to nitrogen ligands allows the formation of several previously inaccessible metalloflavin complexes involving the neutral quinone, dianionic semiquinone, and fully reduced flavins. Apart from the possibility of direct metal-flavin ligation, which has yet to be established in a metalloflavoprotein, aspects of the studies reported here can be extended to the general case of the coordination of a Lewis acid to the N-5 site of a flavin, for which spectroscopic evidence does exist in a number of flavoproteins.[2]

The most obvious effect of coordination at the N-5 site is the wide separation (266 mV at pH 7) between what are overlapping reduction potentials in the free flavin. This causes the flavin to undergo oxidation and reduction in discrete one-electron steps and prevents disproportionation of the flavosemiquinone.

The studies of E_{cv} vs. pH for the Ru-Fl complexes provide the only such data available for metalloflavin complexes with quantitatively characterized proton equilibria and so illustrate how flavin redox potentials can be adjusted by affecting proton availability at the N-1 and N-3 sites of a N-5 ligated coenzyme. Reference to Figure 4 indicates how the accessibility of the lower redox couple can be controlled by the availability of a proton at the N-1 site. The separation between the first and second flavin reduction potentials is minimized when a proton is of such availability as to not protonate Fl_{ox}, to partially protonate Fl·, and to fully protonate Fl_{red}. The small separation (40 mV) between the couples in this pH region may even cause the electron transfer to occur by an apparent two-electron process. If the proton is forced onto the Ru-Fl_{ox} form, then the first reduction becomes more facile and diverges from the lower redox process. If a proton is totally unavailable to add at the N-1 position, then the two potentials are widely separated. Proton loss resulting from the presence of a base at the N-3 site does not affect the separation between the two redox processes of an N-5 ligated flavin but does cause the first to decrease in potential with increasing pH at the same rate as the second. When a proton is unavailable to bind the N-3 site of either the Fl_{ox} or Fl· complexes, the couples again diverge.

Control of the availability of a proton or a base at a particular site on a substrate molecule is a property which is very well-handled by proteins. A better approximation of an average environment on the interior of a protein, as opposed to the exterior aqueous environment approximated in this work, would be provided by similar studies in an amide solvent. These investigations are now under way.

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Registry No. $[(Rib)(NH_3)_4Ru]Cl_2$, 78591-56-7; $[(3,10\text{-}Me_2Alo_{ox})(NH_3)_4Ru]^{2+}$, 69290-19-3; $[(10\text{-}MeAlo_{ox})(NH_3)_4Ru]^{2+}$, 69290-17-1; $[(Rib_{ox})(NH_3)_4Ru]^{2+}$, 78591-57-8; $[(3,10\text{-}Me_2IAlo\cdot)(NH_3)_4Ru]^{2+}$, 78591-58-9; $[(10\text{-}MeIAlo\cdot)(NH_3)_4Ru]^{2+}$, 78591-59-0; $[(Rib\cdot)(NH_3)_4Ru]^{2+}$, 78591-60-3; $[(3,10\text{-}Me_2IAloH_{ox})(NH_3)_4Ru]^{3+}$, 78591-61-4; $[(10\text{-}MeIAloH_{ox})(NH_3)_4Ru]^{3+}$, 78591-62-5; $[(RibH_{ox})(NH_3)_4Ru]^{3+}$, 78609-76-4; $[(10\text{-}MeIAlo_{ox}^-)(NH_3)_4Ru]^+$, 78591-63-6; $[(Rib_{ox}^-)(NH_3)_4Ru]^+$, 78591-64-7; $[(3,10\text{-}Me_2IAlo^-\cdot)(NH_3)_4Ru]^+$, 78591-65-8; $[(10\text{-}MeIAlo^-\cdot)(NH_3)_4Ru]^+$, 78591-66-9; $[(Rib^-\cdot)(NH_3)_4Ru]^+$, 78591-67-0; $(10\text{-}MeIAlo^{2-}\cdot)(NH_3)_4Ru$, 78591-68-1; $(Rib^{2-}\cdot)(NH_3)_4Ru$, 78609-77-5; $[(10\text{-}MeIAlo_{ox})(NH_3)_4Ru]^{3+}$, 78591-69-2; $[(3,10\text{-}Me_2IAlo_{ox})(NH_3)_4Ru]^{3+}$, 78591-70-5; $[(Rib_{ox})(NH_3)_4Ru]^{3+}$, 78591-71-6; $[(3,10\text{-}Me_2Alo_{red}^-)(NH_3)_4Ru]^+$, 78591-72-7; $[(10\text{-}MeAlo_{red}^-)(NH_3)_4Ru]^+$, 78591-73-8; $[(Rib_{red}^-)(NH_3)_4Ru]^+$, 78591-74-9.

Supplementary Material Available: A figure of the E_{cv} vs. pH plot for $(10\text{-}MeIAlo)(NH_3)_4Ru^{II}$ and tables of E_{max} and λ_{max} for Ru-Fl_{ox} and Ru-Fl complexes in various protonation states and cyclic voltammetry data used in E_{cv} vs. pH plots (8 pages). Ordering information is given on any current masthead page.

Contribution from Exxon Research and Engineering Company, Linden, New Jersey 07036

Fluxionality of Uranyl β-Diketonate–Base Complexes. Behavior of Uranyl Trifluoroacetylacetonate–Dimethyl Sulfoxide

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The F NMR spectral behavior of a mixture of the cis and trans uranyl trifluoroacetylacetonate–dimethyl sulfoxide complexes indicates that base migration rather than anion rotation is the preferred intramolecular rearrangement path. The intramolecular nature of the process is consistent with the lack of correlation between the fluxional rate and the heats of solution of a series of bases which yield rearranging hexafluoroacetylacetonate complexes.

It has recently been found that uranyl hexafluoroacetylacetonate–base complexes of the general formula $UO_2(hfacac)_2 \cdot B$ undergo a rearrangement in aprotic media that is fast on the NMR time scale.[1,2] This results in averaging the ^{19}F NMR spectra of the complexes to a single band which can be resolved by cooling. The tetrahydrofuran complex[3] exhibits a coalescence temperature of about −80 °C which is typical of the behavior of other compounds with relatively small bases like dimethyl sulfoxide and trimethylphosphate.[4]

Under the assumption that the reaction is intramolecular, it was proposed that the fluxionality is due to a gyroscopic path taken by the base as it travels about the chelated uranyl ion. This report is concerned with two mechanistic issues; the validity of an intramolecular rearrangement rather than a unimolecular dissociation being rate determining and the

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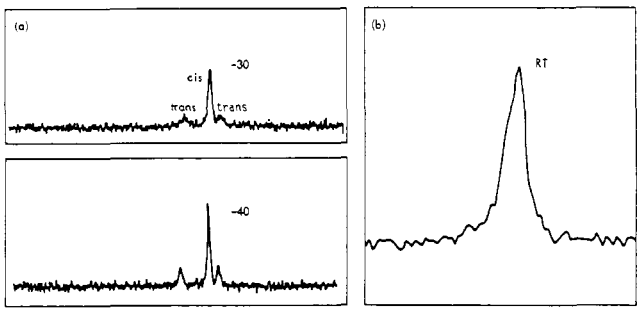

Figure 1. (a) ^{19}F NMR spectra of *cis*- and *trans*-$UO_2[CF_3COCHCOCH_3]_2 \cdot (CH_3)_2SO$ obtained at −30 and −40 °C on a Varian 360-L spectrometer (60 MHz). (b) Spectrum at ambient temperature on a 90-MHz JEOL FX-900 instrument showing the trans compound as a shoulder on the side of the cis isomer.

possibility of anion rotation rather than base migration being the intramolecular process at hand.

The possible existence of a rate-determining unimolecular dissociation followed by rapid displacement processes was considered unlikely because of the lack of a detectable dissociation equilibrium at temperatures at least 80 °C above the coalescence temperature. In fact the tetrahydrofuran complex can be heated in hydrocarbon solutions to about 90 °C without any apparent loss of the base. Consistent with this indication of the absence of dissociation is the fact that these compounds show a strong tendency to remain in hydrocarbon media when contacted with an aqueous phase, even when the uncomplexed neutral base would have a strong affinity for water.

This question has been further examined by measuring the heats of solution of the series of bases used in the prior study. If a unimolecular dissociation were governing the process, it would be reasonable as a first approximation to expect a parallel between their heats of solution and the fluxionality of the complexes. True, the values might be mitigated when strong intermolecular dipolar forces were present in the bases themselves because of the energy expenditure in dissociating the self-associated molecules, but a general relationship should be expected. The dipolar effect should become more pronounced as both the dipole moment and nucleophilicity of the bases increase, but if unimolecular dissociation is rate determining, the fluxional rate should be expected to steadily increase with increasing base–solvent interactions.

Accordingly, the heats of solution, ΔH_S have been measured in methylene chloride. (The fluxional process was studied in a solution in a solution of 90% methylene chloride and 10% of a methylcyclohexane–isopentane mixture.) They were obtained in triplicate measurements by adding enough base to 150 mL of CH_2Cl_2 to prepare nominal 0.1 M solutions, the temperature change being measured by a Beckmann thermometer.

These values are compared with the rate of the fluxional process in Table I. The heats of solution of CH_3OH, THF, Me_2SO, TMP, Et_3PO, and HMPA are in qualitative agreement with the relative basicity of these compounds toward uranyl hexafluoroacetylacetonate.[5] The heat of solution of pyridine *N*-oxide and methanol are the only values which appear to significantly deviate from the basicity series. The ΔH_S values may be rationalized by noting that pyridine *N*-oxide is a solid and the measured ΔH_S contains an unknown contribution from the heat of fusion which must make the experimental result more endothermic than it would be if the compound were a liquid. The heat of solution of methanol is more endothermic than might be expected from its basicity toward the uranyl complex. A reasonable explanation is that its uranyl complex is stabilized by hydrogen bonding but that this is not very significant in methylene chloride.

(5) G. M. Kramer, E. T. Maas, Jr., and M. B. Dines, *Inorg. Chem.*, **20**, 1415 (1981).

Table I. Heat of Solution and Rate of Fluxional Rearrangement

base[b]	k,[c] s^{-1}	ΔH_S	rel basicity[a]
MeOH	11000	+4.0	0.5
THF (0.04 M)	1670	−1.6	0
THF (0.002 M)	5500		
Me_2SO	51000	−2.1	−2.2
TMP	2000	−1.4	−2.8
pyNO (solid)	7800	+2.7	−3.6
Et_3PO	18	−3.1	−4.9
HMPA	9.9	−4.2	−5.6

[a] Determined for the equilibria

$$UO_2[(CF_3CO)_2CH]_2THF + B \underset{DCCl_3}{\rightleftharpoons} UO_2[(CF_3CO)_2CH]_2 \cdot B + THF$$

[b] MeOH = methanol, THF = tetrahydrofuran, Me_2SO = dimethyl sulfoxide, TMP = trimethyl phosphate, pyNO = pyridine *N*-oxide, Et_3PO = triethylphosphine oxide, and HMPA = hexamethylphosphoramide. [c] At 30 °C.

The data show that there is absolutely no correlation between the fluxional process and the heat of solution of these bases in methylene chloride. The eliminates a rate-determining dissociation as a factor and enables us to inquire with confidence about the intramolecular rearrangment path. Kinetic arguments were previously used to argue that base migration was more facile than anion rotation. To probe this possibility in greater detail, we examined the behavior of a trifluoroacetylacetonate complex in which the consequences of base or anion mobility would lead to different NMR results.

X-ray studies[3] of several of the compounds indicate that an oxygen atom of the base occupies one site in a pentagon of oxygen atoms that equatorially surround the linear uranyl ion. Base migration may be visualized as the process in which the base moves to an octahedral face of the $UO_2(hfacac)_2$ molecule and then to a complementary position on the other side of the ion from whence it came. Anion rotation would involve a 180° rotation of the β-diketonate about an axis passing through the uranium atom and the central carbon of the anion. The latter motion might be either a concerted or a stepwise process involving a monodentate anion.

A trifluoroacetylacetonate complex ought to distinguish between these possibilities because both cis and trans isomers should exist, and when they are cooled to a temperature at which the complexes are static, one would expect to observe two equal peaks in the ^{19}F NMR spectrum of the trans complex. There are two possible cis complexes corresponding to Me_2SO being near or remote from the CF_3 groups. There should therefore be two singlets for the cis complexes, but since an equilbrium between them with ΔG of only ±2 kcal/mol would yield a 100:1 ratio of the two forms at −50 °C, it is likely that only a single cis component would be observed. If base migration is the preferred rearrangement path, the spectra of the cis complexes would probably remain a singlet on warming, shifting slightly as the mole fractions of the contributing isomers changed, and the spectra of the trans isomer would coalesce independently to a separate singlet. If however anion rotation is the preferred process, the trans peaks would broaden and coalesce with the cis, ultimately yielding one singlet, not two.

Accordingly, the related uranyl bis(trifluoroacetylacetonate)–dimethyl sulfoxide complex was synthesized. The compound was made by reacting an aqueous solution of uranyl nitrate with a benzene solution of dimethyl sulfoxide, (utilizing a slight stoichiometric excess) and then adding Htfacac (1,1,1-trifluoroacetylacetone). The uranyl compound was extracted into the benzene layer as it formed. It was recovered by evaporating the solvent and excess Me_2SO in flowing N_2.

Yellow crystals with a melting point of 185–190 °C were obtained. Anal. Calcd: C, 22.02; H, 2.14; S, 4.89. Found: C, 21.58; H, 2.42; S, 4.78. Proton NMR of deuteriobenzene solutions on a 60-MHz Varian 360L instrument showed the anion protons at δ 6.16 and 2.06 and the dimethyl sulfoxide at δ 2.16 with relative areas of 1:3:3, respectively.

The Me_2SO peak was identified by synthesizing the complex with Me_2SO-d_6 (which led to the disappearance of the 2.16-ppm band) and by noting that this peak would average with excess Me_2SO when it was added.

This material is a mixture of 62% cis and 38% trans compounds **1** and **2**, which is readily deduced from the ^{19}F NMR spectra of the crystals dissolved in $DCCl_3$ at low temperature. The proton spectrum is not as well resolved but is consistent with the fluorine spectrum.

At −40 °C the trans compound is static and exhibits an F spectrum of two equal size singlets at δ −75 and −75.4 (the shift being measured from internal $FCCl_3$). The cis compound is seen as a singlet near δ −75.2, shifted (shielded) slightly from the average of the trans components. On warming gradually the trans singlets are found to broaden and move toward each other without a detectable spreading of the cis singlet. At room temperature the trans compound is coalesced into a singlet seen as a pronounced shoulder on the side of the singlet corresponding to the cis compound, on the Varian 360 L spectrometer. (The shoulder is readily apparent on a 90-MHz JEOL FX-900 instrument.) The rearrangement process is roughly estimated as having an activation energy of about 5 kcal/mol from the change in peak shape with temperature (with use of the graphs of Pople, Schneider, and Bernstein).[6] This value is consistent with the more rigorous kinetics previously established for the isomerization of the hexafluoroacetylacetonate complexes.

The broadening and coalescence of the trans peak independent of the cis is the anticipated results of intramolecular base migration. If on the other hand the anions were rotating, the cis and trans absorptions would necessarily merge to a single line since every rotation would interconvert the isomers. These observations therefore indicate that base migration is the preferred process in this temperature regime for the trifluoroacetylacetonates and supports the thesis that this is also the low-energy process for the hexafluoroacetylacetonate complexes.

$UO_2[CF_3COCHCOCH_3]_2 \cdot (CH_3)_2SO$

$UO_2(NO_3)_2 \cdot 6H_2O$ (2 mmol) was dissolved in 10 mL of H_2O. This solution was contacted with a solution of 1 mmol of Me_2SO in 5 mL of benzene in a separatory funnel. $CF_3COCH_2COCH_3$ (2 mmol) was added, and the mixture was shaken vigorously. Upon settling a yellow benzene layer separates containing the adduct and excess Me_2SO. Approximately 0.2 mmol of the Me_2SO adduct was obtained by removing the solvent and excess Me_2SO in flowing N_2.

Registry No. *cis*-$UO_2[CF_3COCHCOCH_3]_2 \cdot (CH_3)_2SO$, isomer 1, 78280-03-2; *cis*-$UO_2[CF_3COCHCOCH_3]_2 \cdot (CH_3)_2SO$, isomer 2, 78340-41-7; *trans*-$UO_2[CF_3COCHCOCH_3]_2 \cdot (CH_3)_5SO$, 78340-42-8; $UO_2(NO_3)_2(H_2O)_2$, 59752-71-5; MeOH, 67-56-1; THF, 109-99-9; Me_2SO, 67-68-5; TMP, 512-56-1; pyNO, 694-59-7; Et_3PO, 597-50-2; HMPA, 680-31-9.

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Contribution from Donnan Laboratories, University of Liverpool, Liverpool L69 3BX, England, the Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7, and the Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England

Binuclear Reductive Elimination Reactions in Diplatinum Complexes: Synthesis of Hydridoplatinum(I) Complexes

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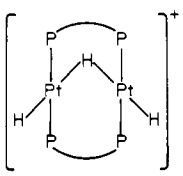
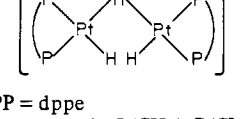
The complex $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) reacts with tertiary phosphine ligands to give H_2 and the hydridoplatinum(I) complexes $[Pt_2HL(\mu\text{-dppm})_2][PF_6]$ (**4**, L = η^1-dppm; **5**, L = PMe_2Ph; **6**, L = $PMePh_2$; **7**, L = PPh_3). Complex **4** is also obtained by the reduction of $[Pt(dppm)_2][PF_6]_2$ with sodium borohydride. Study of the ^1H and ^{31}P NMR spectra of **4**–**7** is in accord with the presence of Pt–Pt bonds and, in the case of 4, shows that its structure in solution is similar to that previously determined in the solid state by an X-ray investigation. Methanethiol reacts reversibly with **4** to give $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$. Attempts to prepare diplatinum(0) complexes by deprotonation of **4** or **7** were unsuccessful.

The many recently reported binuclear platinum hydrides now constitute a rapidly expanding and structurally diverse class of compounds, but most are platinum(II) compounds containing bridging hydrido groups. The most common type contains a $Pt_2H_3^+$ unit bound to four donor atoms which may belong to either monodentate or bidentate ligands. Where the ligands are bidentate, they may be bridging as in $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (**1**)[2] (dppm = $Ph_2PCH_2PPh_2$) or chelating as in $[Pt_2H_2(\mu\text{-H})(dppe)_2]^+$ (**2**)[3] (dppe = $Ph_2PCH_2CH_2PPh_2$) or



1, PP = dppm



2, PP = dppe
3, PP = $(Me_3C)_2P(CH_2)_3P(CMe_3)_2$

$[Pt_2H_2(\mu\text{-H})\{(Me_3C)_2P(CH_2)_3P(CMe_3)_2\}_2]^+$ (**3**).[4] In **1**, terminal and bridging hydrido groups are trans to one another, whereas in **2** or **3** they are cis. When one hydride of **1** is replaced by chloride, the latter occupies the bridging position, but when two hydrides are thus replaced, the remaining hy-

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