linium, terbium, and ytterbium. A single break has been observed when plotting the log $K_{\text{stability}}$ *vs.* the reciprocal of the ionic radius for the lanthanide–EDTA complexes, which is often called the "gadolinium break."[26] Likewise, the molecular rotations show this gadolinium break with the possibility that there are two breaks instead of one in these rare earth complexes.

Conclusions

This strong unambiguous periodic trend of the molecular rotations and the optical rotatory dispersion spectra has not previously been reported for any optically active complexes. An explanation based on a bathochromic shift of a large negative circular dichroic CT band is proposed to explain the observed trends for the lanthanide–D-(–)-PDTA complexes. The same strong unambiguous periodic trends of the molecular rotations have been observed for complexes of octahedral geometry where the ligand is completely stereospecific.[23] Although the perturbing forces that give rise to the ORD spectra are a function of the ionic potential, it is clearly evident that more than simple electrostatic interactions between the ligand and the metal ions are involved, and a greater degree of covalency seems apparent than has been previously proposed for the lanthanide–amino–polyacetato complexes.

The ligand field splitting of the J levels shows a greater degree of resolution in the circular dichroism spectra than in optical rotatory dispersion spectra or plain absorption spectra. Further research using circular dichroism and magnetic circular dichroism in the study of the optical phenomena of optically active lanthanide complexes may be of great help in assigning the exact f–f transitions in solution chemistry.

Acknowledgment. The many helpful suggestions of Henry Eyring are gratefully acknowledged. This research was supported by The Robert A. Welch Foundation, Fellowship Grant No. A-262. Appreciation is expressed to the Dow Chemical Company for its grant of a leave of absence for the summer of 1968 to D. L. C. This study was presented in part at the 158th National Meeting of the American Chemical Society on Sept 10, 1969, at New York, N. Y.

Chelation of Uranyl Ions by Adenine Nucleotides. III. Further Nuclear Magnetic Resonance Investigation of the Uranyl Nitrate–Adenosine 5′-Monophosphate System at Basic pH[1] (7.5–11.4)

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Abstract: Nmr spectra, both proton (^{1}H, 100 MHz) and phosphorus (^{31}P, 40 MHz), were obtained for mixtures of uranyl nitrate and adenosine 5′-monophosphate (AMP) at various stoichiometries and alkalinities. The spectra indicate that in an equimolar mixture (0.1 and 0.05 M) the strong chelate with 1:1 stoichiometry (whose structure was previously given[2] as a 2:2 sandwich-type dimer), which is exclusively present above pD 10.9, disproportionates below this pD to uncomplexed AMP, sandwich-type chelates (two forms) with 2:1 (U:AMP) stoichiometry, and nonsandwich-type complex(es). Only the latter type of complex is present at pD 7.5 in 0.05 M equimolar mixture. The extent of disproportionation and the ligand exchange rate both increase with decrease in pH, probably owing mainly to the competition between uranyl ions and protons for the ribose hydroxyl-oxygen sites. Structures for the 2:1 chelates and also 3:1 chelates, compatible with the spectra, are given. A series of equilibria is suggested to describe the U–AMP system from pH 2 to 11.5.

From an earlier proton magnetic resonance study[2] we concluded that the predominant solute species in an equimolar mixture of uranyl nitrate and adenosine 5′-monophosphate (U–AMP) at high pD is a chelate with 1:1 stoichometry in which the uranium is bound to the phosphate group and to both of the ribose hydroxyl-oxygen atoms. At high pD the uranyl ion does not bind to the adenine group, although it does so at pH below 4.5.[3] A *dimeric sandwich-type* (ST) chelate, similar to structure **1**, was postulated for this high-pD species.[4] It became necessary in our investigation of metal-ion-catalysis of ATP hydrolysis[5] to elucidate the U–AMP system over as wide a pD

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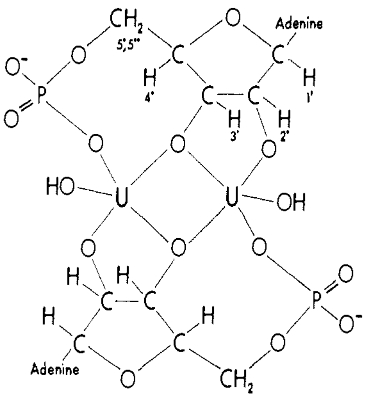
[1] (a) This paper is based on work performed under contract with the U. S. Atomic Energy Commission at the University of Rochester Atomic Energy Project, and has been assigned Report No. UR-49-1123. (b) Part of this paper was presented at the Second Rochester Conference on Toxicity, Rochester, N. Y., June 1969.

[2] R. P. Agarwal and I. Feldman, *J. Amer. Chem. Soc.*, **90**, 6635 (1968); **91**, 2411 (1969).

[3] I. Feldman, J. Jones, and R. Cross, *ibid.*, **89**, 49 (1967).

[4] The only difference between the ST chelate postulated previously[2] and structure **1** of this paper is that in **1** we have taken cognizance of the fact that the titration curve of an equimolar U–AMP mixture shows that this chelate is doubly hydroxylated. This point is explained in the Results section.

[5] K. E. Rich, R. P. Agarwal, and I. Feldman, submitted for publication.



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range as possible. In the present paper we report ^1H and ^{31}P nmr studies of the U–AMP system over the pD range 7.5–11.4.

Experimental Section

All spectra were recorded with a Jeolco 4H-100 (100 MHz) nmr spectrometer kept in a 24° constant-temperature room. Probe temperature was 27°. The methyl group resonance frequency of the $(CH_3)_4NOH$ added for pH adjustment was used as internal standard for chemical shifts in the pmr spectra.

^{31}P nmr spectra (40.5 MHz) were obtained for solutions in both D_2O and H_2O. Solubility and viscosity considerations usually forced us to study only 0.1 *M* solutions, but a few 0.05 and 0.2 *M* solutions were also investigated. ^{31}P spectra were obtained with nonspinning 10-mm tubes, and, therefore, they had relatively low signal-to-noise ratio and were lacking in fine structure. The H_3PO_4 ^{31}P signal was recorded as an external standard for each spectrum before and after spectrum accumulation, and indicated a drift of <0.5 ppm during the time (~4 hr) required for 128 scans.

A Jeolco JRA-1 spectrum accumulator was used to increase the signal-to-noise ratio. The necessity of constantly monitoring the bridge balance and lock signal made it impractical to accumulate more than 128 scans.

Solutions in D_2O were prepared by triple lyophilization as described previously.[2] The pD values were taken to be the Beckman pH meter readings plus 0.4.[6] The meter readings were always within 0.2 unit of the pH of the original aqueous solution before lyophilization.

The pH titrations were "pointwise titrations" performed as described previously.[3]

Results

^1H and ^{31}P nmr spectra were recorded for equimolar U–AMP mixtures in D_2O over the pD range 7.5–11.4 at ~0.5 pD-unit intervals, the values of r (mol of base added/total mol of AMP) varying from 2.7 to 5.3. A representative number of these 1:1 spectra are presented in Figures 1 (for ^1H) and 2 (for ^{31}P) to show the spectral changes produced by changing pD in this alkaline range. ^{31}P spectra of 2:1 and 3:1 aqueous mixtures at pH 10.5 are also given in Figure 2.

Proton Spectra. As discussed previously,[2] bonding of uranium to the ribose hydroxyl oxygens and to the phosphate group of AMP, as shown in **1**, in an equimolar U–AMP solution at high pD, causes the 2′, 3′, 4′, and 5′ signals in the pmr spectrum of this mixture (Figure 1B) to move considerably downfield of their locations in the free-AMP spectrum (Figure 1A). In contrast, the spectrum (Figure 1H) of an equimolar, 0.05 *M* U–AMP solution at pD 7.8 ($r = 3$) differs only very slightly from the free-AMP spectrum, even though, as evidenced by absence of precipitate, all the uranium is complexed by AMP in this solution. It is evident from this comparison that in this (*i.e.*, 0.05 *M*) near-neutral solution the uranium must be bound only to phosphate. The complexes in this solution will be referred to as non-ST complexes to distinguish them from the high-pD complex, **1**, in which uranium is bound to ribose hydroxyl oxygens as well as to the phosphate. Spectral bands attributable to non-ST complexes will be referred to as non-ST bands.

Above 0.05 *M*, however, there is some ST complex even in a near-neutral U–AMP solution. This seems evident from the C bands in Figure 1G, the spectrum of a 0.1 *M*, equimolar solution at pD 7.9 ($r = 3.25$). We attribute these C bands to ST complexes since they are at the same frequencies as the bands in Figure 1B. In Figure 1G there are also small bands, labeled X, not common either to Figure 1A or to Figure 1B. These unidentified X bands are not spurious bands caused by high-viscosity effects, because the lower viscosity at higher pD makes these bands clearly evident in the spectra (Figures 1E and 1F) of both 0.05 and 0.1 *M* mixtures with pD values up to 8.9 ($r = 4$).

For 0.05 *M* mixtures the lowest pD at which ST pmr spectral bands (*i.e.*, the C bands) were detected was 8.4 (when $r = 3.8$), but no pmr spectra were taken between pD 7.8 and 8.4. Though highly viscous, a pD 7.5 ($r = 2.7$), 0.05 *M*, equimolar solution has a pmr spectrum similar to Figure 1H, except for a lower signal-to-noise ratio in the pD 7.5 spectrum. Gelation with accompanying low signal-to-noise ratio and spurious bands precluded taking meaningful spectra at pD <7.5. The pmr spectra of 0.05 *M* (1:1) solutions with pD >8.4 and 0.1 *M* solutions with pD >7.8 (typified by Figures 1C to 1G) seem to be superpositions of Figure 1B with Figure 1A and/or Figure 1G primarily (*i.e.*, plus the small X bands), with the ratio of the intensities of the L bands to those of the corresponding C bands increasing as pD is decreased. The symbol L in these spectra refers to both free-AMP bands and to bands of non-ST complexes, since these two types of bands cannot be discriminated in pmr spectra.

The pmr spectra of 2:1 and 3:1 U–AMP solutions at pD 11 are almost identical with the 1:1 spectrum near the same pD.

Phosphorus Spectra. The pD 11.4 phosphorus nmr spectrum (Figure 2B) contains only one band (I), −10.1 ppm, which is ~6 ppm downfield of the only band (III), at −4.5 ppm, in the free-AMP spectrum near this pD (Figure 2A). This confirms our earlier deduction[2] that only one complex species, such as **1**, with uranium bound to the phosphate group of AMP, is present in an equimolar U–AMP mixture at high pH. Spectra for the pD 8.4–10.9 range consist of three bands. Their chemical shifts (considered to be the median frequencies of the spectral bands) and relative intensities are given in Table I. At pD 10.9 and 10.4 (Figure 2C) the middle band, II, is a barely perceptible shoulder on the upfield side of band I. The chemical shifts of band II in the spectra for these two pD's were

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(6) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

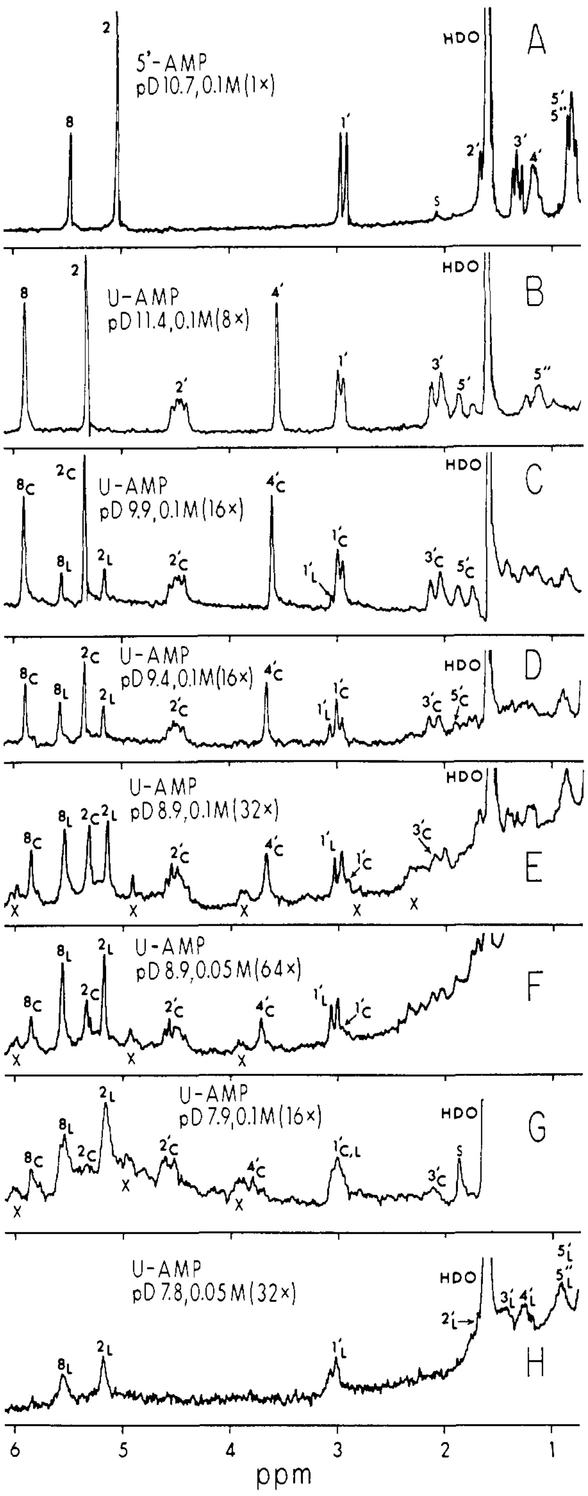


Figure 1. Pmr spectra (100 MHz) of AMP and of equimolar uranyl nitrate-AMP solutions in D_2O at various pD values (pD adjusted with $(CH_3)_4NOH$). Chemical shifts are measured downfield (positive numbers) of the ^1H signal of $(CH_3)_4N^+$ (internal standard). Proton resonance frequency assignments for spectra A and B were made in previous papers [see ref 2; C. D. Jardetzky and O. Jardetzky, *J. Amer. Chem. Soc.*, **82**, 222 (1960); and I. Feldman and R. P. Agarwal, *ibid.*, **90**, 7329 (1968)] and are indicated by the numbers on the figures. Assignments for spectra C–H were made by comparison with spectra A and B. Subscript C refers to ST-complex bands (see text), subscript L refers to uncomplexed AMP and/or non-ST-complex bands (see text). Symbol X is also explained in the text. Symbol s designates spinning side bands. Solution concentration, pD, and number of scans accumulated are shown on each figure, the latter number in parentheses.

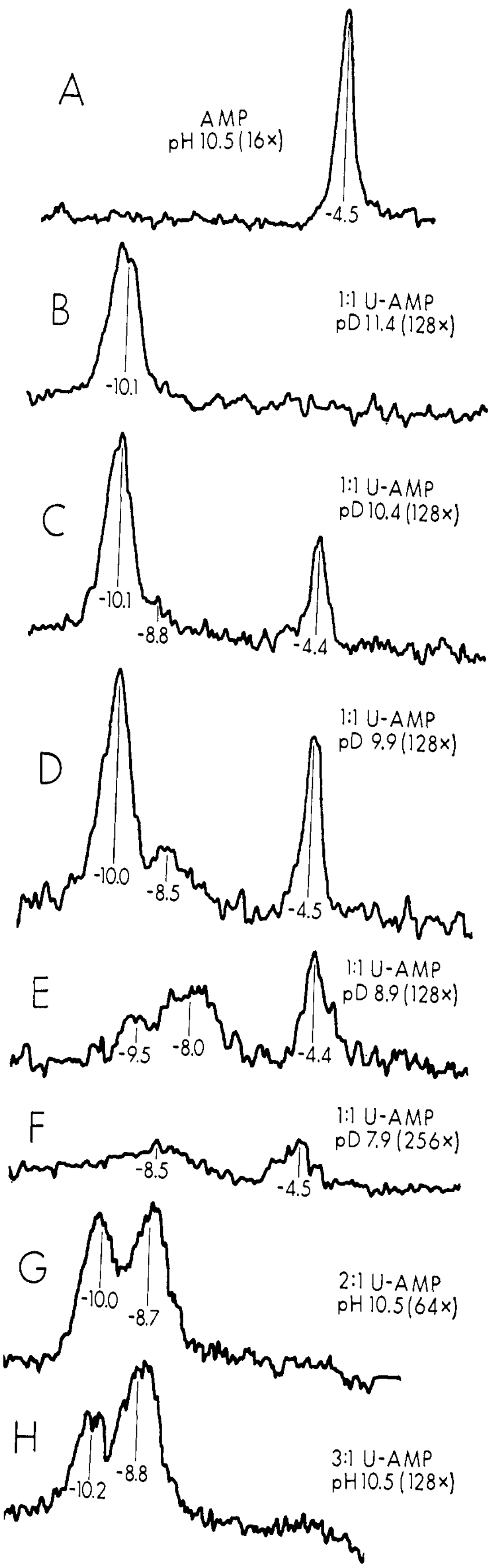


Figure 2. ^{31}P nmr spectra (40.5 MHz) of AMP and of uranyl nitrate–AMP solutions. AMP concentration was 0.1 *M* for each solution. Basicity (pD or pH), U:AMP molar stoichiometry, and number of accumulated scans (in parentheses) are shown on each figure. Chemical shifts are measured downfield (negative numbers) of the ^{31}P signal of H_3PO_4 used as an external standard.

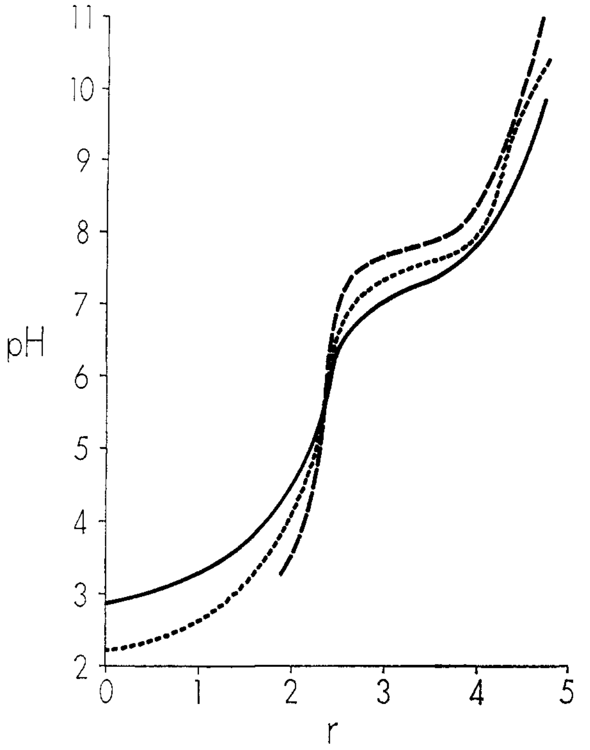


Figure 3. Titration curves of equimolar mixtures (aqueous) of uranyl nitrate and AMP: — —, 0.1 *M*; - - -, 0.005 *M*; —, 1 × 10^{-4} *M*; *r* = mol of $(CH_3)_4NOH$ added/mol of total AMP.

estimated by assuming a band width of 1 ppm, these approximate values being sufficiently accurate for any purpose for which they are used in this paper. Visible maxima can be seen, however, for all three bands at pD 9.9, 9.4, 8.9, and 8.4 (*e.g.*, see Figures 2D and 2E).

Table I. ^{31}P Nmr Spectral Data for Equimolar (0.1 *M*) U–AMP Solutions in D_2O at Various pD's[a]

pD	*r*	Band I (%)	Band II (%)	Band III (%)
11.4	5.3	−10.1 (100)		
10.9	5.0	−10.0 (83)	−9.3 (6)?	−4.4 (11)
10.4	4.7	−10.1 (67)	−8.8 (13)	−4.4 (20)
9.9	4.4	−10.0 (55)	−8.5 (18)	−4.5 (27)
9.4	4.2	−9.6 (19)	−8.0 (51)	−4.4 (30)
8.9	4.0	−9.5 (17)	−8.0 (47)	−4.4 (36)
8.4	3.8	−9.5 (25)	−8.0 (44)	−4.4 (31)
7.9	3.0		−8.5[b] (70)	−4.5 (30)

[a] Chemical shifts in ppm relative to H_3PO_4 and relative areas of bands in %. [b] Probably refers to coalescence of bands I and II (see text).

The pD 7.9 phosphorus spectrum (Figure 2F) seems to be comprised of only two bands. The one at −4.5 ppm is obviously the free-AMP band (III). The second band has a maximum near −8.5 ppm. However, this latter band is exceptionally broad, extending from −6.5 ppm to ∼−11.5 ppm, and its (integrated) area is twice that of band III in the same spectrum, leading us to believe that this band actually results from a coalescence of bands I and II, with I contributing to only a small extent. This band is further broadened by gelation of the mixture. It was not feasible to obtain a meaningful ^{31}P spectrum of the U–AMP system below pD 7.9 or at a lower concentration than 0.1 *M* because of the very low signal-to-noise ratio below these limits. Hence, we have not been able to establish the phosphorus resonance frequency of the non-ST complex(es).

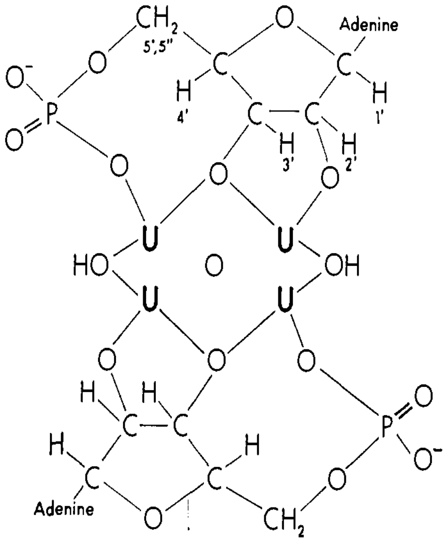
^{31}P spectra of equimolar aqueous mixtures are quite similar to those of D_2O solutions, except that the free-AMP band, which was clearly evident in the pD 10.9 spectrum, was so small as to be dubious in the pH 10.5 spectrum. This latter spectrum (*i.e.*, aqueous, 1:1) contained only a −10.3-ppm band. Both the 2:1 and the 3:1 (aqueous) spectra contain two bands, at about −10.1 and −8.8 ppm (Figures 2G and 2H). These bands are of equal area in the 2:1 spectrum, but in the 3:1 spectrum the −8.8-ppm band has twice the area of the −10.2-ppm band.

pH Titrations. In Figure 3 are presented pH titration curves for equimolar U–AMP mixtures at three concentrations. In each case pH ∼11 corresponds to *r* ≈ 5. Since AMP (*i.e.*, the divalent anion) contains only four hydrogen atoms which can possibly be considered as ionizable (namely, the adenine and phosphate protons and the two ribose hydroxyl hydrogens), this *r* value indicates that **1** must be either doubly hydroxylated, doubly olated, or oxolated near pH 11. We have depicted it as doubly hydroxylated, since a molecular model built with Corey–Pauling–Koltun space-filling atomic models indicates that there is no space between the uranium atoms of **1** to accommodate another atom.

The three titration curves intersect at the first inflection where *r* ≈ 2.4, pH ∼6. Since the nmr spectra discussed above show that even in a uranium-containing complex there is no ionization of the ribose hydroxyl protons at this point, this *r* value, being >2, shows that there is some hydrolysis of the uranyl group. The fact that the curve for the most concentrated solution lies lowest before the crossover point and highest after this point is evidence that there is a depolymerization in this system after the crossover point. This, of course, is consistent with the fact that liquefaction of the gel, which exists in acid solution, seems to begin just above the crossover point and is complete in a 0.05 *M* mixture when *r* reaches ∼2.7. At this point all the solute is in the form of non-ST complexes. From these results we conclude that the non-ST complexes are olated (or oxolated) to some extent, since complete liquefaction would not have resulted until at least *r* = 3 if the non-ST complexes were hydroxylated monomers.

Discussion

The ^1H and ^{31}P nmr spectra of a 2:1 U–AMP solution lead us to postulate two 4:2 ST species, **2** and **3**, in equal amounts for this mixture at high pH. In agreement with our results near pD 11, both **2** and **3** would be expected to have the same pmr spectrum as **1**, since for each ribose moiety in **2** and **3** the pmr spectrum should be influenced only by the two uranyl ions bonded directly to that given ribose group, the other two uranyl ions having no significant electron-withdrawing effect on the ribose protons and being too distant from them to exert any diamagnetic anisotropy effect. Structure **2** should give a ^{31}P band near the resonance band of **1** because of the similarity of the phosphate bonding in **1** and **2**. However, **3** should give a ^{31}P band at a different frequency, since each phosphate in **3** is attached to a second uranyl ion. The two bands, −10.0 and −8.7 ppm, in Figure 2G are compatible, therefore, at least qualitatively, with these two postulated 4:2 species, **2** and **3**, respectively, if they exchange ligands slowly.



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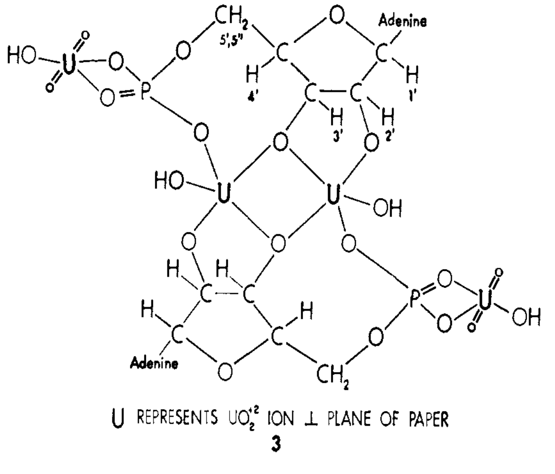
A 3:1 solution at pH 10.5 must consist of species very similar to the 4:2 species, for the 3:1 ^{31}P spectrum (Figure 2H) contains only the two bands, −10.2 and −8.8 ppm, and the 3:1 pmr spectrum at pD 11 is virtually identical with the 1:1 and 2:1 pmr spectra. The 3:1 species responsible for the −10.2-ppm ^{31}P band could be a 6:2 ST complex differing from the 4:2 complex, **2**, simply by having three uranyl groups in the two interligand chains in place of the two interligand chains in **2**. The −8.8-ppm band in this spectrum could reflect a 6:2 ST complex having interligand chains as in **2** and a uranyl ion chelated bidentately by each phosphate as in **3**, and/or a 6:2 complex differing from **3** by having $-U(OH)_2UOH$ chains in place of those two uranyl ions which are chelated bidentately by phosphate in **3**. It should also be of interest that at high pH, where uranyl ion normally precipitates completely, one AMP ion can solubilize about 3.5 (on the average) uranyl ions.



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The appearance of the free-AMP band, III, in the ^{31}P spectrum of the 1:1 solution when the pD is lowered to 10.9, and the increased intensity of this band as the pD is decreased further (Table I), must denote the formation of some complex(es) with higher U:AMP ratio than unity, most likely 2:1. This is further demonstrated by the simultaneous appearance of band II and by the changing intensity ratio of the three bands with decreasing pD, also seen in Table I.

Comparison of the relative intensities of the bands in the ^{31}P spectra with those in the pmr spectra indicates that when the pD is slightly less than 11 there is some disproportionation according to the expression

$$2\ \text{ST complex (2:2)} \xrightarrow[\text{pD} < 11]{2\text{D}^+} \text{ST complex (4:2)} + 2\text{A}^{2-}$$

where A^{2-} represents deprotonated, uncomplexed AMP. In such a case the molar ratio of free AMP to complex (L:C) in the system calculated from the pmr spectrum (*i.e.*, either 8_L area : 8_C area or 2_L area : 2_C area) should be the same as the ratio calculated from the ^{31}P spectrum [*i.e.*, area ratio, III/(I + II)]. For a pD 9.9 solution (0.1 *M*, equimolar, r = 4.43), the pmr spectrum gives an L:C ratio of 0.34 ± 0.05 (0.29 from H_8 signals, 0.39 from H_2 signals) and the ^{31}P spectrum gives 0.36. This agreement seems good.

According to the above reaction there should be the same number of moles of AMP in the 4:2 ST form (**2** plus **3**) as in the uncomplexed form. Hence, since band II, with a relative intensity of 18%, represents structure **3**, then the percentage of AMP in the **2** form equals the percentage of AMP uncomplexed, 27% (from I), minus 18%. Thus, in the pD 9.9 solution the AMP should be distributed as follows: 27% uncomplexed, 27% as the 4:2 ST species (9% as **2**, 18% as **3**), and 46% as the 2:2 ST species, **1**. From these results we can calculate an r value of 4.46, which agrees with a titration value of 4.43 for pD 9.9, *if we assume* that the uranium atoms in **1**, **2**, and **3** are hydroxylated, olated, and oxolated as shown.

Between r = 3, where non-ST complexes predominate, and r = 4.2 the system is very complicated. The spectra do not reveal the exact composition at any point between these r limits, but they do furnish some plausible ideas. The same type of calculations as above suggests that the non-ST complex(es) begin to form when pD is made less than 9.9. For instance, both the H_8 and H_2 signals in the pmr spectrum of a pD 9.4, equimolar, 0.1 *M* U-AMP solution give a value of 42% for the percentage of AMP not in the ST form (*i.e.*, non-ST-type complex plus free AMP), but the ^{31}P spectrum gives 30% for free AMP only. Thus, about 12% of the AMP should be in the non-ST form in this pD 9.4 solution.

The comparison cannot be made at lower pD because of the unidentified X bands at pD 7.9 and 8.4 (Figures 1E and 1F). However, it seems relevant to this point that the resonance frequencies of both bands I and II move upfield ~0.5 ppm in going from the pD 9.9 ^{31}P spectrum to the pD 9.4 spectrum, but they remain constant from pD 9.4 to 8.4. This sudden change between pD 9.9 and 9.4 could be due to an increased ligand exchange rate between non-ST and ST complexes, *if* the non-ST band is slightly upfield of, and hidden by, the normal band II of structure **3**. Unfortunately, we cannot verify this conjecture, for as noted above, we cannot identify a ^{31}P non-ST band alone. However, consistent with this view are the sudden very large intensity changes of bands I ($55\% \rightarrow 19\%$) and II ($18\% \rightarrow 51\%$) between 9.9 and 9.4 (Table I), while III increases only 3%. Thus, it seems that the major reaction which occurs when the pD is made less than ~9.9 is

$$\mathbf{2} \xrightarrow[\text{pD} < 9.9]{} \text{non-ST complex(es)}$$

To reconcile the constancy of the ^{31}P data (*i.e.*, chemical shifts and relative areas) between pD 8.4 and 9.4 ($r = 3.8$–4.2) with the definite changes in the pmr spectra in this region we would first note that this region is the first half of the third, relatively steep buffer region in the titration (Figure 3). This is also the region in which the pmr spectra contain the unidentified X bands. We suggest, purely as speculation, that as the pD is decreased below 9.9 several reactions occur. First, protonation of one of the ribose hydroxyl-oxygen atoms (probably 2′) occurs, weakening the ST-type of chelation and causing the formation of non-ST complex(es) according to the previous equation. As the non-ST complex concentration increases mixed complexes form. For instance, a 2:2 dimer may form in which one uranium atom is attached bidentately to the phosphate of one AMP molecule and also (bidentately) to the 3′ oxygen and one phosphate oxygen of a second AMP, while this latter phosphate group is also bidentate to a second uranium as in **3**. Such a dimer should give both the II band of **3** and the non-ST band, which, we suggested earlier, may be near the location of II. Thus, as the reaction, **3** → mixed dimer, proceeds with decreasing pD, the change in the ^{31}P spectrum may be only slight. On the other hand, the pmr spectrum should change because of the breaking of the U–O$_{2'}$ bond. The X bands may be mixed complex bands.

Our interpretation of the nmr spectra may be coupled with the earlier titration results[3] to give the following summarizing series of reversible reactions (several of which may overlap) as a description of the equimolar U–AMP system from pH 2 to 11.5. (Equations are not balanced.)

$$H_2A + UO_2{}^{2+} \xrightarrow[\text{pH} < 4.5]{2OH^-} A{\equiv}UO_2(\text{ppt}^3) \xrightarrow[\text{pH} \sim 6]{\sim 0.4OH^-} \text{olated gel} \xrightarrow[\text{pH} \sim 7.5]{\sim 0.6OH^-}$$

$$\text{non-ST complex (soluble)} \xrightarrow[\text{pH } 7\text{–}9.5]{OH^-}$$

$$\text{mixed complex} \xrightarrow[\text{pH} \sim 10]{\sim 0.5OH^-} (\mathbf{2} + \mathbf{3}) + A^{2-} \xrightarrow[\text{pH} \sim 11]{\sim 0.5OH^-} \mathbf{1}$$

Hydrolysis of a Borane Cation Derived from Ethyl N,N-Dimethylglycinate[1]

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Received February 7, 1970

Abstract: The rate of hydrolysis of $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5{}^+$ was determined by monitoring hydrogen evolution in an apparatus which requires only micro quantities of substrate. After an induction period, the hydrogen evolution was fit by first-order decay of substrate, with $k = 6.5 \times 10^{-4}$ sec^{-1} at 29.8°. Temperature dependence and kinetic isotope effects were explored, and syntheses of several possible intermediates were attempted. A mechanism consistent with all the experimental data invokes saponification of the ester function to produce a polar intermediate, $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2$, as a first step. Slow intramolecular loss of trimethylamine governed by k gives a cyclic intermediate, $(CH_3)_2\overline{NCH_2CO_2B}H_2$, which then undergoes a second-order step and subsequent fast hydrogen-producing steps. The cyclic intermediate was isolated from a hydrolysate in dilute base and was characterized.

The class of borane cations, $H_2B(NR_3)_2{}^+$, derived from tertiary amine bases has been shown to be exceptionally inert to hydrolysis, even under forcing conditions.[2] It has now been found that a cation derived from an amino acid ester is hydrolyzed in base, and this observation opens interesting questions about

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(1) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13–18, 1969.

(2) N. E. Miller and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 1033 (1964).