a clear view of the  $UO_2^{2+}$  ion as behaving as a model Lewis acid.

### **Experimental Section**

NMR measurements were usually made on a Varian A-60 instrument at ambient temperature. The bulk of the work was done with equal mole ratios of the base-THF complex in DCCl<sub>3</sub>, and shifts were measured in Hz from internal Me<sub>4</sub>Si. The concentration of the uranyl compound was normally 0.5 M but was reduced to 0.05 M with systems that had low solubilities.

While the NMR procedure permits rather precise measurements of equilibria in the range of  $10^{-3} < K < 10^3$ , an overlapping procedure was used to permit measurement with stronger bases. For this purpose the reference complex was changed from the THF to the dimethyl sulfoxide adduct. In general, a good correlation was found between both sets of data, the equilibria being related by eq 2.

$$\Delta G^{\circ}_{\text{THF}} = \Delta G^{\circ}_{\text{MesSO}} - 2.2 \pm 0.8 \text{ kcal/mol}$$
(2)

When this work was begun, the utility of the NMR studies was investigated by measuring the equilibrium between 1 and pyridine at different concentrations. A narrow range of equilibrium constants were obtained with use of 0.5 M solutions of 1 and 0.5, 0.25, and 0.05 M concentrations of pyridine, K being 8.3, 5.9, and 1.0 corresponding to free energy changes of -1.3, -1.1, and 0 kcal/mol in the respective measurements. Since the error is smallest when equimolar concentrations of reagents are used, these conditions were employed in the subsequent work. The error of a free energy determination by the NMR procedure is small when the strength of the unknown base is close to that of the reference compound but increases as the difference between the bases increases. In these experiments the error is estimated as increasing from  $\pm 0.1$  kcal/mol when  $\Delta G^{\circ}$  is smaller than  $\pm 2$  to

- J. A. Pople, W. G. Schneider, and H. J. Bernstein, Eds., "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1966, Chapter 10.
- V. Gutmann, A. Steininger, and E. Wychera, Monatsh. Chem., 97, 460 (5)(1966)
- (a) R. S. Drago and B. Wayland, J. Am. Chem. Soc., 87, 3571 (1965); (7)(b) R. S. Drago Struct. Bonding (Berlin), 15 (1973).

Table I.	Relative Basicity of Oxygenated Bases toward
UO,[(CF	<sub>3</sub> CO),CH], THF in Chloroform

base	$\Delta G^{\circ},$ kcal/mol	base	$\Delta G^{\circ},$ kcal/mol		
(CH <sub>3</sub> O) <sub>2</sub> SO <sub>2</sub> CF <sub>3</sub> CH <sub>2</sub> OH	≥4.8 3.5	CH₃OH THF C₂H₅OH	0.5 0 -0.2		
	2.9		-0.5		
	2.7	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SO	-1.6		
$(C_2H_5)_2O$	2.2	(CH <sub>3</sub> ) <sub>2</sub> SO	-2.2		
CH2CH2 CH2CH2	2.0		-2.4		
0    сн₃с—сн₃	1.9	$(MeO)_{3}P=O$ $(Me)_{3}P=O$	-2.8 -2.8		
Cr3	1.9	HC-N <ch3< td=""><td>-2.9</td></ch3<>	-2.9		
H <sub>2</sub> C-CH <sub>2</sub> H <sub>2</sub> C-CH <sub>2</sub> C=0	1.8		-3.6		
H <sub>2</sub> O	1.3	Et <sub>3</sub> P=O	-4.9		
H2C C C C	1.0	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> P=O	-5.6		

Table II

	$\Delta G^{\circ},$	$\Delta(\Delta G^{\circ}),$	
base	$\overline{\text{UO}_2\cdots\text{THF}}$ + B	$\frac{1}{B UO_2 \cdots Me_2 SO + B}  \frac{L(2O)}{kcal/n}$	
aniline	1.4	4.3	2.9
pyridine	-1.3	1.8	3.1
Me,SO	-2.2	0	2.2
pyridine N-oxide	-3.6	-2.2	1.4
			av 2.4 ± 0.8

 $\pm 0.5$  kcal/mol when  $\Delta G^{\circ}$  is as large as  $\pm 4-5$  kcal/mol.

#### **Results and Discussion**

Table I contains the measured equilibria for oxygenated bases. The data provide the relative strength of these compounds vs. tetrahydrofuran in chloroform. Since chloroform is a weakly hydrogen-bonding solvent the equilibria of eq 1 are likely to be biased relative to values which would be obtained in the gas phase. Nevertheless they provide a good estimate of the relative strength of Lewis bases and, as will be shown, correlate well with other estimates of basicity such as Gutmann's donor number scale.

The basicity of dimethyl sulfate is rather uncertain because the shift measured was within the uncertainty of measurement  $(\pm 0.2 \text{ Hz})$ . Nevertheless it is clear that oxygen atoms in the sulfate group are much less basic than those in a sulfone or a sulfoxide.

The sulfoxides generally are less basic than phosphine oxides and possibly amine oxides. It is interesting that tetramethylurea and dimethylformamide, both of which are presumed to bond through a carbonyl oxygen, are stronger bases than the alkyl sulfoxides. This is apparently a manifestation of donation of the dimethylamino electrons through the carbonyl bond to the oxygen atom.

The data also indicate that a strained cyclic ketone is less basic than an open chain or less strained analogue while the reverse is true in series of ethers, diethyl ether being less basic than either tetrahydrofuran or trimethylene oxide.

Methanol and ethanol bracket THF while the addition of fluorine atoms to an alcohol leads to an expected decrease in the nucleophilicity of the hydroxyl moiety. These effects are generally consistent with inductive properties expected of the various substituents on the oxygen atoms.

<sup>(1)</sup> G. M. Kramer, M. B. Dines, R. B. Hall, A. Kaldor, A. J. Jacobson, and J. C. Scalon, Inorg. Chem., 19, 1340 (1980).

<sup>(2)</sup> A. Ekstrom, H. Loeh, C. H. Randall, L. Szego, and J. C. Taylor, Inorg. Nucl. Chem. Lett., 14, 301 (1978).

<sup>(3)</sup> G. M. Kramer, manuscript in preparation.

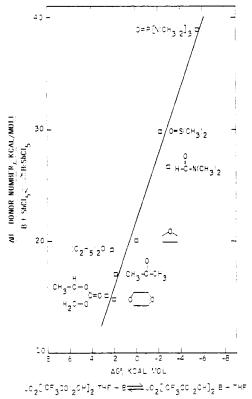


Figure 1. Correlation of Lewis acidities of  $UO_2L[(CF_3CO)_2CH]_2$  and  $SbCl_5$ .

**Overlapping Base Scale.** The stronger bases were measured vs. the Me<sub>2</sub>SO complex after comparative studies of several compounds established the existence of an overlapping basicity scale. One finds reasonable agreement between equilibria measured for a series of bases with both the THF and Me<sub>2</sub>SO complexes. From a comparison of these measurements the difference in basicity of Me<sub>2</sub>SO and THF can be estimated as  $-2.4 \pm 0.8$  kcal/mol. [Note that the data in Table I for strong bases is tabulated on the assumption that the difference in  $\Delta G^{\circ}$  is -2.2 kcal/mol, the directly measured value.] Table II lists the comparative data observed for aniline, pyridine, Me<sub>2</sub>SO, and pyridine *N*-oxide.

With the Me<sub>2</sub>SO adduct as a reference, the basicity of trimethyl phosphate was found to be -2.8 kcal/mol relative to THF. For an unknown reason we have found it difficult to make this measurement directly with the THF adduct, but the value is consistent with the measured basicities of triethylphosphine oxide and hexamethylphosphoramide. It is, however, not clear why trimethylphosphine oxide also yields  $\Delta G^{\circ} = -2.8$  kcal/mol since the methyl groups are ordinarily much less effective than methoxy groups at withdrawing and distributing negative charge. Perhaps this is a steric effect arising because the methyl groups of trimethylphosphine oxide are drawn closer to the anions than they are with trimethyl phosphate.

Comparison of Existing Scales:  $UO_2[(CF_3CO)_2CH]_2$ , a Representative Lewis Acid. It is of interest to compare the Lewis acidity of the chelated uranyl ion with that of typical Lewis acids to develop a picture of its bonding characteristics. This was done by comparing the measured  $\Delta G$  values with known heats of reaction of a number of the bases with SbCl<sub>5</sub> (the Gutmann donor number<sup>5</sup>) and other Lewis acids with use of Drago and Wayland's correlations.<sup>6,7</sup> The relationship to DN is shown in Figure 1 and to Me<sub>3</sub>Al in Figure 2. The graphs indicate a good correlation with the behavior of either of these acids.

Table III shows the Drago and Wayland bonding parameters of representative Lewis acids. Empirical observations

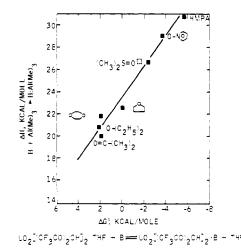


Figure 2. Correlation of Lewis acidities of  $UO_2[(CF_3CO)_2CH]_2$  and  $Al(CH_3)_3$ .

Table III. Drago and Wayland Bonding Parameters Characterizing UO<sub>2</sub>[(CF<sub>3</sub>CO)<sub>2</sub>CH]<sub>2</sub>

acid	$C_{A}^{a}$	EA	rel corr <sup>b</sup>
(CH <sub>3</sub> ) <sub>3</sub> Al	1.43	16.9	1
$(C_2H_3)_3Al$	2.04	12.5	2, 3
$(C_2H_5)_3Ga$	0.59	12.6	2, 3
$Cu[(CF_3CO)_2CH]_2$	1.40	3.39	4
(CH <sub>3</sub> ) <sub>3</sub> B	1.70	6.1	5

<sup>a</sup> R. S. Drago and B. Wayland, J. Am. Chem. Soc., 87, 3571 (1965); R. S. Drago, Struct. Bonding (Berlin), 15, 73 (1973); W. B. Jensen, Chem. Rev., 78, 1 (1978). <sup>b</sup> The relative correlation is obtained from graphs of calculated  $H_{\rm IXII}$  with nine Lewis bases vs. measured ( $\Delta G$ )<sub>THF</sub> with these compounds. The bases are acetonitrile, acetone, 1, 3-p-dioxane, tetrahydrofuran, ethyl ether, pyridine, dimethyl sulfoxide, N,N-dimethylformamide, and pyridine N-oxide.

of graphs of estimated  $\Delta H$ 's with use of the Drago and Wayland parameters for these acids vs.  $\Delta G$  suggest the uranyl ion to be more like trimethylaluminum than several other acids, the goodness of fit decreasing in the series Me<sub>3</sub>Al > Et<sub>3</sub>Al  $\approx$ Et<sub>3</sub>Ga > Cu[(CF<sub>3</sub>CO)<sub>2</sub>CH]<sub>2</sub> > Me<sub>3</sub>B. By examining the parameters characterizing these acids in Table III, one can deduce that the uranyl ion behaves most like acids that predominantly bond in the electrostatic manner.

Drago<sup>7b</sup> stresses that the  $E_A$  and  $C_A$  parameters are not to be compared directly but that these tell you how an acid bonds relative to I<sub>2</sub> for which  $E_A$  and  $C_A$  are arbitrarily defined as 1.00. Thus, the uranyl ion behaves like Lewis acids which exhibit considerably more polar than nonpolar characteristics in their bonding than does iodine.

This discussion leads to the apparently reasonable conclusion that the uranyl ion is behaving like a relatively hard acid as would be expected for an ion with a formal 6+ charge on its central atom. There are some grounds for questioning this assessment however, and further information is being sought. One concern is that the solvent used in these studies may have modified the equilibria sufficiently to prevent this quantitative type of deduction. This is a real concern because, if the reported equilibria in Table I are used to estimate Drago and Wayland bonding parameters for the uranyl ion, one obtains values which appear to be low (rough estimate,  $E_A = 9.1$  and  $C_{\rm A} = 0.5$ ). If they are used to estimate the heat of reaction of THF with uranyl hexafluoroacetylacetonate, one obtains a  $\Delta H$  of -9 kcal/mol which must be low since the heat of vaporization of the complex which sublimes intact is about 14.5 kcal/mol.8

<sup>(8)</sup> G. M. Kramer, M. B. Dines, R. B. Hall, A. Kaldor, A. J. Jacobson, and J. C. Scanlon, *Inorg. Chem.*, 19, 1340 (1980).

It is interesting that the correlations in Figures 1 and 2 extend to a base as large and basic as HMPA. First it is surprising that HMPA does not appear to suffer from a severe steric barrier in complexing the uranyl ion. An X-ray structural analysis of UO<sub>2</sub>(hfacac)<sub>2</sub>HMPA has recently been done, and it in fact shows a very close approach of the methyl groups to the CF<sub>3</sub> groups of the anion.<sup>9</sup> Second, HMPA is known to be able to coordinate the uranyl ion to form a complex in which four HMPA molecules are tightly bound and the counterions are removed from the inner coordination sphere.<sup>10</sup> We believe similar species can form when HMPA reacts with the  $UO_2[(CF_3CO)_2CH]_2$  system, but they do not appear to exert a strong effect on the equilibrium measurements of 1:1 solutions with the uranyl ion. Why the size and tendency toward multiple coordination of the base does not disturb the measured correlations is not immediately evident and is being

studied further.

In summary the chelated uranyl ion has been found to bind to oxygenated bases through a strongly electrostatic interaction which increases with the general basicity of these compounds as shown by the way they bind to other relatively hard Lewis acids. Equilibrium measurements in chloroform afford a convenient basicity scale with which to assess the overall nucleophilicity of both protic and aprotic bases.

**Registry No.** 1, 69244-67-3;  $UO_2[(CF_3CO)_2CH]_2$ ·Me<sub>2</sub>SO, 75172-91-7;  $UO_2[(CF_3CO)_2CH]_2$ , 67316-66-9; cyclobutanone, 1191-95-3; 4-methyl-1,3-dioxolan-2-one, 108-32-7;  $(C_2H_3)_2O$ , 60-29-7; 1,4-dioxane, 123-91-1; CH<sub>3</sub>COCH<sub>3</sub>, 67-64-1; tetrahydro-3-methyl-thiophene 1,1-dioxide, 872-93-5; H<sub>2</sub>O, 7732-18-5; cyclopentanone, 120-92-3; tetrahydro-2H-pyran-2-one, 542-28-9; CH<sub>3</sub>OH, 67-56-1; C<sub>2</sub>H<sub>3</sub>OH, 64-17-5; oxetane, 503-30-0;  $(C_4H_9)_2$ SO, 2168-93-6; (C-H<sub>3</sub>)\_2SO, 67-68-5; CO[N(CH<sub>3</sub>)\_2], 632-22-4; (MeO)<sub>3</sub>P=O, 612-56-1; HCO[N(CH<sub>3</sub>)\_2], 68-12-2; (Me)<sub>3</sub>P=O, 676-96-0; pyridine 1-oxide, 694-59-7; Et<sub>3</sub>P=O, 597-50-2; [(CH<sub>3</sub>)\_2N]\_3P=O, 680-31-9; (CH<sub>3</sub>-O)\_2SO<sub>2</sub>, 77-78-1; CF<sub>3</sub>CH<sub>2</sub>OH, 75-89-8; aniline, 62-53-3; pyridine, 110-86-1; acetonitrile, 75-05-8; THF, 109-99-9; (CH<sub>3</sub>)<sub>3</sub>Al, 75-24-1; (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al, 97-93-8; (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Ga, 1115-99-7; Cu[(CF<sub>3</sub>CO)<sub>2</sub>CH]<sub>2</sub>, 14781-45-4; (CH<sub>3</sub>)<sub>3</sub>B, 593-90-8; Cl<sub>5</sub>Sb, 7647-18-9.

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# Equilibrium Studies with the Uranyl Ion: Nitrogen Bases and Uranyl Hexafluoroacetylacetonates

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Displacement equilibria between the THF adduct of uranyl hexafluoroacetylacetonate and nitrogen-containing bases have been measured by NMR. Experiments have been conducted in chloroform and 2,2,2-trifluoroethanol. The basicity increases markedly from pyrrole and nitriles (which are weaker bases than THF) to amines which are much stronger. Steric effects appear to be important only when the amine is very large.

The chelated uranyl ion in  $UO_2[(CF_3CO)_2CH]_2$  has been shown to behave as a relatively hard Lewis acid in its reactions with oxygenated bases.<sup>1</sup> Displacement equilibria with these bases have been conveniently studied by proton magnetic resonance, and a basicity order has been established.

This paper reports on the extension of the basicity scale to cover a wide range of nitrogen bases. The base strength of these compounds is tabulated relative to THF for the equilibria

$$\mathbf{B} + \mathrm{UO}_{2}[(\mathrm{CF}_{3}\mathrm{CO})_{2}\mathrm{CH}]_{2}\cdot\mathrm{THF} \xrightarrow[\mathrm{DCCl}_{3}]_{2}\cdot\mathrm{B}$$

$$\mathrm{THF} + \mathrm{UO}_{2}[(\mathrm{CF}_{3}\mathrm{CO})_{2}\mathrm{CH}]_{2}\cdot\mathrm{B}$$
(1)

### Experimental Section

The equilibria of relatively weak N bases were assessed from direct measurements of the <sup>1</sup>H NMR shift of the  $\alpha$ -CH<sub>2</sub> group of tetrahydrofuran as before.<sup>1</sup> An overlapping procedure using the Me<sub>2</sub>SO adduct of the uranyl chelate was again used to evaluate stronger bases, but in many cases the N-base complexes tended to precipitate from chloroform and equilibria could not be easily measured. So that relative basicity of these bases could be evaluated, similar equilibrium studies were made in 2,2,2-trifluoroethanol. Preliminary measurements in this weakly nucleophilic solvent and those in DCCl<sub>3</sub>, despite the fact that the alcohol is a stronger proton donor. It was assumed that this proportionality exists to the extremes of the basicity scale examined in this study so that basicity values for strong nitrogen bases in chloroform could be estimated. Table I lists the derived values of free energy change for base exchange and orders the nitrogen bases according to their nucleophilicity toward the chelated uranyl ion. These values are integrated in Table II with those observed for oxygen donor bases.

A basicity scale of nitrogen-containing, organic Lewis bases toward the UO<sub>2</sub>[(CF<sub>3</sub>CO)<sub>2</sub>CH]<sub>2</sub> moiety was constructed from solution equilibrium data in DCCl<sub>3</sub> By use of CF<sub>3</sub>CH<sub>2</sub>OH as a solvent, this scale was extended to include a variety of primary, secondary, and tertiary amines which form insoluble species with the uranyl moiety in chloroform. In this less nucleophilic solvent, it was necessary to employ UO<sub>2</sub>- $[(CF_3CO)_2CH]_2$ ·Me<sub>2</sub>SO as the reference material whereas  $UO_2[(CF_3CO)_2CH]_2$  THF had been employed in DCCl<sub>3</sub>. The equilibria between UO<sub>2</sub>[(CF<sub>3</sub>CO)<sub>2</sub>CH]<sub>2</sub>·Me<sub>2</sub>SO and 2,6-dimethoxypyridine, aniline, pyridine, trimethyl phosphite, trimethyl phosphate, and pyridine N-oxide were studied in both solvents in order to correlate the basicity scales of the two solvents. The equilibria with the  $Me_2SO$  complex in DCCl<sub>3</sub> have been shown previously to be related to those of the analogous THF complex by the expression

$$(\Delta G^{\circ})_{\text{THF}} = (\Delta G^{\circ})_{\text{Me},\text{SO}} - 2.2 \text{ kcal/mol}$$
(2)

Calculated equilibria of the THF complex in DCCl<sub>3</sub> is plotted vs. equilibria of the  $Me_2SO$  complex in CF<sub>3</sub>CH<sub>2</sub>OH in Figure 1, and an extrapolation is made to include several amines

<sup>(9)</sup> G. M. Kramer, E. T. Maas, Jr., D. A. Rapp, and J. C. Scanlon, manuscript in preparation.

<sup>(10)</sup> L. R. Nassimbeni and A. L. Rodgers, Cryst. Struct. Commun., 5, 301 (1976).

**Results and Discussion** 

<sup>(1)</sup> G. M. Kramer, E. T. Maas, Jr., and M. B. Dines, Inorg. Chem., in press.