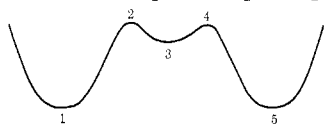


onal arrangement of ligands for cases where large amplitude rocking vibrations ν_8 represent the exchange coordinates (routes 5 and 6, Table V). In these instances either the S_{8a} or S_{8b} symmetry coordinates (Figure 5) would be principally responsible for bringing the axial atoms into a planar position with the equatorial ligands. Accompanied by some ligand repulsion a D_{5h} intermediate results.

The potential diagram would contain a saddle point (3) associated with the planar pentagon while the



difference in energy between the hump heights (2 and 4) and the saddle point would represent ligand rearrangement energy. The exchange barrier between equivalent trigonal bipyramids (1 and 5) is shown as the energy difference between either 1 and 2 or 4 and 5 in the above figure. Of course, in all of the above processes, certain mixing of stretching coordinates may serve to reduce the barrier energy.

Possible candidates for routes 3 or 4 of Table V are CuCl_5^{3-} in $[\text{Cr}(\text{NH}_3)_6][\text{CuCl}_5]$ or $\text{Ni}(\text{CN})_5^{3-}$ in $[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3][\text{Ni}(\text{CN})_5] \cdot 1.5\text{H}_2\text{O}$. X-Ray investigations,^{36,37} recently available, show trigonal-bi-

(36) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).

pyramidal structures with shorter axial distances in each case. In addition to a distorted trigonal-bipyramid environment in the latter compound, $\text{Ni}(\text{CN})_5^{3-}$ also exists in a square-pyramidal environment, each structure hydrogen bonded to water.³⁷ However, no evidence appears to exist showing exchange phenomena for these substances.

It does not seem worthwhile to consider more extensive processes. At present, little experimental evidence exists for some of the ones already mentioned. If the need arises, more complex calculations may be profitable, taking into account anharmonicity assuming suitable spectroscopic information becomes available.

What has been discussed here are possible routes for intramolecular exchange as a result of considerable amplitude in bending vibrations.³⁸ As pointed out,² pseudorotation may occur or energy barriers may be reduced at least in collisional processes especially important in condensed-state media.

Acknowledgment.—Support of this research by the National Science Foundation is gratefully acknowledged as is use of the CDC 3600 computer.

(37) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 1362 (1968).

(38) Recent papers [P. C. Lauterbur and F. Ramirez, *J. Am. Chem. Soc.*, **90**, 6722 (1968); E. L. Muetterties, *ibid.*, **90**, 5097 (1968); **91**, 1639 (1969)] discuss topological aids to visualizing stereoisomerization via pseudorotation routes for trigonal-bipyramidal molecules.

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Synthesis and Properties of Certain Uranyl Aminopolycarboxylates

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The uranyl chelates of iminodiacetic acid with a ratio (metal:ligand) of 1:2, of nitrilotriacetic acid with ratios of 1:1 and 3:2, of ethylenediaminetetraacetic acid with ratios of 1:1 and 2:1, and of *trans*-cyclohexanediaminetetraacetic acid with ratios of 1:1 and 2:1 have been prepared and characterized by elemental analyses, infrared spectroscopy, and thermal analyses. Their probable structures are discussed.

Introduction

Although the coordination chemistry of oxycations of hexavalent uranium has been studied rather extensively, researches on uranyl chelates of analytically important aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (H_4EDTA) and its analogs have been restricted principally to solutions. Brintzinger and Hesse² isolated the 1:1 uranyl-nitrilotriacetic acid (H_3NTA) and the 1:1 uranyl-EDTA chelates. The 2:1 uranyl-EDTA chelate has been prepared recently by Bhat and Krishnamurthy.³ However, the physical

properties of these solids have not been reported.

Differential thermal analysis (dta) and thermogravimetric analysis (tga) of some of the aminopolycarboxylic acids and many metal-EDTA chelates have been reported⁴ in recent years. Charles⁵ studied recently a series of alkali metal salts of Nd-EDTA chelates by tga, dta, and thermogravimetric analysis. Bhat and Iyer⁶ used the tga technique for many metal-EDTA chelates and concluded that although no generalizations could be made about the stability, decomposition involves either a two-step process or a one-step process.

(1) This report is based on portions of a thesis to be submitted by M. Krishnamurthy to the Graduate School of Howard University in partial fulfillment of the requirements for the Ph.D. degree.

(2) H. Brintzinger and G. Hesse, *Z. Anorg. Allgem. Chem.*, **249**, 113, 299 (1942).

(3) T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **26**, 587 (1964).

(4) W. W. Wendlandt, *Anal. Chem.*, **32**, 848 (1960).

(5) R. G. Charles, *J. Inorg. Nucl. Chem.*, **28**, 407 (1966).

(6) T. R. Bhat and R. K. Iyer, *ibid.*, **29**, 179 (1967).

TABLE I
ANALYSES OF URANYL CHELATES

Compound no. ^a	Formula ^b	% C		% H		% N		% U	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1	UO ₂ ((IMDA)H) ₂	17.98	17.38	2.25	2.45	5.24	5.29	44.58	44.48
2	UO ₂ ((NTA)H)·2H ₂ O	14.54	14.47	2.42	2.79	2.83	2.82	48.08	47.89
3	(UO ₂) ₃ (NTA) ₂ ·10H ₂ O	10.55	11.13	2.34	2.34	2.05	2.31	52.28	51.68
4	UO ₂ (EDTA)H ₂ ·2H ₂ O	20.14	19.29	3.02	3.09	4.70	4.71	39.94	40.52
5	(UO ₂) ₂ (EDTA)·2H ₂ O	13.89	13.37	1.85	2.63	3.24	3.50	55.09	54.61
6	UO ₂ (CDTA)H ₂ ·3H ₂ O	25.15	24.26	3.89	4.12	4.19	4.54	35.63	35.60
7	(UO ₂) ₂ (CDTA)·6H ₂ O	16.97	16.55	3.03	3.43	2.83	3.11	48.10	47.78

^a Hereafter these compounds are referred by their number in this report. ^b IMDA, NTA, EDTA, and CDTA denote NH(CH₂COO⁻)₂, N(CH₂COO⁻)₃, [-CH₂N(CH₂COO⁻)₂]₂, and *trans*-C₆H₄[N-(CH₂COO⁻)₂]₂, respectively.

TABLE II
INFRARED SPECTRAL DATA (CM⁻¹) FOR THE AMINO ACIDS AND THEIR URANYL CHELATES^a

H ₂ -IMDA	Compd 1	H ₂ NTA	Compd 2	Compd 3	H ₄ EDTA	Compd 4	Compd 5	H ₄ CDTA	Compd 6	Compd 7	Tentative assignments
1712 s		1720 vs			1690 vs			1752 vs 1730 vs 1707 vs			$\nu_{\text{asym}}(\text{C}=\text{O})$
1582 vs	1590 vs		1646 vs	1628 vs 1564 vs	1658 vs 1630 vs, sh	1620 vs 1560 vs	1590 80 vs	1660 vs 1625 vs	1625 s 1625 vs, sh	1625 s 1555 s	$\nu_{\text{asym}}(-\text{COO}^-)$
	1450 vs 1412 vs	1460 s 1408 s	1432 m 1412 s	1430 m 1412 s	1442 s		1430 s 1400 vs	1435-1450 m, sh 1445 sh 1402 s		1435-1450 m, sh 1405-1390 s, sh	CH ₂ scissor $\nu_{\text{sym}}(\text{COO}^-) +$ -OH bending
1392 vs 1359 s	1395 vs		1360 vs	1361 s	1395 s	1398 s, sh	1398 s	1367 s	1353 vs	1360 m	$\text{pw}(\text{CH}_2) +$ $\text{pt}(\text{CH}_2)$
	1342 m	1330 s		1337 w	1345 m	1342 s	1334 m	1342 s			
1205 s		1200 vs			1215 w			1218 vs	1205 w	1200 w	
1100 m	1072 m 916 vs	1072 s	1074 w 950 s	938 s	1080 m, sh		917 s	1117 s 920 vs	1076 w 939 s	1115 w 920 s	$\nu(\text{C}-\text{N})$ $\nu_{\text{antisym}}(\text{UO}_2)$

Other Bands

H ₂ IMDA:	3440 w, 3100 s, 2980 w, 1432 s, 1329 m, 1280 m, 1242 s, 1060 s, 1030 m, 952 w, 900 m, 852 w, 690 m, 572 w, 540 w
Compd 1:	3445 m, 3042 s, 3005 s, 2960 m, 2850-2780 s, 1610 sh, vs, 1550 vs, 1490 s, 1320 vs, 1240 w, 1228 m, 1048 w, 1025 vw, 962 w, 880 vs, 708 w, 675 m, 572 m
H ₂ NTA:	3050 m, 3000 m, 1432 s, 1380 s, 1240 vs, 1225 vs, sh, 1006 s, 962 s, 898 s, 859 s, 738 s, 672 m, 586 w
Compd 2:	3480-3430 b, vs, 3140 s, 2978 m, 1308 vs, 1042 w, 965 m, 918 m, 915-910 m, sh, 856 w, 695 w, 550 w
Compd 3:	3520 s, 3370 s, 1308 s, 1292 m, 1272 w, 1105 vw, 1044 vw, 1020 vw, 964 w, 902 m, 874 vw, 849 vw, 786 vw, 635 vw, 580 vw
H ₄ EDTA:	3460-3440 w, 3025 m, 1420 s, 1315 s, 1257 w, 1140 w, 1048 m, 1006 m, 964 s, 870 s, 780 s, 710 m, 580 s
Compd 4:	3480-3440 s, 3035 m, 1386 s, 1305 s, 1015, 955 sh, 690 w
Compd 5:	3440 b, s, 1295 m, 725 w, 620 w, 605 w
H ₄ CDTA:	3520-400 b, m, 3010 s, 2970 s, 2880 s, 2550 m, b, 1655 s, 1318 m, 1308 s, 1297 m, 1267 vs, 1233 vs, 1170 s, 1147 m, 1010 w, 995 m, 980 w, 967 w, 945 m, 928 w, 907 m, 890 w, 880 w, 712 m, 699 m, 681 m
Compd 6:	3460-3400 b, s, 3010 m, 2970 m, 1381 vs, 1338 s, 1312 s, 1301 s, 1230 m, 1153 w, 1038 w, 987 m, 910 m, 880 w, 782 w, 701 m, 619 w, 568 w
Compd 7:	3450-3430 b, vs, 2940 m, 1382 s, 1305 m, 1160-1140 w, 710 w, 630-618 w

^a Abbreviations: ν , stretching; pw, wagging; pt, twisting; sh, shoulder; v, very; s, strong; m, medium; w, weak; b, broad.

Infrared data for several aminopolycarboxylic acids and their chelates can be found in the literature. Nakamoto⁷ and his associates obtained the infrared spectra for EDTA and its analogs while Sawyer⁸ studied the infrared spectra of the EDTA chelates of di- and trivalent metal ions and of higher valent metal oxyocations. The infrared spectra of uranyl salts and of many uranyl chelates have also been reported extensively.⁹

A comparison of the thermal properties and infrared spectra of these aminopolycarboxylates whose structures have been established with those whose structures are not known should enable one to deduce some structural information about the latter. Such comparisons involving some of the uranyl polyamino-carboxylates form the basis of this report.

Experimental Section

Reagents.—A stock solution of pure uranyl nitrate (0.35 M) was made from laboratory grade uranyl acetate by precipitation

of ammonium diuranate, ignition to U₃O₈, and dissolution of this product in nitric acid. Several recrystallizations of the uranyl nitrate yielded a product that was sufficiently pure for the preparation of a standard solution of the salt. The amino acids were obtained from Aldrich Chemical Co. and used without further purification.

Measurements.—A Perkin-Elmer Model 621 grating double-beam spectrophotometer was used to record the ir spectra. The instrument was calibrated with polystyrene film. Thermal properties were studied by using the Du Pont dta instrument (Model 900) with the tga accessory (Model 980). Both pellet and mull techniques were used in the preparation of samples of appropriate concentrations for the ir work. The spectra of samples prepared by both methods agreed very well except in one case. The ir spectrum of a pellet sample of uranyl-IMDA chelate shows -OH stretching absorption around 3400 cm⁻¹ while the spectrum of a mull sample does not show any absorption in this region in accordance with the molecular formula. This was attributed to the presence of traces of adsorbed moisture regardless of the technique and precautions exercised in drying the KBr. Therefore, for all of the samples, assignments were not attempted beyond 2000 cm⁻¹.

(7) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).

(8) D. T. Sawyer and J. M. McKinnie, *ibid.*, **82**, 4191 (1960).

(9) J. T. Bullock, *J. Inorg. Nucl. Chem.*, **29**, 2257 (1967).

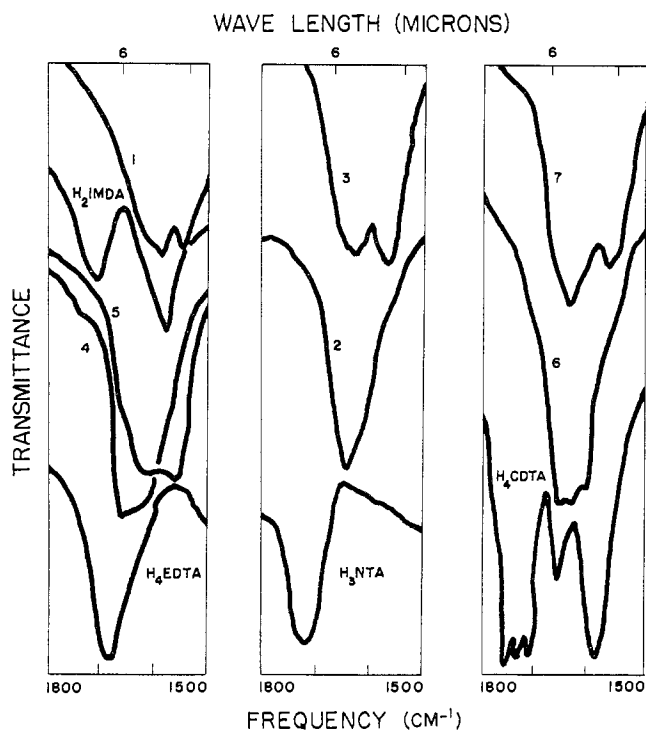


Figure 1.—Antisymmetric stretching frequencies of the ligand carbonyl groups in the amino acids and in compounds 1-7.

Both tga and dta were carried out in N_2 as well as in air atmosphere. The instruments were calibrated with benzoic acid and calcium oxalate samples. Since chromel-alumel thermocouples were employed in the measurements, temperature corrections were necessary. Although the temperatures represented in Figures 2 and 3 are uncorrected, the corrected values are reported in the Results. In the tga measurements, the effluent gases were bubbled into a small quantity of water for which the pH was monitored continuously according to the procedure employed by Charles.⁵ This technique enables one to obtain information about dehydration and/or decomposition of the chelate. Such information is presented along with the thermograms in Figure 3. For the tga measurements, the heating rate was $8^\circ/\text{min}$; for dta data, the rate was $20^\circ/\text{min}$.

Preparation of the Compounds. **Uranyl Iminodiacetate (1).**—Stoichiometric amounts of uranyl nitrate and iminodiacetic acid solutions were mixed with stirring and the pH was adjusted with sodium hydroxide pellets to approximately 3-3.5. After 1 day, the 1:2 (metal:ligand) chelate separates as a yellow amorphous powder. Interestingly, if one mixes the solutions in a 1:1 ratio, the product isolated is still the same, compound 1.

Uranyl Compounds of NTA, EDTA, and CDTA.—Stoichiometric amounts of uranyl solution and a solution containing the disodium salt of the corresponding amino acid were mixed while stirring uniformly and then diluted to 300 ml. For the 1:1 chelates, the ligand was kept slightly in excess; for the other chelates, the uranyl salt was kept in excess to avoid the contamination of other species. All of these chelates, except the 2:1 compound for EDTA, precipitated soon after mixing of the solutions. Each mixture was adjusted to a pH of 3, boiled, and filtered under suction while hot. The yield of the 2:1 EDTA compound was greatest in cold mixtures after 1 day had elapsed. Each chelate was washed thoroughly with hot water and acetone and dried either in the range $95-100^\circ$ or in a vacuum desiccator. The average yield for these chelates was above 95%.

Uranium was analyzed in the chelates by (1) careful ignition to U_3O_8 and (2) dissolving the ash in acid, precipitating as ammonium diuranate, and igniting to U_3O_8 . The microanalyses for C, H, and N were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and the Du-Good Chemical Laboratory, St. Louis, Mo. Analytical data are presented in Table I.

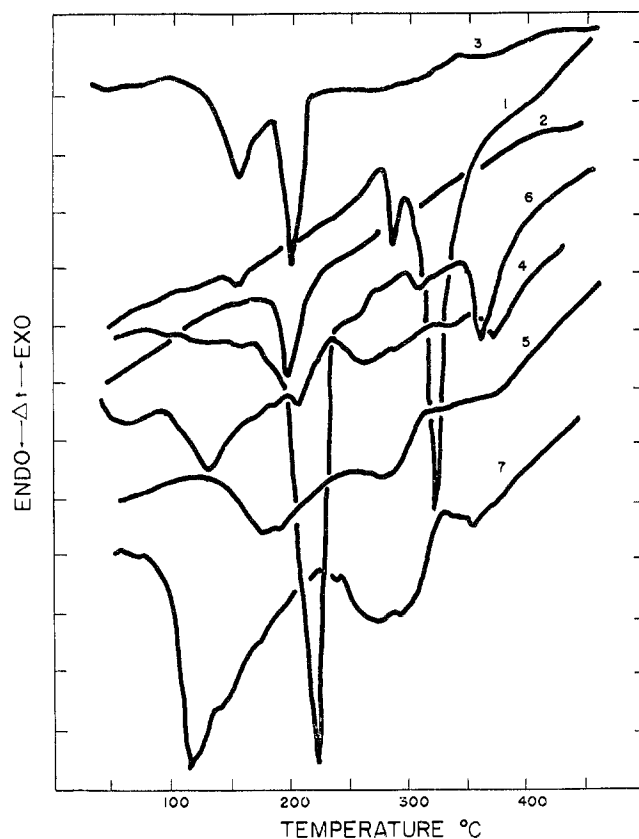


Figure 2.—Differential thermal analyses curves for compounds 1-7.

Results

All of the compounds are insoluble in water, DMSO, DMF, dioxane, ethyl and methyl alcohols, and nonpolar solvents. They are soluble with decomposition in strong mineral acids. The infrared absorption frequencies of all of the compounds and of the free ligands are given in Table II. In Table II, the relative intensity of each peak has been estimated by comparison with the strongest peak, and, whenever possible, tentative assignments have been made. The amino acid complexes of this report give broad peaks for the asymmetric carboxylate stretching. This is in agreement with the observations of others⁸ in their studies with analogous complexes. Figure 1 shows the absorption spectra of these compounds.

The dta and tga thermograms are shown in Figures 2 and 3. The dotted lines in Figure 3 represent the variation in pH of 10 ml of water into which the effluent carrier gas from the tga furnace was bubbled. The dta measurements were carried out in nitrogen and air atmospheres; the tga determinations were carried out principally in an atmosphere of nitrogen. For the compounds of this report, the thermograms are essentially the same for either air or nitrogen as the atmosphere. Naturally, the end product will contain more carbonaceous material for measurements carried out in an atmosphere of nitrogen than when air is used.

Compound 1 shows endothermic peaks at 149 , 278.5 , and 315° in nitrogen. The tga curve shows that the compound is stable up to 197° . As the reproducible but

irreversible endothermic peak at 149° does not correspond to any weight loss in the tga curve, the peak may be the result of sintering of particles or crystalline transformation. Compound 2 shows only one endotherm at 194° in nitrogen. The sample is stable up to 125° beyond which dehydration occurs up to 197°. For compound 3, there are two endotherms in N₂ at 151 and 193°. A small endothermic shoulder appears at 170° and a small and broad exothermic peak over the range 329–334°. It loses water over the range 54–192°. Seven moles of water is lost per mole of compound. Although the tga thermogram does not reveal any conspicuous intermediate steps during dehydration, the sharp peaks in the dta thermogram indicate that the water loss is a stepwise process.

Compound 4 exhibits endotherms in N₂ at 122, 202, and 360° and an exotherm at 277°. Dehydration of the compound begins at 50° and is complete at 122°. The anhydrous compound is stable up to 197°. In the tga curve, the weight losses occur in two stages with the stages ending at 246 and 367°, respectively. If one makes the reasonable assumption that the acidic product evolved between 200 and 250° is CO₂, the weight loss from the initial stage represents the loss of approximately 1 mol of CO₂ per mole of compound. For compound 5 in N₂, there are broad endotherms for the ranges 172–187, 275–280, and 357–367°.

The dta thermograms of compounds 4 and 5 are difficult to analyze because of the presence of broad bands instead of sharp peaks in the thermograms. The decomposition of compound 5 is peculiar in another respect. Although all of the compounds studied, with the exception of compounds 1 and 5, gave acidic gaseous products initially, followed by basic gaseous products, compound 5 evolved predominantly basic products. In the case of compound 1, basic products evolved initially, and subsequently both acidic and basic products were evolved.

Compound 6 exhibits endotherms at 220, 302, and 354° in N₂. Complete dehydration of this compound takes place between 122 and 197°. Compound 7 shows an endotherm at 114° corresponding to dehydration which takes place between 50 and 147°. There are also two endotherms for the range 266–295° and at 348°, both of which correspond to decomposition.

Discussion

Infrared Data.—The absence of any absorption beyond 1660 cm⁻¹, in the cases of compounds 1, 2, 4, and 6, indicates that there are no un-ionized carboxyl groups in these compounds. This suggests that the protons of these compounds may be attached to the nitrogens rather than to the carboxylate oxygens. The asymmetric stretchings, in the range 1600–1660 cm⁻¹, observed for compounds 2, 4, and 6 could be attributed to either monodentate complexes or ionic α -ammonium carboxylates.¹⁰ By similar reasoning, the shift to lower frequencies observed in the cases of compounds 3,

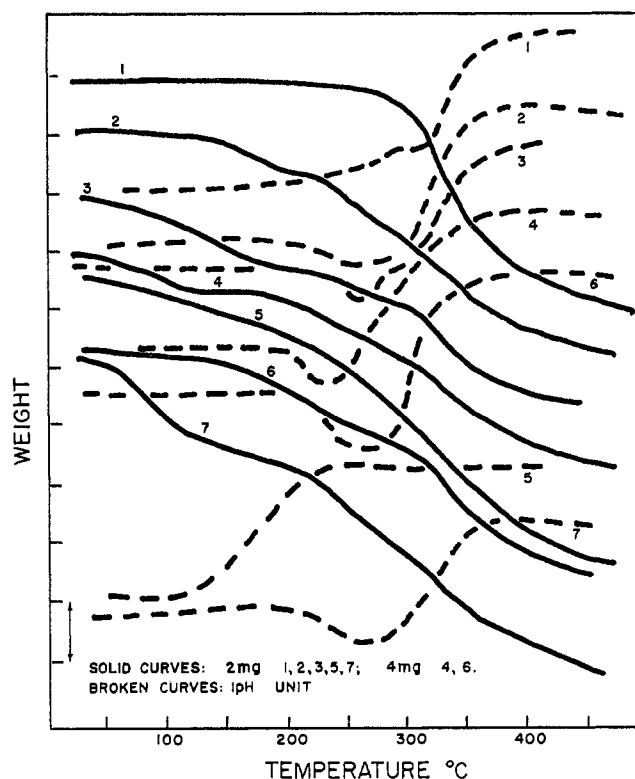


Figure 3.—Thermogravimetric analyses curves (solid lines) and pH variation due to effluent gases (broken lines) as a function of pyrolysis temperature for compounds 1–7.

5, and 7 could be due to either a change in the nature of the coordination of the carboxylates or to the presence of ion-pair α -aminocarboxylates.¹⁰ In the above cases, it is not possible to distinguish between the two possible effects by ir data alone.

The increase in intensity of the uv spectra of these UO₂²⁺ complexes in aqueous solution and other observations¹¹ (e.g., lowering of the initial pH of the mixtures, elevation of the pH of precipitation in the potentiometric studies, etc.) are factors which suggest strongly the coordination of the carboxylates. Thus, this rules out the likelihood of coulombic interaction offered above as a possibility. The strong absorption peaks ranging from 1550 to 1610 cm⁻¹ for compound 1 would indicate that the carboxylate groups are coordinating in more than one manner. It follows from the preceding discussion that coordination of amino groups in compounds 1, 2, 4, and 6 is inhibited by the protons. However, it is not possible to conclude from these studies whether the amino groups of compounds 3, 5, and 7 are involved in coordination. Hexavalent uranium falls under class A cations which prefer coordination with oxygen rather than nitrogen or sulfur.¹² Therefore, it is reasonable to assume that the amino groups of compounds 3, 5, and 7 are not involved in coordination. The shift of asymmetric carboxylate absorption to lower frequencies may be the result of either a reduction of the inductive effect associated with removal of the formal charge on amino

(10) K. Nakamoto in "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, Chapter IV, p 277

(11) M. Krishnamurthy, Ph.D. Thesis to be submitted, Howard University, Washington, D. C.

(12) G. Schwarzenbach, *Advan. Inorg. Chem. Radiochem.*, **3**, 265 (1961).

nitrogen and enhancement of carboxylate coordination or the change in type of coordination from mono- to bidentate.¹³

The uranyl ion asymmetric stretching absorption varies in frequency from 916 cm^{-1} in compound **1** to 950 cm^{-1} in compound **2**. Since a consideration of the ir series proposed by McGlynn and others¹⁴ is not fruitful in accounting for this variation in frequency, the only explanation possible now appears to be that there is hydrogen bonding between equatorial ligand oxygens and uranyl oxygens. This is consistent with the proposals of Hoekstra¹⁵ for hydrated and anhydrous uranyl fluorides.

Thermal Studies.—The thermal data reveal that (a) anhydrous compounds **2**, **4**, **6**, and **7** are quite stable, (b) the complete dehydration of compound **5** results in decomposition, and (c) compound **3** decomposes before losing 3 mol of water. Presumably, the water molecules of compounds **2**, **4**, **6**, and **7** are joined to the rest of the molecule by hydrogen bonds rather than by coordination to the metallic cation. In the case of compound **5**, it would appear that 1 of the 2 mol of water is coordinated to the metal ion and this accounts for the inability to obtain the anhydrous compound without getting decomposition. For compound **3** it would appear that at least three molecules of water must be coordinated strongly to the cation in view of the fact that decarboxylation begins even when 3 mol of water is still present in the compound. Except for compound **1**, all compounds decompose at lower temperatures.

Bhat and Iyer,⁶ in their researches with EDTA complexes, are of the opinion that decarboxylation is the first step in the decomposition. The same is true for the compounds of the present report. This decarboxylation may be caused by the inductive effect that results from either a formal positive charge on nitrogen in α -ammonium carboxylate chelates or the enhanced coordination of amino nitrogen to the metal. It is concluded by the other workers⁶ in their report that decomposition occurs in a single step when three or more carboxylate groups are coordinated to the metal and in two steps when less than three carboxylate groups are coordinated to the metal. This generalization is not supported by the present work with EDTA complexes.

Numerous investigators have studied the UO_2^{2+} -EDTA system by various techniques in solution. These studies established the existence of 1:1 or 2:1 (metal:ligand) species or both species, depending upon the limitations of the techniques used and the experimental conditions employed. Bhat and Krishnamurthy³ concluded on the basis of spectrophotometric studies that the nature of bonding between UO_2^{2+} and EDTA is the same in both 1:1 and 2:1 species. Ac-

cordingly, only half of the EDTA is bound directly to UO_2^{2+} in the 1:1 complex. DaSilva and Simoes¹⁶ also proposed a similar structure in which there is hydrogen bonding between $\text{>N}^+\text{H}$ of the other unbound half of EDTA and the oxygen of UO_2^{2+} . This proposal appears to be highly unlikely. A hydrogen attached to a positively charged nitrogen will definitely carry a partial negative charge, and, because of this, it will not participate in hydrogen bonding with another atom carrying a partial negative charge, such as oxygen of UO_2^{2+} . However, hydrogen bonding between the two $-\text{COO}^-$ groups of the other half of EDTA and uranyl oxygens, through water molecules, appears to be very reasonable. This also would explain the fact that of the two $\text{>N}^+\text{H}$ groups in compound **4**, one of them (the one closer to the coordinated $-\text{COO}^-$) has a low ionization constant while the other does not ionize without decomposition of the chelate at a very high pH.

On the basis of these arguments, it is clear that only half of EDTA is coordinated to UO_2^{2+} in solution where the ratio is 1:1. The fact that part of the coordination sphere of UO_2^{2+} is occupied only by solvent molecules is further substantiated by the formation of mixed complexes¹⁷ with H_2O_2 as in the case of $\text{UO}_2^{2+}:\text{H}_2\text{O}_2$:oxalate. Although it is possible to deduce successfully the structure of these UO_2 -EDTA chelates in solutions, one cannot do the same with solids isolated from the solutions in this report. These solids appear to be polymeric in nature because (1) while all of the simple chelates of EDTA and its analogs are water soluble, the uranyl chelates of this report are insoluble in water and (2) the precipitation of the compounds reported here is slow (e.g., compounds **1** and **5**) by comparison with rapid chelation in solution. (Note: This system is comparable to Fe^{3+} -NTA.^{11,18})

Similar relationship exists between the uranyl iminodiacetate reported by Lai and Chen¹⁹ in solution at pH 3 and compound **1**. One possible explanation for the occurrence of such polymerization is that the simple monomeric species are linked through hydrogen bonding with water molecules. Another possible interpretation is that the uncoordinated part of the ligand of one monomer imparts a weak interaction upon the uncoordinated side of the UO_2^{2+} of the other monomer, thereby perpetuating the polymerization.

In conclusion, the uranyl ion is coordinated with four carboxylate groups in compound **1**, three carboxylates in compound **2**, two carboxylates and one water molecule in compounds **3** and **5**, either all four or at least two carboxylate groups in compounds **4** and **6**, and only two carboxylate groups in compound **7**.

(16) J. J. R. F. DaSilva and M. Simoes, *Talanta*, **15**, 609 (1968).

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(14) S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, **35**, 105 (1961).

(15) H. R. Hoekstra, *Inorg. Chem.*, **2**, 492 (1963).