TABLE III

OPTICAL ROTATION DATA FOR THE SECOND-ORDER ASYMMETRIC TRANSFORMATION OBSERVED IN A 1-DM. TUBE

	Ligand species			
Source of sample	2,3-Dihydroxy-naphthalene	3-Methyl-catechol	4-Methyl-catechol	4-Chloro-catechol
Cinchonine salt solution	0.05°	−2.40°	0.50°	0.40°
Sodium salt from above solution	−0.01°	−0.04°	−0.02°	−0.02°
Quinine salt solution	−2.25°	−2.65°	−0.40°	−0.30°
Sodium salt from above solution	0.04°	0.03°	0.03°	0.03°

complex anions involves a structure suggested by examination of that proposed for a rather similar rhodium complex.[13] The water is regarded as coördinated to the central atom through oxygen but also is hydrogen bonded to the hydroxyl groups of one of the catechol groups which is otherwise free. One of the hydrogens then can act as the acidic hydrogen and yet the unchelated phenol will be held firmly enough to allow a stable asymmetric structure to exist. Under favorable circumstances this water can be removed to give the simple tris complex without destruction of the compound.

(13) A. L. Porte, H. S. Gutowsky, and G. M. Harris, *J. Chem. Phys.*, **34**, 66 (1961).

Another obvious feature is that these complex anions all possess a considerable degree of inertness and are all resistant to the attack of hydroxide ion. The final feature is the common occurrence of a second-order asymmetric transformation in the presence of suitable alkaloids. This is the only group of generically related complexes which has yet been shown to behave in this fashion. This would seem to be a characteristic reaction for octahedral complexes of arsenic(V) with 1,2-diphenols. Within this class the ease with which this inversion occurs varies noticeably, but for each complex ion such a process is indisputable. From the separation experiments reported here, the inversion seems to occur at a slower rate with the complexes containing catechol or 3-methylcatechol than with those involving other ligands. The fact that such effects are demonstrably greater in non-ionizing solvents implies that the chief reason for the paucity of inorganic examples of this phenomenon is the common use of water as the solvent in the resolution of complexes.

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CONTRIBUTION FROM THE DIVISION OF RADIATION CHEMISTRY AND TOXICOLOGY OF DEPARTMENT OF RADIATION BIOLOGY, UNIVERSITY OF ROCHESTER SCHOOL OF MEDICINE AND DENTISTRY, ROCHESTER 20, NEW YORK

Reaction of the Uranyl Ion with Amino Acids. Bidentate Carboxylate Chelation[1]

BY ISAAC FELDMAN AND LARYSA KOVAL

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The stability constants determined by the pH method for 1:1 complexes of the uranyl ion with acetate, acid succinate, aspartate, and glutamate ions in acid solution at 25° and $\mu \cong 0.2$ all have practically the same value, log K_1 between 2.61 and 2.70. These results are interpreted as being due primarily to the fact that in each case complexing involves only bidentate carboxylate chelation, which produces significantly less steric hindrance than is present in either uncomplexed, hydrated uranyl ion or in other possible chelate structures. The concept of bidentate acetate chelation of the uranyl ion also is used to explain the apparent anomaly that pK_1 for the uranyl–acetate complex is as high as pK_1 for the uranyl–glycolate chelate. Precipitation studies from pH 3 to 8 indicate that both carboxyl and imidazole nitrogens probably are involved in protein binding of the uranyl ion, but that binding by α-amino groups is insignificant, probably for steric reasons.

Some time ago, Dounce and Lan concluded from qualitative titration and precipitation studies that the uranyl ion is bound to proteins almost exclusively by carboxyl groups.[2]

On the other hand, Li, *et al.*, have concluded that the binding sites of histidine toward the uranyl ion are the amino group and the 'pyridine' nitrogen of the imidazole group.[3] Their pH titration results gave no evidence for complexing of the uranyl ion by glycine, serine, or other α-amino acids in the pH region 3 to 4.3, but from solvent extraction experiments they obtained formation constants of 27 and 7.4, respectively, for glycine and serine complexes near pH 2.[4,5]

(1) This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York. Presented at the 7th International Conference on Coördination Chemistry at Stockholm, Sweden, 1962.

(2) A. L. Dounce and T. H. Lan, Chapter 13 in "Pharmacology and Toxicology of Uranium Compounds," ed. by C. Voegtlin and H. C. Hodge, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(3) N. C. Li, E. Doody, and J. M. White, *J. Am. Chem. Soc.*, **79**, 5859 (1957).

(4) N. C. Li, W. M. Westfall, A. Lindenbaum, J. M. White, and J. Schubert, *ibid.*, **79**, 5864 (1957).

(5) N. C. Li, E. Doody, and J. M. White, *ibid.*, **80**, 5901 (1958).

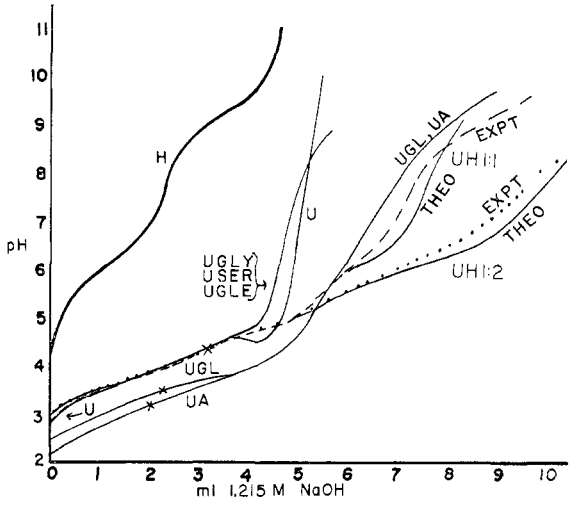

Fig. 1.—pH titrations of uranyl nitrate–amino acid mixtures, of uranyl nitrate alone, and of histidine. In each case 50 ml. of solution was titrated. Titratable constituents in the solutions are indicated by the code letters accompanying the curves. As indicated by the letter U, all curves, except H, represent solutions containing 0.0572 *M* uranyl nitrate initially. The amino acid constituents are indicated as follows: GLY, glycine; SER, serine; GLE, glutamic acid γ-methyl ester; A, aspartic acid; GL, glutamic acid; H, histidine monohydrochloride. All solutions initially contained 0.0572 *M* amino acid, except the UH 1:2 solution, which contained 0.114 *M* histidine monohydrochloride. THEO represents theoretical curves for 'no reaction' obtained by adding the abscissa of the U curve at a given pH to the abscissa of 0.057 and 0.114 *M* H curves for the same pH. EXPT represents actual experimental curves for UH mixtures. × indicates pH of incipient precipitation.

The present paper is a continuation of our investigation of the reactions of the uranyl ion with physiologically significant substances.[6] pH titrations and spectral and precipitation experiments were performed on various mixtures of uranyl nitrate and amino acids.

Experimental

Materials.—L-Glutamic acid γ-methyl ester was obtained from California Corp. for Biochemical Research, Los Angeles. All other amino acids used were Eastman White Label grade; these were glycine, *d,l*-serine, *d,l*-α-alanine, *d,l*-aspartic acid, *l*-glutamic acid, and *l*-histidine monohydrochloride. All were checked for purity by comparing p*K* values, obtained by titration, with literature cited values. Tetramethylammonium hydroxide was received from Distillation Products. All other chemicals, including uranyl nitrate hexahydrate, were analytical reagent grade. All solutions were prepared under nitrogen with CO_2-free, de-ionized water.

Methods.—Spectra were obtained with a Beckman DK recording spectrophotometer in a 25° room.

The pH titrations represented by Fig. 1 were performed in the conventional continuous manner at room temperature using a Beckman Model G pH meter. However, those titrations analyzed quantitatively (Table I) were carried out as pointwise titrations as described previously.[6] Solutions, after mixing, were stored at 25° in a constant-temperature bath for 2 days before pH readings were taken. A water-jacketed solution cell with fittings for nitrogen flow was used for pH measurements in order to obtain CO_2-free constant-temperature pH values. By comparison of pH meter readings of standard HNO_3 (0.01, 0.005, 0.001, 0.0005 *M*), containing known KNO_3, with the stoichiometric hydrogen ion concentrations, the pH meter was calibrated in concentration units, pH_c.

Precipitates obtained at pH 3.50 and 3.94 were washed with HNO_3 solutions of the same pH while being filtered under nitrogen. Precipitates obtained near neutral pH were washed with boiled de-ionized water in the same manner. Precipitates were dried at 130° and then ignited at 850° to U_3O_8 for uranium analysis. Nitrogen determinations were run on undried samples by the Kjeldahl method, using no reducing catalyst. Preliminary experiments showed that any unremoved precipitating agent should not affect either uranium or nitrogen analysis.

Filtrates obtained near neutral pH contained no uranium. Analyses for α-amino groups were performed spectrophotometrically by the ninhydrin method of Yemm and Cocking.[7]

In bringing solutions to constant ionic strength, 0.2, the assumption was made that the free amino acid species had effective charges equal to the formal over-all valences, *i.e.*, H_3X^+, H_2X^0, HX^-, and X^{-2}, the latter having a neutral NH_2 group and both carboxyls ionized. The uranyl amino acid complex was univalent, +1. The error in this assumption probably is insignificant at total amino acid concentrations of 0.028 *M* or less but could cause an uncertainty of several hundredths in the ionic strength of the more concentrated solutions. The required amounts of added KNO_3 were calculated from preliminary experiments.

Experimental Considerations.—Unfortunately, quantitative studies (Table I) were limited to small concentration and pH ranges because of the high tendency of free uranyl ions to hydrolyze and the low pH at which precipitation occurred. As a result the $\bar{n}$ range was too low to allow any reliable calculation of complexes with more than one ligand group. In fact, the acetate study was limited to $\bar{n} \leqq 0.32$, and the succinate study to $\bar{n} \leqq 0.25$. Although 1:2 uranyl–aspartate and 1:2 uranyl–glutamate systems did not contain precipitates until near $\bar{n} = 0.65$, *K* values corresponding to $\bar{n} > 0.50$ were not considered since the assumption in our calculations of only one ligand per uranium in a given complex would be in error at $\bar{n} > 0.50$.

Evidence for 1:1 complexing in equimolar uranyl–aspartate and uranyl–glutamate mixtures was obtained by a continuous variations study at 417 mμ, a maximum absorbance being observed at a uranium mole fraction of 0.45. In addition, it is noted in Table II that for the 1:1 uranyl–aspartate system the precipitate which forms at pH 3.50, just above the pH of incipient precipitation in a continuous titration, contains a uranium to amino acid ratio of 0.91, which indicates a value of unity at the slightly lower pH of incipient precipitation since this U:N ratio increases with decreasing pH.

Calculations.—The method of calculation of concentration stability constants by the pH method is well discussed in the book of Chaberek and Martell.[8] Our experiments, of necessity, were carried out at pH values too high to allow us to ignore dimer formation by uncomplexed uranium. We therefore used Sutton's value[9] of 1.14×10^{-6} for $\mu \cong 0.15$ for the dimerization constant, $K_d = [U_2O_5^{+2}][H^+]^2/[UO_2^{+2}]^2$. Correction of this value to $\mu = 0.2$ would have amounted to less than its experimental error.

Consider the symbolism: T_u, T_x, and A represent initial uranyl nitrate, uncharged amino acid, $HOOC{\cdot}CH(NH_2){\cdot}(CH_2)_x{\cdot}COOH$, and excess nitric acid molar concentrations, respectively; B = moles of added NaOH/volume of solution in liters; U, D, and C represent the equilibrium molar concentrations of unreacted UO_2^{+2} ion, the dimer $U_2O_5^{+2}$, and the complex, respectively.

If we assume that the complexation involves removal of both

(6) Previous paper in this series: I. Feldman, C. A. North, and H. B. Hunter, *J. Phys. Chem.*, **64**, 1224 (1960).

(7) E. W. Yemm and E. C. Cocking, *Analyst*, **80**, 209 (1955).

(8) S. Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 102–108.

(9) J. Sutton, *J. Chem. Soc.*, Suppl. No. 2, s275 (1949).

TABLE I
STABILITY CONSTANTS OF URANYL CARBOXYLATE COMPLEXES AT 25°; μ = 0.20

Ligand	pH	n	T_u	$\log K_1$	
Acetate^{-1}	2.54 → 2.92	0.16 → 0.32	0.0570	2.72	±0.03
(pk = 4.64)	2.83 → 3.17	.15 → .26	.0285	2.67	± .02
				Av. 2.70	
HSuccinate^{-1}	2.13 → 2.26	.19 → .25	.0572	2.63	± .02
(pk_1 = 4.07)	2.43 → 2.53	.18 → .23	.0286	2.61	± .02
	2.62 → 2.72	.18 → .22	.0172	2.63	± .02
				Av. 2.62	
Aspartate^{-1}	2.04 → 2.66	.18 → .49	.0570	2.63	± .04
(pk_1 = 1.92)	2.26 → 2.88	.21 → .44	.0285	2.57	± .02
(pk_2 = 3.69)	2.42 → 3.02	.16 → .40	.0172	2.57	± .02
	2.25 → 2.50	.36 → .50	.0286[a]	2.62	± .01
	2.41 → 2.76	.30 → .50	.0143[a]	2.66	± .02
				Av. 2.61	
Glutamate^{-1}	2.31 → 2.90	.18 → .40	.0572	2.72	± .03
(pk_1 = 2.06)	2.50 → 3.11	.13 → .35	.0286	2.63	± .01
(pk_2 = 4.26)	2.62 → 3.25	.12 → .31	.0172	2.65	± .03
	2.49 → 2.91	.25 → .50	.0286[a]	2.64	± .03
	2.64 → 3.08	.19 → .50	.0172[a]	2.68	± .03
				Av. 2.66	

[a] T_u/T_x = 1:2. In all other cases, $T_u:T_x$ = 1:1.

TABLE II
AMINO ACID:URANIUM MOLAR RATIO PRECIPITATED FROM 1:1 SOLUTION AS A FUNCTION OF PRECIPITATION pH; ROOM TEMPERATURE; INITIAL U = 0.0567 M

	pH				
Ligand	3.50[a]	3.94[a]	6.8[b]	7.5[a]	8.0[b]
Glycine			0.12		0.07
Aspartate	0.91 ± 0.03	0.60 ± .005	.30	0.11 ± 0.04	.11
Histidine			.32		.23

[a] Precipitates analyzed for U and N; precipitating agent was tetramethylammonium hydroxide. [b] Filtrates analyzed for N (spectra show no U in filtrate); precipitating agent was sodium hydroxide.

carboxylic protons while one proton adds to give the NH_3^+ group and assume formation of one 1:1 complex only, then the reaction can be expressed as: $UO_2^{+2} + H_2X \rightarrow HXUO_2^+ + H^+$.

Material balances then are, in molarity units

$$T_u = U + C + 2D$$
$$T_x = C + [H_3X^+] + [H_2X] + [HX^-],$$
since $[X^{-2}] = 0$ at acid pH
$$[H^+] = A - B + C + 2D - [H_3X^+] + [HX^-]$$

Solving these equations simultaneously, with the aid of the first two amino acid ionization constants k_1 and k_2, one gets the quadratic equation: $aU^2 + bU + c = 0$.

For a 1:1 mixture: $a = 2K_d/[H^+]^2$; $b = 1 + g$; and $c = g(B + [H^+] - A - T_u)$; where $g = ([H^+]^2 + k_1[H^+] + k_1k_2)/([H^+]^2 - k_1k_2)$.

For a 1:2 mixture, but again assuming only a 1:1 complex, a and b are the same but $c = T_u + g(B + [H^+] - A - T_u)$.

In both cases, $[HX^-] = (A + T_u - U - [H^+] - B)k_1k_2/([H^+]^2 - k_1k_2)$, and $C = T_u - U - (2K_dU^2/[H^+]^2)$.

The stability constant is $K = C/U[HX^-]$.

For 1:1 uranyl–acetate and uranyl–acid succinate complexes, the coefficient a in the quadratic is unchanged, but $b = -[H^+]/k_1$, and $c = k_1(T_u - [H^+] - B)/(k_1 + [H^+])$. The free monovalent ligand concentration is $k_1(U + (2K_dU^2/[H^+]^2))/(k_1 + [H^+])$.

No formula tried for the complexes except that for a 1:1 monomeric complex gave stability values which could be considered as constant.

Results

In Table I it is seen that the same stability constants were obtained for the 1:1 complexes of the uranyl ion with the monovalent acetate, monovalent acid succinate, and the 'monovalent' aspartate and glutamate ($^-OOC\cdot CH(NH_3^+)\cdot(CH_2)_x\cdot COO^-)^{-1}$ ions. Despite the fact that reliably constant stability constants were obtained for the amino acid complexes only for the case involving complete removal of two protons, we believe that in these complexes the uranyl ion is bound only to one carboxyl group, the one furthest from the positive amino group. Apparently, simple electrostatic repulsion by the uranium atom attached to the other end of the molecule causes complete ionization of the strongly acid α-carboxyl group.

There are several points of evidence for this belief. First, if the uranyl ion were chelated by the two carboxyl groups, a seven-membered aspartate chelate ring and an eight-membered glutamate chelate ring would be showing the same stability. Even though seven-membered rings are weaker than five- or six-membered rings, they are definitely more stable than eight-membered rings. Second, as seen in Fig. 1, except for a very small region at the start, the pH titration curve of a uranyl nitrate solution is almost identical up to the point of precipitation (pH 4.3 for 0.057 M solution at 25°) with titration curves of 1:1 mixtures of uranyl nitrate and the amino acids: glycine, α-alanine, serine, histidine, and glutamic acid γ-methyl ester. Ordinary buffer action by the amino acids probably causes the higher pH, 0.3 log unit, at the start for the mixtures and also the insignificantly higher values, $\leqq$0.05 log unit, from pH 3.2 to 4.3.

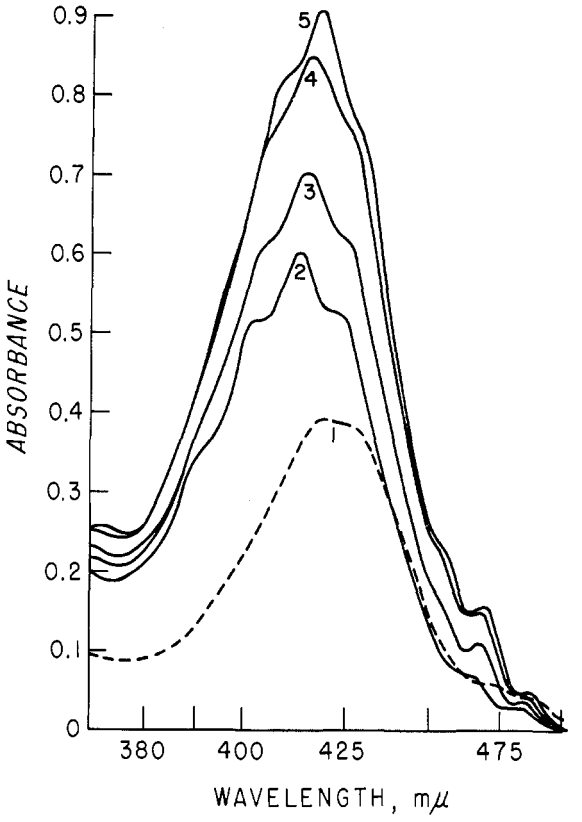

Fig. 2.—Absorption spectra of uranyl nitrate–amino acid mixtures. The same curve 1 was obtained for a 0.0114 *M* $UO_2(NO_3)_2$ + 0.12 *M* $NaClO_4$ solution, pH 4.13, and for the same mixture plus 0.0114 *M* histidine at the same pH. Curve 2 represents a 0.0572 *M* uranyl nitrate solution at pH 3.00, either with or without 0.2 *M* KNO_3 added. Curves 3, 4, and 5 are for 1:1 mixtures, also at pH 3.00, containing 0.0572 *M* uranyl nitrate and 0.0572 *M* amino acid as follows: curve 3, either glycine or glutamic acid γ-methyl ester (same curve); curve 4, glutamic acid; curve 5, aspartic acid.

This is evident from the similar small differences in 1:1 and 1:2 titrations. In fact, this buffer action masks the very weak complexing in these mixtures which Li, *et al.*,[4,5] detected by solvent extraction and which is demonstrated spectrally by the uranyl–glycine curve of Fig. 2. As discussed by Li, *et al.*, this weak complexing probably is due to the α-carboxyl group alone and involves no chelation.

In serine the basicity of the carboxylate group is decreased so much by the alcoholic hydroxy group that the stability constant of the uranyl complex of serine[4] is only 7.4, whereas that of the glycine[5] complex is 27. Since the uranyl–glutamic acid methyl ester mixture has a titration curve (Fig. 1) and a visible spectrum (Fig. 2) identical with those of the uranyl–glycine mixture and since pk_1 of glutamic acid is about the same as the pk_1 of serine, the relative affinities of the α- and γ-carboxyl groups in glutamic acid for the uranyl ion is roughly equal to the ratio of the stability constants of the uranyl complexes of serine and glutamic acid, *i.e.*, 1:62.

The titration curves of 1:1 and 1:2 uranyl nitrate–histidine mixtures are almost identical with those of uranyl nitrate–glycine mixtures up to the point of precipitation. Further, the entire visible spectrum of a 1:1 uranyl nitrate–histidine mixture (0.0114 *M*) at pH 4.13 (just below the pH where no precipitate appears after 1-day storage of the solution) is identical with that of a uranyl nitrate solution at the same pH. Thus, even though there might be a weak uranyl–histidine complex of the same strength as the uranyl–glycine complex at the low pH of 2, such a complex is non-existent at pH 4.13, *i.e.*, at the pH where the uranyl ion hydrolyzes strongly but where imidazole and NH_3^+ hydrogens do not normally ionize.

However, analysis of precipitates and filtrates indicates that histidine does bind to uranium to a significant extent near neutral pH. In Table II it is seen that the amino acid:uranium molar ratio in the precipitate at pH 6.8 is the same, 1:3, for aspartate and histidine mixtures and even has a meaningful value of 1:8 for the glycine mixture. The aspartate value at this pH, however, has decreased from near unity at pH 3.94. By pH 8.0 the aspartate value has decreased to 1:9, only slightly more than the glycine value, 1:14, and now a little less than the histidine value, 1:4.

These precipitation results can be interpreted as indicating that the ability of the β-carboxyl group of aspartate (and therefore the γ-group in glutamate also) to bind to uranyl ion decreases as the hydrolyzing tendency of the uranyl ion increases until at about pH 8 it probably binds no more strongly than does the α-carboxyl group. The amino group, apparently, has little tendency to enter into chelation even after its positive charge is lost. At pH 8 the imidazole group binds with twice the efficiency as does the carboxyl group, which however still retains a significant affinity for uranyl ions.

Discussion

A consideration of steric factors and literature data leads us to the conclusion that, if its basicity is not greatly decreased by other factors, the carboxylate binds to the uranyl ion in a bidentate manner.

The natural tendency of the uranyl entity to remain colinear is now a universally held belief.[10] In addition to its two very strong axial bonds, the uranyl entity itself can form 4, 5, or 6 secondary bonds about its equator. Zachariasen[11] has shown that, in order to minimize the repulsions between uranyl oxygens and ligands *wherever sterically possible* the secondary bonds lie in a plane perpendicular to the uranyl axis, *e.g.*, in $Rb(UO_2)(NO_3)_3$, UO_2CO_3, and $NaUO_2(OAc)_3$. In these crystalline compounds all three ligand radicals chelate in a bidentate manner. All six secondary bonds can, and do, lie in the equatorial plane, because the pair of ligand oxygens in each ligand group are so close together (≦2.21 Å.) that no steric hindrance

(10) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 177.
(11) W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.*, **12**, 526 (1959).

exists between oxygens of neighboring ligand groups. In the acetate case, the latter oxygens are 2.76 Å. apart and each ligand oxygen is 3.0 Å. from each uranyl oxygen. However, when unidentate ligands (*e.g.*, in $CaUO_4$ or UO_2F_2) form six secondary bonds, the ligand polygon is puckered so as to yield O–O or F–F distances which are sufficiently large to decrease van der Waals repulsions to an acceptable amount.

As pointed out by Connick and Hugus,[12] when not displaced by other ligands six water molecules also should form a puckered ring about the uranyl equator in aqueous solution. By arranging the six waters so that their oxygen atoms are alternately 13.2° above or below the equator, steric hindrance in the hydrated uranyl ion can be reduced to an acceptable amount, 2.68 Å., between nearest-neighbor water oxygens and between each water oxygen and its closest uranyl oxygen if we assume a 2.5 Å. secondary bond length as in the $NaUO_2(OAc)_3$ crystal.

Bidentate chelation of the uranium using the α-nitrogen and one carboxyl oxygen of glycine would result in even more steric hindrance than in the hydrated uranyl ion. The N to O distance in glycine is 2.7 Å. A 13° puckering of the ligand polygen in this case therefore also would put the nitrogen atom 2.7 Å. from a uranyl oxygen *and* from its neighboring water oxygen. However, this distance is now to be compared to 2.9 Å., the sum of the N and O van der Waals radii. Some of this steric hindrance undoubtedly could be relieved by angle bending in the glycine molecule but then ring strain would be introduced. In addition, an amino hydrogen would now be only 2.5 Å. from a uranyl oxygen.

It usually is thought that, although capable of utilizing both oxygens to bind two metal atoms simultaneously, as in M–OC(R)O—M, a carboxylate group occupies only one site in the coördination sphere when it is attached to only one metal atom.[13] Binding of the uranyl ion by the carboxylate group seems, however, to be an exceptional case for two reasons. First, the stability constant K_1 for the uranyl–acetate complex is more than twice as large as K_1 for the acetate complex of any of the ten rare earths studied by Sonesson,[14a] but K_1 of the uranyl–glycolate system is exceeded by K_1 of eight of the rare earth glycolate complexes.[14b] Second, K_1 is practically the same in both the uranyl–acetate and the uranyl–glycolate systems; *viz.*, Ahrland's log K_1 values[15] of 2.38 and 2.42, respectively, at 20° and $\mu = 1.0$, and our acetate value of 2.70 at 25° and $\mu = 0.2$, compared to Li's glycolate value[4] of 2.75. Sonesson, on the other hand, found K_1 to be more than 0.5 log unit higher for the glycolate complex than for the acetate complex for each of the ten rare earths studied by him. Similar comparisons can be made from literature data[16] for seven of eight other metals. Failure occurs only for In^{+3}, which has an inordinately high K_1 for its acetate complex.

These two apparent anomalies can be explained easily by attributing bidentate character to the complexing of the uranyl ion by a carboxyl group. Bidentate acetate chelation to a monatomic cation should have a greater entropy effect than that due to the 'normal type of bidentate glycolate chelation' (*i.e.*, involving the α-hydroxyl group and one carboxyl oxygen), for, although the translational (statistical) entropies should be nearly the same in the two cases, the greater freedom of rotation about the C–C bond should produce a more favorable configurational entropy term ($\cong$ 0.2 kcal.) in the former case. Nevertheless, as evidenced by seventeen of the eighteen comparisons available in the literature,[14,16] ΔF usually favors the normal type of bidentate glycolate chelation. Hence, the latter must be due to a much more beneficial enthalpy term. Perhaps this difference in the two enthalpies of formation might be due to more favorable bond angles existing in the normal glycolate chelate of a monatomic cation than are possible in a bidentate carboxylate chelate of the same cation, but this is only a surmise. Steric hindrance must be considered in uranyl chelates.

Normal bidentate glycolate chelation of the uranyl ion would be accompanied by the same amount of steric hindrance as described above for the hydrated uranyl ion. On the other hand, bidentate carboxylate chelation of the uranyl ion actually decreases the steric hindrance as more hydration waters are replaced. This steric factor probably affects both enthalpy and entropy, since the van der Waals repulsions are decreased and the vibrational freedom of the bound waters is increased. However, since both uranyl–acetate and uranyl–glycolate complexes have the same temperature coefficient for K_1 between 20 and 25°, the steric hindrance effect is mainly enthalpic. Apparently, this steric enthalpic effect just equals the more favorable bond-energy enthalpic effect normally found for glycolate complexes. The result is that K_1 is the same for both uranyl–acetate and uranyl–glycolate complexes at a given temperature.

When the second anionic ligand is attached to the uranyl ion, the mutual repulsion of the first and second ligands causes a decrease in the bond-energy enthalpies of both types of bidentate chelation and therefore in their difference also. The steric enthalpic factor becomes even more important, however, since addition of a second bidentate carboxylate group actually results in less steric hindrance than when only one ligand group is attached. Hence, although the bond-energy enthalpy difference and the translational entropy difference between successive complexes causes K_2 to be less than K_1 for both types of bidentate

(12) R. E. Connick and Z Z. Hugus, Jr., *J. Am. Chem. Soc.*, **74**, 6012 (1952).

(13) J. C. Bailar, Jr., and D. H. Busch, Chapter I in "Chemistry of the Coördination Compounds," ed. by J. C. Bailar, Jr., Reinhold Publishing Corp., New York, N. Y., 1956, p. 33.

(14) (a) A. Sonesson, *Acta Chem. Scand.*, **12**, 1937 (1958); (b) **13**, 998 (1959).

(15) S. Ahrland, *ibid.*, **7**, 485 (1953).

(16) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, Ed., "Stability Constants, Part I, Organic Ligands," The Chemical Society, London, 1957.

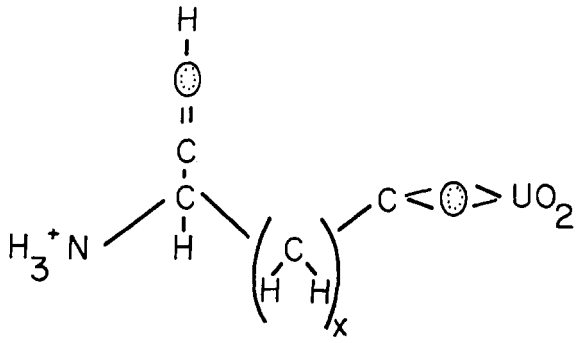

Fig. 3.—Extended structure caused by mutual repulsion of uranium and NH_3^+ group. The symbol ⓞ represents two oxygen atoms, one above the plane of the paper and one below this plane.

chelation, the reduction in steric hindrance when the second bidentate acetate group is attached makes the ratio K_1/K_2 smaller for the uranyl–acetate system than for the uranyl–glycolate system. Ahrland found this ratio to be 2.5 for the uranyl–acetate complexes and 7.7 for the uranyl–glycolate complexes.[15] He interpreted the difference as being due to bidentate glycolate chelation as contrasted with unidentate acetate complexing, but he virtually ignored the fact that K_1 is the same for both systems.

Glycolate chelates uranyl ion in its normal manner instead of by utilizing its carboxyl group bidentately simply because this group is so much weaker as a base than in acetate that the difference in the bond-energy enthalpies of the two possibilities exceeds the less favorable steric effect of normal-type glycolate chelation.

As direct experimental evidence of bidentate acetate chelation of the uranyl ion one can cite not only the precise X-ray study of Zachariasen,[11] but also the very important fact that in aqueous solution, despite its coördination number of six, the uranyl ion is capable of binding a maximum of only three acetate ions[17a] or three monochloroacetate ions.[17b] Further, uranyl acetate precipitates from excess acetic acid solution as the dihydrate, $UO_2(OAc)_2 \cdot 2H_2O$.[18]

(17) (a) S. Ahrland, *Acta Chem. Scand.*, **5**, 199 (1951); (b) **3**, 783 (1949).
(18) Reference 2, p. 60.

The reason for the apparently complete inability of glycine to chelate the uranyl ion in its normal manner (*i.e.*, by both N and O) is several-fold. As discussed above, there would be large steric hindrance in such a chelate. Further, in acid solution the acidity of the NH_3^+ is weak and in basic solution the competing hydrolytic tendency of the uranyl ion is large. These latter two factors do not prevent chelation in the copper–glycinate system because there is no steric hindrance in this system to be overcome.

The mutual repulsion of the NH_3^+ group and the uranium atom in the uranyl–aspartate and –glutamate complexes would be expected to favor an extended structure such as in Fig. 3. In this structure the nitrogen and uranium atoms are sufficiently far apart and sufficiently insulated from one another by the intervening atoms so that the NH_3^+ group does not weaken the uranium attachment significantly. On the other hand, because of rotation about C–C bonds the uranium atom and the α-carboxyl group are not always completely insulated from one another. As a result, repulsion by the uranium causes the easily-dissociable hydrogen in the α-carboxyl group ($pK = 2.1$) to ionize completely even though this group is not bound to uranium.

Plausibility for this small increase in the acidity of the α-carboxyl group due to repulsion by uranium is gleaned from the microscopic pk values for glutamic acid tabulated by Edsall and Wyman.[19] Although the pk_1 of the α-carboxyl group of glutamic acid is normally 2.15 at 25°, it would have been 2.62 if the γ-carboxyl hydrogen had dissociated first. That is, the γ-carboxyl proton lowers the pk of the α-carboxyl group 0.47 log unit. The uranium atom should have an even greater effect on this pk. It also is true that the NH_3^+ group causes a decrease in the pK of the γ-carboxyl group from 4.65 to 3.85, so that one might conclude that uranium complexing to the γ-carboxyl group should be weakened by the NH_3^+ group. However, the more easily dissociable and univalent proton should have less extensor influence than the more highly charged, and more strongly attached, uranium atom on the glutamate or aspartate chains.

(19) J. T. Edsall and J. Wyman, Ed., "Biophysical Chemistry," Volume I, Academic Press Inc., New York, N. Y., 1958, p. 496.