

Table IV. Isomerization Rate Constants at 25 °C and Activation Parameters for $trans\text{-}[\text{Co}(\text{en})_2(\text{X})(\text{ONO})]^{n+}$ Complexes

| X | $10^5 k$, s ⁻¹ | ΔH^\ddagger , kJ mol ⁻¹ | ΔS^\ddagger , J K ⁻¹ mol ⁻¹ | $10^5 k_{\text{H}}$, ^a s ⁻¹ | $10^6 k_{\text{H}}$, ^b s ⁻¹ (ref) |
|------------------------------|----------------------------|--|---|--|--|
| ONO ⁻ | 13 ^c | 94.3 | -2.6 | 13.0 ^d | |
| | | 97.5 ^e | +8.5 ^e | 12.8 ^e | |
| NCS ⁻ | 0.42 | 103.3 | -1.3 | 0.15 ^g | 0.046 (21a) |
| NO ₂ ⁻ | very fast | | | 1.1 ^f | 980 (21a) |
| CN ⁻ | very fast | | | | 82 (21a, 22) |
| NH ₃ | 4.2 | 94.1 | -13.4 | | 0.34 (21a, 22) |

^a Isomerization rate constants at 25 °C reported earlier. ^b Acid hydrolysis rate constants of the corresponding chloro complexes at 25 °C. ^c Half the rate constant obtained for the dinitrito complex. ^d Half the rate constant estimated in ref 13 from the data obtained by Adell.¹² ^e Activation parameters and half the rate constant reported in ref 13. ^f Estimated on the assumption $k_1 = 2k_2$ for the dinitrito complex in ref 12. ^g Reference 9b.

$trans\text{-}[\text{Co}(\text{en})_2(\text{X})(\text{ONO})]^{n+}$ type complexes together with acid hydrolysis rate constants k_{H} of the corresponding chloro complexes at 25 °C. For cis complexes, k is relatively insensitive to the change in the X ligands. By contrast, acid hydrolysis rates of the corresponding chloro complexes differ greatly for different X ligands; $cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)(\text{Cl})]^+$ releases Cl⁻ ion almost 180 times more easily than $cis\text{-}[\text{Co}(\text{en})_2(\text{CN})(\text{Cl})]^+$ at 25 °C, as seen in Table III. A close inspection of Table III reveals that the isomerization rate increases in the order NH₃ < NO₂⁻ < CN⁻ < NCS⁻ < ONO⁻, which is not in agreement either with the order of ligand field strength or with the order of acid hydrolysis rate of the chloro complexes (NH₃ < CN⁻ << NCS⁻ << NO₂⁻). It is not possible at present to account for the order of the isomerization rate constants obtained for these cis complexes.

For trans complexes, on the other hand, the rate constant is greatly dependent on the kind of X ligands trans to the ONO group. When X = NO₂⁻ and CN⁻, the isomerization is so fast that its rate constant cannot be determined by the usual techniques. This finding, which was not correctly recognized by Adell,¹² is ascribed to the so-called trans effect of NO₂⁻ and CN⁻.^{14,16,17,22,44} Actually, it is seen in Table IV that $trans\text{-}[\text{Co}(\text{en})_2(\text{X})(\text{ONO})]^{n+}$ isomerizes faster if the corre-

sponding chloro complex, $trans\text{-}[\text{Co}(\text{en})_2(\text{X})(\text{Cl})]^{n+}$, releases Cl⁻ more easily and vice versa.

Finally, it is worthy of note that the isomerization of $trans\text{-}[\text{Co}(\text{en})_2(\text{NCS})(\text{ONO})]^+$ is exceptionally slow. Even $trans\text{-}[\text{Co}(\text{cyclam})(\text{NH}_3)(\text{ONO})]^{2+}$ isomerizes faster than the NCS complex. In parallel with the extremely low reactivity of the NCS complex, acid hydrolysis of $trans\text{-}[\text{Co}(\text{en})_2(\text{NCS})(\text{Cl})]^+$ is exceptionally slow among monovalent $trans\text{-}[\text{Co}(\text{en})_2(\text{X})(\text{Cl})]^+$ type complexes.^{23a,45} In the acid hydrolysis of chloro(amine)cobalt(III) complexes, the Co(III)-Cl⁻ bond strength is one of the dominant factors determining the rate constant, since the so-called I_d mechanism prevails for Co(III) complexes. Therefore, the low reactivity of the two NCS complexes leads us to suppose that the slower loosening of the Co(III)-ONO⁻ bond in $trans\text{-}[\text{Co}(\text{en})_2(\text{NCS})(\text{ONO})]^+$ is responsible for its extremely slower isomerization. Much slower isomerization is thus expected for $trans\text{-}[\text{Co}(\text{cyclam})(\text{NCS})(\text{ONO})]^+$. It is also informative to remember that $trans\text{-}[\text{Co}(\text{en})_2(\text{NCS})(\text{ONO})]^+$ isomerizes in the solid state with a rate fairly slower than those of other nitrito complexes.^{1,5,9b}

Effect of Net Charge on the Complexes. It is well-known^{16,41} that the acid hydrolysis rate of chloro(amine)cobalt(III) complexes is greatly affected by the change in their net charge. This is because charge separation takes place when a five-coordinated intermediate is formed. A comparison of the isomerization rate constants listed in Tables I-IV establishes that the net charge on the complex has no practical effect on its isomerization rate. This observation is consistent with the assertion that the isomerization is an intramolecular process which involves no appreciable charge separation in the transition state, and a dissociative mechanism is ruled out completely.⁴

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Registry No. $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$, 16633-04-8; $cis\text{-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{ONO})]^{2+}$, 85610-84-0; $trans\text{-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{ONO})]^{2+}$, 85610-85-1; $\omega\text{-}[\text{Co}(\text{en})(\text{dien})(\text{ONO})]^{2+}$, 85533-77-3; $\pi\text{-}[\text{Co}(\text{en})(\text{dien})(\text{ONO})]^{2+}$, 85610-86-2; $trans\text{-}[\text{Co}(\text{cyclam})(\text{NH}_3)(\text{ONO})]^{2+}$, 85533-78-4; $cis\text{-}[\text{Co}(\text{tn})_2(\text{NH}_3)(\text{ONO})]^{2+}$, 85552-54-1.

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Correlation of Spectroscopic Parameters with Ligand Basicity for Uranyl Bis(hexafluoroacetylacetonate) Adducts

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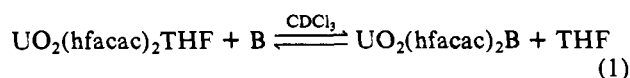
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The infrared transition frequencies (vapor and solution phases) of the uranyl and hexafluoroacetylacetonate (hfacac) moieties, as well as ¹³C and ¹H NMR shifts, correlate linearly with the relative basicity of the neutral bases (B) for 15 UO₂(hfacac)₂ adducts. Solvation effects and relative entropy changes appear to be minimal for the base-exchange equilibrium, suggesting that the observed shifts in these easily measurable spectroscopic properties predominantly reflect the Lewis acid-base relative bond strengths. We interpret the observed shifts in terms of electronic structure perturbations of both the uranyl and hfacac moieties arising from changes in neutral base (L-M) bonding.

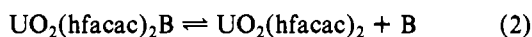
Introduction

The chelated uranyl ion, UO₂(hfacac)₂, recently has been shown to behave as a model hard Lewis acid to a variety of oxygen and nitrogen bases.¹ The free energies (ΔG°) for the

base-exchange reaction



were measured by NMR techniques, thereby establishing a basicity scale, relative to THF (tetrahydrofuran). This scale correlates well with other basicity scales such as the Gutmann donor number.^{1a} These Lewis acid–base adducts are of particular interest since they possess significant volatility (ca. 1 torr) at moderate temperatures (80–200 °C) at which the thermal dissociation equilibria



are observable.^{2–6} The dissociation enthalpy and entropy have been determined for several bases^{2,4–6} and for the dimerization equilibrium (3),^{2,4} in which $\text{UO}_2(\text{hfacac})_2$ is both a Lewis acid and a (weak) Lewis base.^{4,7} Direct comparison of vapor- and solution-phase basicities is possible and enables solvation effects to be discerned. Furthermore, various molecular properties of the Lewis acid are sensitive to the particular neutral base and can now be quantitatively correlated with the relative basicities.

This paper presents the correlations of infrared transition frequencies (vapor and solution phases) of the uranyl and hfacac moieties, as well as ¹³C and ¹H NMR shifts, and adduct and neutral base dipole moments for 15 complexes with the relative basicity (CHCl_3 solution). Consideration of solvation effects and relative entropy changes for the equilibrium (1) and comparison of solution-phase basicities with the few known vapor-phase measurements suggest that the basicity scale corresponds closely to the relative enthalpy changes. The spectroscopic properties, therefore, provide a direct measure of the adduct Lewis acid–base relative bond strengths. Previous correlations among a more limited set of spectroscopic parameters for similar uranyl complexes⁸ have provided no quantitative relationship with basicity. We interpret these correlations in terms of electronic structure perturbations of both uranyl and hfacac moieties, arising from the changes in neutral base (L–M) bonding.

Experimental Section

Infrared spectra were measured on a Digilab FT IR spectrometer, with nominal resolution of 0.5 or 1 cm^{-1} , using either CHCl_3 or C_6H_6 (or the perdeuterated compounds) as solvents. For vapor-phase measurements samples were distilled into a specially constructed heated cell maintained at constant temperature within the range 80–160 °C with typical pressures 0.1–1.0 torr. The onset of thermal dissociation or decomposition determined the maximum temperature and pressure for recording uncontaminated spectra of the adduct. Reference 9 describes in greater detail the apparatus and procedures.

NMR spectra were obtained for the same solutions used in the infrared determinations. The concentrations of the uranyl compounds

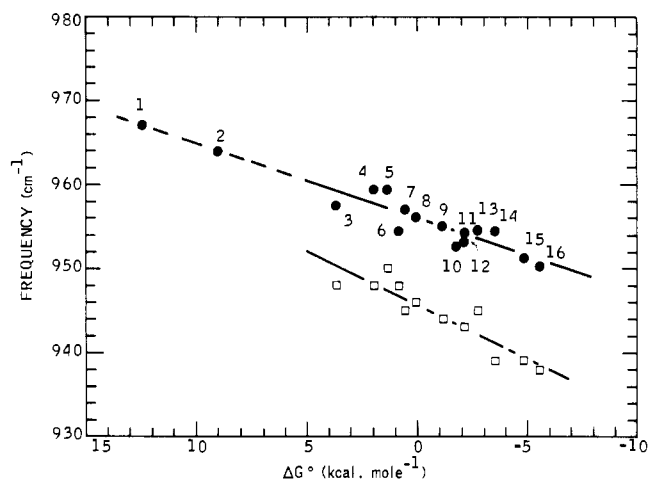


Figure 1. Correlation of uranyl asymmetric stretch frequency (cm^{-1}) for $\text{UO}_2(\text{hfacac})_2\text{B}$ complexes with relative base strength (ΔG° , kcal mol^{-1}): (●) vapor phase; (□) C_6H_6 solution. Table I interprets the compound number code.

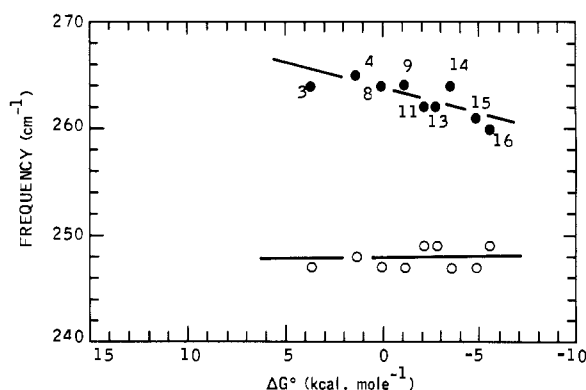


Figure 2. Correlation of uranyl bending frequency (●) and invariance of CF_3 rocking frequency (○) (C_6H_6 solution) with relative base strength (ΔG° , kcal mol^{-1}). Table I interprets the number code.

were normally between 0.04 and 0.4 M, and measurements were made at ambient temperature on a Varian EM-360L spectrometer. Spectral shifts were determined under the assumption that the solvent protons could be used as an internal standard.

Dipole moments of the uranyl complexes were determined from measurements of the dielectric constant and refractive indices of solutions in benzene. For reference the dipole moments of the bases were determined separately. The dielectric constants were measured on a Sargent Model V oscillometer at 25 °C and the refractive indices determined by Exxon's analytical laboratory using the ASTM-D1218 procedure. These quantities were used to determine the molar polarization and molar refraction of the solutions from which the orientation polarization of the solute and its dipole moment were deduced by standard means.¹⁰

The values obtained for the Lewis bases are more reliable than those for the uranyl complexes because, in the former case, the solute concentration could be readily varied and the molar refractions and polarizations extrapolated to values at infinite dilution, from which the dipole moments were deduced. The lowest concentration utilized for the Lewis bases was 0.1 M. Since the molar polarization of the bases at infinite dilution approximated the polarization at 0.1 M, it was assumed that the dipole moment of the uranyl compounds is reliably estimated from measurements at only 0.1 M concentration. Measurements at lower concentrations of these solutions were irreproducible and limitations on sample availability precluded the use of higher concentrations. The standard deviations of the dipole moments are ± 0.3 D for the bases and ± 0.6 D for the uranyl complexes.

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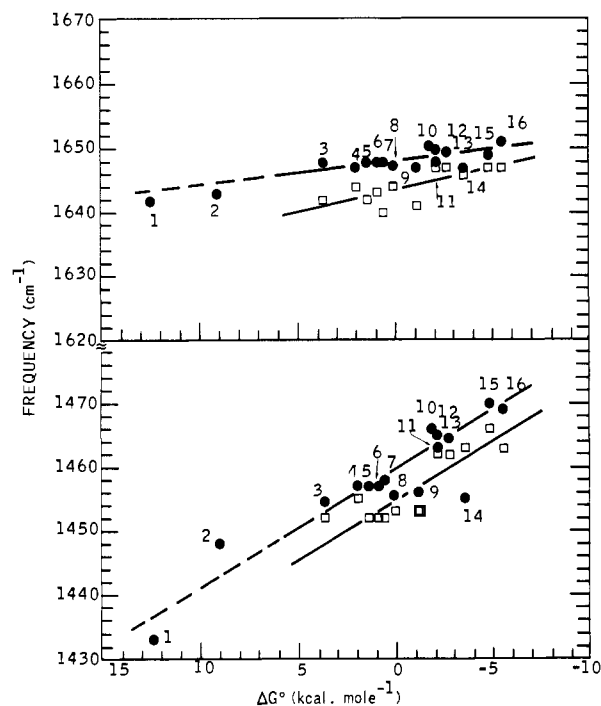


Figure 3. Correlation of C=O symmetric (upper panel) and asymmetric (lower panel) stretch frequencies with relative base strength (ΔG° , kcal mol $^{-1}$): (●) vapor phase; (□) C₆H₆ solution. Table I interprets the number code.

Results

The hfacac ligand ring stretches, and the uranyl asymmetric stretch and bend vibrations, all display significant shifts with neutral base. Table I lists the infrared frequencies (vapor and C₆H₆ solution) of these transitions for 15 bases as well as for monomeric UO₂(hfacac)₂ and also includes the relative base strengths (CHCl₃ solution), molecular weights, and abbreviations used in the text.

The uranyl asymmetric stretch frequency (near 955 cm⁻¹) decreases with increasing base strength for the vapor phase and C₆H₆ solution, as shown in Figure 1. The extension of the solid line for the vapor-phase data enables the dimer (964 cm⁻¹) and monomer (967 cm⁻¹) transitions to be displayed. No comparable data exist for solutions, since solid [UO₂(hfacac)₂]_m dissolved in CHCl₃, shows only a single broad band at 944 cm⁻¹ and the identity of the corresponding molecular species is uncertain. Deviations from linearity are mimicked in both phases with the solution-phase data red shifted by ~12 cm⁻¹. The uranyl bending frequency (262 cm⁻¹, C₆H₆ solution) follows the same, but weaker, trend with base strength as does the asymmetric stretch (see Figure 2).

Although the ligand ring stretch vibrations are complex normal modes involving all the ring bond-stretch coordinates, they are denoted here by their major components C=C and C=O, respectively; see ref 9 for a discussion of these assignments). Stronger bases increase the symmetric (~1645 cm⁻¹) and asymmetric (~1450 cm⁻¹) C=O stretch frequencies, as shown in Figure 3. The relative basicity values, derived from the linear extrapolation in Figure 1, locate the monomer and dimer frequencies. They overlap well with the linear extrapolation for the C=O stretch frequencies. Assignments of the C=C stretch frequencies are not as secure as those for the C=O stretch modes. Three relatively weak bands at ~1610, ~1550, and ~1530 cm⁻¹ are all candidates, and at least one of these possesses some C=C asymmetric stretch character. Similarly the C=C symmetric stretch is coupled to CF₃ stretch motions, and two bands at ~1220 and ~1170 cm⁻¹ possess some C=C stretch motion. Nevertheless, the frequencies of these five bands all decrease with increasing base strength.

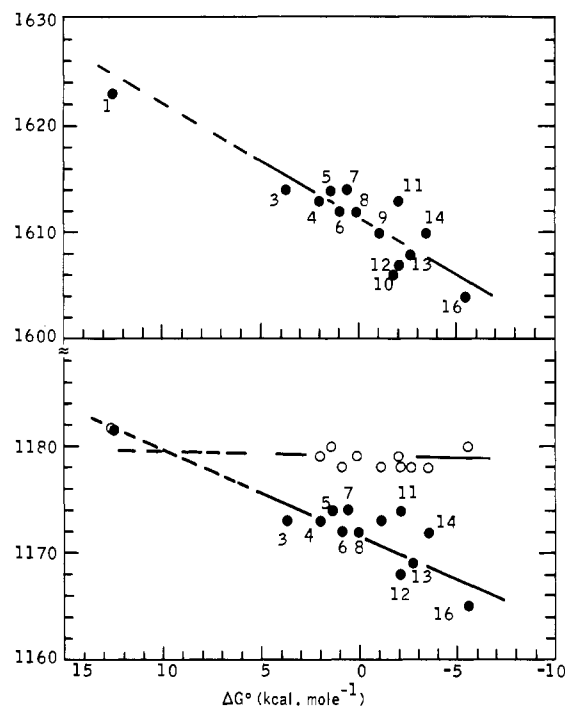


Figure 4. Correlation of C=C asymmetric (upper panel) and symmetric (lower panel) stretch frequencies (●) with neutral base strength (ΔG° , kcal mol $^{-1}$). Data for the overlapping CF stretch (○) are shown in the lower panel. Table I interprets the number code.

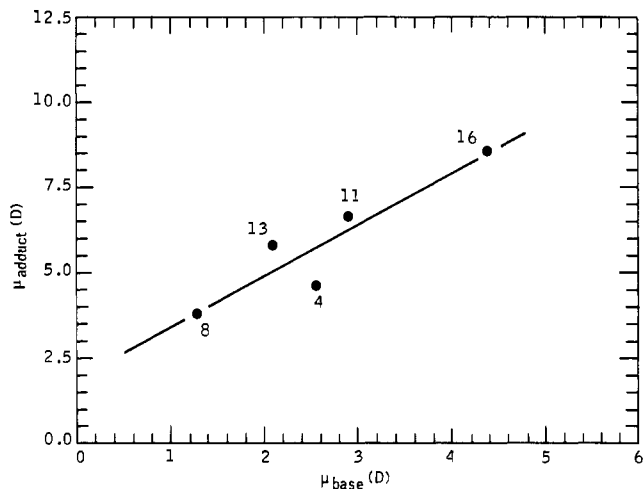


Figure 5. Dipole moments (D) for UO₂(hfacac)₂B complexes plotted against the neutral base (B) values, measured in C₆H₆ solution. The linear correlation corresponds to $\mu_{\text{adduct}} = 1.5\mu_{\text{base}} + 1.9$. Table I interprets the compound number code.

Figure 4 shows this behavior for the 1610- and 1170-cm⁻¹ band frequencies and demonstrates the opposing correlations of C=O vs. C=C stretch frequencies of the hfacac ligand. Only the vapor-phase data are displayed for the latter, with the monomer frequencies located as before.

The invariance of other vibrational frequencies (typically ± 1 cm⁻¹) for this series of complexes is displayed for two cases where these bands overlap the neutral base dependent uranyl bend (Figure 2) and C=C symmetric stretch bands (Figure 4, lower panel).

Table II lists the neutral base and adduct dipole moment data together with the proton and ¹³C (CO and CH) NMR shifts of the hfacac ligand. The (benzene) solution values for the neutral base dipole moments (μ) correlate well with the vapor-phase values; linear regression analysis gives $\mu_{\text{benzene}} = 0.79\mu_{\text{vapor}} + 0.06$ (with a correlation coefficient, $r^2 = 0.98$) with use of the data of Table II. Figure 5 compares the dipole

Table I. Infrared Frequency Shifts,^a Relative Base-Exchange Free Energies (ΔG°),^b and Base Molecular Weights (M_B) for $UO_2(hfacac)_2B$ Complexes

| B | abbr | ΔG° | M_B | C=O _{ss} | | C=O _{as} | | C=C _{ss} | | UO ₂ (as) | | UO ₂ (bend) |
|-----------------------------|--------------------|---------------------|-------|-------------------|------|-------------------|------|-------------------|------|----------------------|------|------------------------|
| | | | | vapor | soln | vapor | soln | vapor | soln | vapor | soln | vapor |
| 1. no base | | (12.4) ^c | | 1642 | | 1433 | | 1225 | | 967 | | |
| 2. $UO_2(hfacac)_2$ | | (9.0) ^c | 684 | 1643 | | 1448 | | 1182 | | 964 | | |
| 3. tetrahydrothiophene | THT | 3.6 | 88 | 1649.5 | 1642 | 1455 | 1452 | 1222 | 1173 | 948 | 958 | |
| 4. acetone | ACE | 1.9 | 58 | 1647 | 1644 | 1457 | 1455 | 1222 | 1173 | 948 | 960 | 264 |
| 5. water | H ₂ O | 1.8 | 18 | 1642 | 1648 | 1451 | 1451 | 1223 | 1174 | 950 | 960 | 265 |
| 6. dimethyltetrahydrofuran | DMTHF | 0.8 | 100 | 1643 | 1648 | 1452 | 1452 | 1222 | 1172 | 948 | 955 | |
| 7. 1,4-epoxycyclohexene | ECH | 0.5 | 96 | 1640 | 1648 | 1450 | 1450 | 1223 | 1174 | 945 | 957 | 264 |
| 8. tetrahydrofuran | THF | 0.0 | 72 | 1643 | 1647 | 1453 | 1453 | 1221 | 1172 | 946 | 956 | 264 |
| 9. pyridine | py | -1.2 | 79 | 1641 | 1647 | 1456 | 1456 | 1221 | 1172 | 944 | 955 | 264 |
| 10. tributyl phosphate | TBP | -1.9 | 266 | 1649.5 | 1647 | 1466 | 1466 | 1216 | 1168 | 953 | 953 | |
| 11. dimethyl sulfoxide | Me ₂ SO | -2.2 | 74 | 1648.5 | 1647 | 1463 | 1463 | 1219 | 1174 | 943 | 954 | 262 |
| 12. triethyl phosphate | TEP | -2.2 | 182 | 1650 | 1650 | 1465 | 1465 | 1217 | 1168 | 953 | 953 | |
| 13. trimethyl phosphate | TMP | -2.9 | 140 | 1647 | 1647 | 1463 | 1463 | 1219 | 1169 | 945 | 955 | 262 |
| 14. pyridine N-oxide | PNO | -3.6 | 95 | 1646 | 1647 | 1463 | 1463 | 1219 | 1172 | 939 | 955 | |
| 15. triethylphosphine oxide | TEPO | -4.9 | 134 | 1647 | 1649 | 1466 | 1466 | 1219 | 1172 | 939 | 951 | 261 |
| 16. hexamethylphosphoramide | HMPA | -5.6 | 179 | 1647 | 1647 | 1463 | 1463 | 1215 | 1165 | 938 | 950 | 260 |

^a For assignments, see ref 9. Solution data refer to C_6H_6 . Units are in cm^{-1} . Abbreviations: as, asymmetric stretch, ss, symmetric stretch. ^b Reference 1. Units are in kcal mol⁻¹. ^c Extrapolated values given by linear regression of data for $UO_2(as)$ (Figure 1) and used for plotting other data correlations.

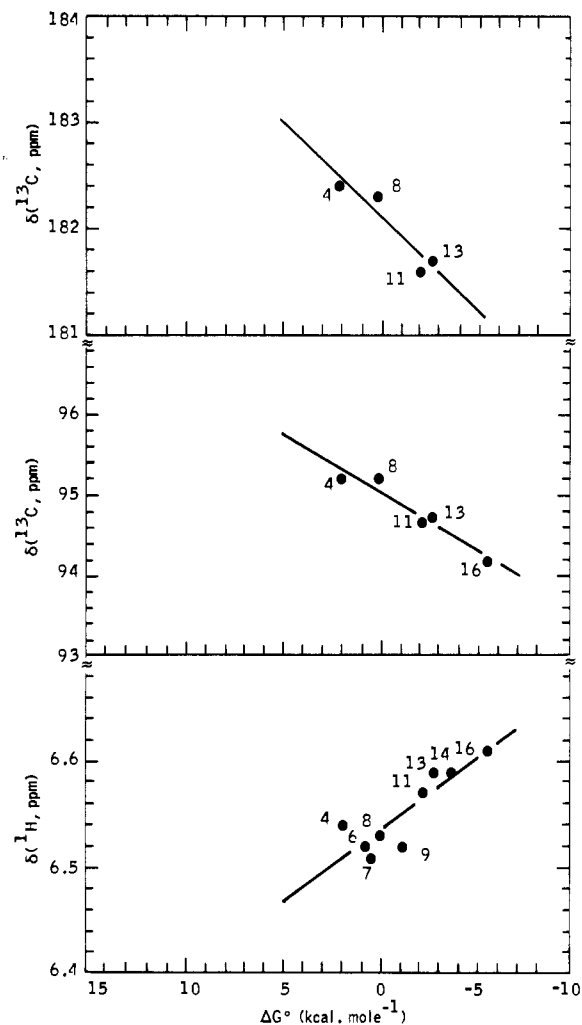


Figure 6. Correlation of ¹³C (CO, upper panel; CH, middle panel) and ¹H (lower panel) NMR shifts (δ vs. Me₄Si) with relative base strength (ΔG° , kcal mol⁻¹). Table I interprets the number code.

moments of the adducts and neutral bases. A linear regression analysis of this data gives $\mu_{\text{adduct}} = 1.5\mu_{\text{base}} + 1.9$ ($r^2 = 0.85$). The adduct dipole moment exceeds the neutral base moment by $\sim 2-4$ D, the difference increasing with the size and strength of the bases. Figure 6 displays the relatively small, but approximately linear, dependence of the hfacac ligand proton and ¹³C shifts on relative basicity for a small number of adducts.

Discussion

The molecular structures of these complexes, as shown by X-ray crystal structure data,^{3,11,12} consist of an inner-sphere pentagonal bipyramid of oxygen atoms (with the THF adduct as an example) surrounding the central uranium atom. The linear uranyl moiety is perpendicular to the plane containing the hfacac and neutral base oxygen atoms. The planar hfacac rings are bent with respect to the pentagonal plane of oxygen atoms. The uranium-neutral base bond length decreases only slightly with base strength (2.35 Å, THF;³ 2.31 Å, TMP;¹¹ 2.28 Å, HMPA¹²) while the U-O(hfacac) bond lengths increase slightly. Infrared spectra for these complexes in both vapor and solution phases show only small frequency shifts and are consistent with these known structures. The observed shifts do not correlate with the size of the neutral base, which

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Table II. NMR Shifts and Dipole Moments for $\text{UO}_2(\text{hfacac})_2\text{B}$ Complexes

| B | NMR shifts ^a (δ) | | | dipole moments ^b (μ , D) | | |
|------------------------|--------------------------------------|--------------------|---------------------|--|---------|-----------------------|
| | ¹ H | ¹³ C(H) | ¹³ C(=O) | $\text{UO}_2(\text{hfacac})_2\text{B}$ | B(soln) | B(vapor) ^c |
| 4. ACE | 6.54 | 95.20 | 182.4 | 4.6 | 2.56 | 2.88 |
| 6. DMTHF | 6.52 | | | | | |
| 7. ECH | 6.51 | | | | | |
| 8. THF | 6.53 | 95.20 | 182.3 | 3.8 | 1.29 | 1.63 |
| 9. py | 6.52 | | | | | |
| 11. Me ₂ SO | 6.57 | 94.66 | 181.6 | 6.7 | 2.91 | 3.96 |
| 13. TMP | 6.59 | 94.72 | 181.7 | 5.8 | 2.1 | |
| 14. PNO | 6.59 | | | | | |
| 16. HMPA | 6.61 | 94.17 | | 8.6 | 4.4 | 5.39 |

^a Error limits: ± 0.02 (¹H); ± 0.03 (¹³C). All spectra were run in CHCl_3 solution, with δ vs. Me_4Si . ^b Error limits: ± 0.3 D (B); ± 0.6 D ($\text{UO}_2(\text{hfacac})_2\text{B}$). All measurements were made in C_6H_6 solution. ^c Reference 19.

occupies the fifth coordination site with minimal apparent steric interference, except for the dimer. The latter adduct, which is only observed in the gas phase in equilibrium with the monomer (reaction 3), is more loosely bound. Infrared spectral analysis⁷ and thermodynamic equilibrium measurements^{2,4} indicate that one monomeric unit acts as a typical Lewis base forming a weak bond to the $\text{UO}_2(\text{hfacac})_2$ Lewis acid via one of the uranyl oxygen atoms. The large size of the $\text{UO}_2(\text{hfacac})_2$ base moiety presumably hinders a close approach to the uranium atom of the Lewis acid.

The following discussion explores the relationship between the basicity scales and acid-base bond strengths for this series of complexes and interprets the correlations of infrared transition frequencies, NMR shifts, and dipole moments with relative basicity in terms of electronic structure perturbations due to the neutral bases.

Vapor and Solution Basicity Scales. The basicity scale given by the relative free energies (ΔG°) for the base-exchange equilibrium (1) (CHCl_3 solution) correlates with both solution- and vapor-phase infrared frequencies. The equilibrium can be expressed as the sum of the dissociation equilibria (2) for the respective complexes

$$\Delta G^\circ = \Delta G^\circ_{\text{THF}} - \Delta G^\circ_{\text{B}}$$

where $\Delta G^\circ_{\text{THF}}$ and $\Delta G^\circ_{\text{B}}$ refer to the free energies for dissociation of the THF and B complexes, respectively. Since the vapor-phase dissociation enthalpies ($\Delta H^\circ_{\text{B}}$) and entropies ($\Delta S^\circ_{\text{B}}$) are known for only three adducts, the corresponding vapor-phase basicity scale has not been established. The difference between the relative free energies for solvation of the adducts and of the bases in the exchange equilibrium (1) determines the relative ordering of the bases for the vapor- and liquid-phase scales. Solvent-base and solvent-adduct interactions should be minimized in aprotic and weakly polar solutions (e.g. CHCl_3), but the stronger bases do possess significant dipole moments and dipole-dipole interactions will become increasingly more important contributors to the relative solvation free energies. However, the polarities of the bases and corresponding adducts are proportional to each other (vide infra and Figure 5); solvation effects on the basicity scale should be minimized, and the basicity scales possess the same ordering in both phases.

Thermochemical calculations of adduct dissociation (2) suggest that the relative enthalpies for base exchange (1) are the dominant contribution to the relative basicity scales; i.e., the relative entropy changes are nearly constant. The electronic, translational, rotational, and vibrational contributions to the dissociation entropies ($\Delta S^\circ_{\text{B}}$) for the dimer and THF adducts were calculated by Woodin et al.⁴ These data, and estimates of the entropy contributions for other representative complexes obtained with use of the same formulas, provide the basis for subsequent discussion.

The electronic contribution to the dissociation entropy change is zero since all molecules exist in the ground electronic

state. Since the masses of the various bases are small in comparison to that of $\text{UO}_2(\text{hfacac})_2$ (see Table I), the translational entropy change is nearly constant ($\sim 40 \pm 2$ eu) while the rotational contribution shows a greater variation ($\sim 23 \pm 3$ eu), which increases with molecular size. As only small (less than a few percent) perturbations in vibrational frequencies occur between $\text{UO}_2(\text{hfacac})_2$, neutral base, and the adduct,⁹ only the six vibrational modes associated with adduct formation contribute significantly to the vibrational entropy change. Infrared spectroscopy⁹ indicates that the average vibrational frequency for these six modes should fall into the range 400–200 cm^{-1} , corresponding to a vibrational entropy change of -5 to -15 eu with the more negative values corresponding to the larger, less rigid bases. We conclude that, except for the special case of the dimer, the dissociation entropies will fall in the range 53 ± 5 eu, the greater deviations occurring for the larger bases and contributing at most about 3 kcal mol^{-1} to relative dissociation free energies. The equivalence of dissociation entropies should be an excellent assumption for nearly half the bases which have similar masses (58–100) and rigid structures yet span the entire range of basicities.

Since the relative entropy changes are expected to be very small, the relative free energies correspond closely to the relative enthalpies for complex dissociation and the solution basicity scale is a measure of relative bond strengths. The available data support this conclusion. The dissociation enthalpies for the dimer,^{2,4} THF,⁴ and TMP^{5,6} complexes are 23, 33, and 36 kcal mol^{-1} , respectively, in good agreement with the observed relative basicity for the TMP complex (-2.8 kcal mol^{-1} , CHCl_3 solution) and the extrapolated value (9.0 kcal mol^{-1}) based upon the dimer uranyl asymmetric stretch (Figure 2). Contrary to the case for the other adducts, the dimer complex is loosely bound and its dissociation entropy is ~ 20 eu less than that of $\text{UO}_2(\text{hfacac})_2\text{THF}$, presumably due to a very low frequency hindered internal rotation.⁴

We have previously noted solvent effects on the relative basicity for uranyl adducts.¹ The relative basicity scale is compressed in trifluoroethanol as compared to that in chloroform. In polar and protic media, hydrogen bonding with the solvent will occur, especially for the stronger bases. The solvent-base interaction will be minimized in less polar and more aprotic solvents where the solution equilibria will more closely mimic the gas phase, as demonstrated by the relative basicities for TMP vs. THF adducts in CHCl_3 and trifluoroethanol solutions (-2.8 and -0.88 kcal mol^{-1} , respectively).¹

Dipole Moments. The solution values for the neutral base dipole moments correlate well with the vapor-phase values, providing a useful check on our experimental procedures. The $\sim 20\%$ reduction is attributed to dipole-induced dipole interactions with the benzene solvent.

The dipole moments of the adducts and neutral bases are compared in Figure 5. The adduct dipole moment exceeds the neutral base moment by ca. 2–4 D, and the difference

increases as a function of the size and strength of the base (see Table I). Although spectroscopic data do not indicate whether or not the monomer is polar, the $\text{UO}_2(\text{hfacac})_2$ moiety clearly contributes to the polarity of the adduct. For the protonated molecule, Hhfacac , the dipole moments of the fluoromethyl groups more than counterbalance the carbonyl dipoles; the resultant $\mu(\text{calcd})$ is 0.7 D.¹³ In $\text{UO}_2(\text{hfacac})_2$, the positively charged uranium atom, centered $\sim 2.4 \text{ \AA}$ from each oxygen atom, replaces the proton centered on the O—O axis and must significantly increase the dipole moment of this component of the neutral base adduct. If we assume point dipole moments of $\sim 3.0 \text{ D}$ centered along the ligand U—CH axes which are subtended at 144° , the $\text{UO}_2(\text{hfacac})_2$ moiety contributes $\sim 1.8 \text{ D}$ to the adduct dipole moment. The difference in free base and adduct dipole moments is ascribed in part to the increased size of the complex and also to contributions from the individual U(hfacac) components that may be comparable to, or in some instances exceed, the contributions from the free base.

Infrared and NMR data (vide infra) indicate the transmission of electronic effects from the neutral base into the anionic ligand; these perturbations in electron density increase with base strength and should further increase the adduct dipole moment. This effect contributes to the increasing difference between neutral base and adduct dipole moments with base strength.

Infrared Frequencies. Several vibrational modes of the uranyl and hfacac moieties display linear frequency shifts with increasing relative basicity. Less extensive trends have previously been noted⁸ but not quantitatively correlated with adduct bond strength (as measured by the relative basicity scale). Furthermore, vapor-phase measurements allow examination of solvent effects upon these trends.

The observed decrease in the uranyl asymmetric stretch frequency (see Figure 1), which has been observed for other complexes with increasing ligand field strength,^{8,14,15} is attributed primarily to $\sigma(\text{L}-\text{M})$ electron donation into an empty "atomic"-like orbital on the uranium atom that does not contribute to the O=U=O bonding. Increased electron density at the uranium atom destabilizes the O=U=O bonds by electron repulsion with the highly negative axial oxygen atoms, thereby decreasing the vibrational frequency. The same argument also applies to the low-frequency UO_2 bend correlation (see Figure 2). Haigh and Thornton⁸ studied the effect of substitution in both anionic and neutral ligands for the pyridine adduct; from infrared and NMR data, they concluded that $\pi(\text{M}-\text{L})$ bonding was strong, shifting the asymmetric stretch to higher frequencies. No deviation from the correlation is expected for this effect, which will be absent for most other bases, since the U—py bond will be correspondingly weaker and the effect reflected in the basicity scale. The frequency shifts they observe for three neutral bases, H_2O , py, and PNO, in $\text{UO}_2\text{L}_2\text{B}$ adducts, where L corresponds to a series of anionic ligands, follow the same trend as for the hfacac complexes.

The observed decrease in $\text{C}\equiv\text{C}$ stretch frequencies and increase in $\text{C}=\text{O}$ stretch frequencies with neutral base strength

(see Figures 3 and 4) indicates that transmission of electronic effects beyond the uranyl groups occurs in β -diketone complexes. Both $\sigma(\text{L}-\text{M})$ and $\pi(\text{L}-\text{M})$ and $\pi(\text{M}-\text{L})$ electron donation contribute to the equatorial bonding of uranyl chelates.^{9,14} For the stronger bases, the increased electron density at the uranium atom will increase the electrostatic interactions with the bonding electrons. Charge redistribution occurs at the equatorial oxygen atom, weakening the U—O(C) bond and strengthening the $\text{C}=\text{O}$ bond, as observed by infrared spectroscopy. Although weakening of the U—O bond is expected, the U—O stretch frequencies, identified at 362 and 337 cm^{-1} , show no base dependence. This is not surprising given previous findings⁸ that the U—O stretch at 403 cm^{-1} for the $\text{UO}_2(\text{acac})_2$ pyridine adduct does not depend on neutral base for a variety of pyridine substituents, despite large changes in $\nu_3(\text{U}=\text{O})$. To explain the opposing trend for the $\text{C}\equiv\text{C}$ stretch frequency would require detailed molecular orbital calculations of the hfacac electronic structure, which is beyond the scope of this paper.

NMR Shifts. Figure 6 indicates that increased base strength results in decreased shielding of the proton while the CO and CH carbon atoms become progressively more shielded, indicative of increased electron densities at the carbon atoms and transmission of electronic effects from the neutral base into the anionic ligand. Since electron density distributions at the carbon and hydrogen atoms are difficult to calculate accurately unless the most sophisticated ab initio methods are used, no attempt is made to rationalize these trends in terms of the hfacac bonding structure. Furthermore, intramolecular first-order electric field effects contribute significantly to NMR shifts in dipolar molecules.^{16,18} Such effects previously demonstrated for dipolar acetylacetonate complexes^{17,18} most likely are important for $\text{UO}_2(\text{hfacac})_2$ complexes as well.

Summary

We have established that infrared transition frequencies and NMR shifts of $\text{UO}_2(\text{hfacac})_2\text{B}$ complexes correlate linearly with relative basicity of the neutral bases (B). Solvation effects and the relative entropy changes appear to be minimal for the base-exchange equilibrium (1), thereby suggesting that the observed shifts in these easily measurable spectroscopic properties predominately reflect the adduct Lewis acid–base relative bond energies and provide insight into the electronic structure of these complexes.

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Registry No. $\text{UO}_2(\text{hfacac})_2$, 67316-66-9; $\text{UO}_2(\text{hfacac})_2\text{THT}$, 78527-96-5; $\text{UO}_2(\text{hfacac})_2\text{ACE}$, 69244-73-1; $\text{UO}_2(\text{hfacac})_2\text{H}_2\text{O}$, 78527-93-2; $\text{UO}_2(\text{hfacac})_2\text{DMTHF}$, 85565-67-9; $\text{UO}_2(\text{hfacac})_2\text{ECH}$, 85565-68-0; $\text{UO}_2(\text{hfacac})_2\text{THF}$, 69244-67-3; $\text{UO}_2(\text{hfacac})_2\text{py}$, 78527-94-3; $\text{UO}_2(\text{hfacac})_2\text{TBP}$, 35185-38-7; $\text{UO}_2(\text{hfacac})_2\text{Me}_2\text{SO}$, 75172-91-7; $\text{UO}_2(\text{hfacac})_2\text{TEP}$, 78527-95-4; $\text{UO}_2(\text{hfacac})_2\text{TMP}$, 64708-00-5; $\text{UO}_2(\text{hfacac})_2\text{PNO}$, 34011-51-3; $\text{UO}_2(\text{hfacac})_2\text{TEPO}$, 75172-92-8; $\text{UO}_2(\text{hfacac})_2\text{HMPA}$, 75172-93-9.

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