STUDIES ON URANYL COMPLEXES

I. URANYL COMPLEXES OF E. G. T. A.

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The uranyl complexes of EGTA — (ethyleneglycol-bis-aminoethy-lether) tetracetic acid — were studied by potentiometric and absortiometric methods. Evidence is presented for the formation in solution of the species $UO_2(H_2O)HY^-$, $(UO_2)_2(H_2O)_2Y$, $(UO_2)(HO)HY^{2-}$, $(UO_2)_2(HO)(H_2O)Y^-$ and $(UO_2)_2(HO)_2Y^{2-}$; their respective formation constants were determined by potentiometric measurements. The species $Na(UO_2)(H_2O)HY$ and $(UO_2)_2(H_2O)_2Y$ were isolated in solid form; IR spectra give evidence for considerable covalent character in uranium-oxygen bonds and support the formulation of the complexes with coordinated water and free carboxylate groups.

1 — INTRODUCTION

Although uranium compounds have been extensively investigated for several years, quantitative data on the solution chemistry of uranyl ion is still scarce.

This is especially true for the reactions with the poly-aminocarboxylic acids («complexones»); yet, the complexes formed by these ligands may be of great interest for elucidating the behaviour of the uranyl ion. On one hand, the species formed are fairly stable at low values of pH, when hydrolysis and polymerization effects can be neglected; hence, the equilibria involved are not very complicated and can be accurately studied. On the other hand, some of the ligand atoms in the complexones can be changed, thus providing an indirect means of studying the effect of the donor on the stability of the complexes formed.

Up to the present only some commercial complexones were studied on quantitative grounds, namely iminodiacetic acid (1) (IMDA), nitrilotriacetic acid (2) (NITA), N-hydroxyethyliminodiacetic acid (1) (HIMDA), ethylenediaminetetracetic acid (3) (EDTA) and 1,2-diaminocyclohexane-NN'-tetracetic acid (2) (DCTA); however, not all were fully explored and, excepting HIMDA, the coordinating structure is the same in every case. This is, of course, useful to predict the influence of basicity on the stability of the uranyl complexes, but precludes more general conclusions on the behaviour of this ion towards different ligands of the same class.

An evaluation of these possibilities is the purpose of the present series of studies and measurements carried with ethyleneglycol-*bis*-(aminoethylether) tetracetic acid (EGTA) are now reported, in the sequence of our previous work with this complexone (4).

This particular investigation seemed worthwhile for one reason besides the necessity of extending the range of data available for both the complexone and the ion. Indeed, it was recently reported that EDTA forms a stable 2 : 1 complex in which both uranyl groups seem to be attached to the ligand with similar type of bonds (3); this should also occur with EGTA (I) and should be even more pronnounced, since this complexone has two further oxygen atoms symmetrically located in the molecule and available for coordination

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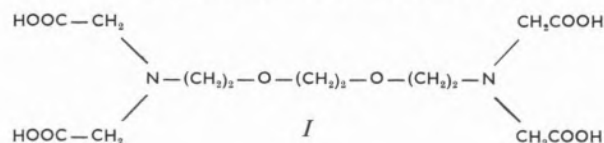
The occurrence of such 2 : 1 species raises serious questions concerning the tendency of the UO_2^{2+} ion for high coordination numbers in its complexes, a problem of considerable interest under the theoretical point of view and of practical importance for the understanding of many of the reactions of this group.

As a further point of interest, it was hoped that the system UO_2^{2+} - EGTA was amenable to rigorous mathematical treatment for determining the formation constant of all the species formed, since most of the previous results were obtained with too many and not allways justified simplifying assumptions.

2 — EXPERIMENTAL

2.1 — Reagents

1 : 2 - bis - [2 - di (carboxymethyl) - aminoethoxy] ethane (EGTA)

The commercial G. Frederick Smith Chem. Co. product was purified by repeatedly dissolving the solid in the equivalent amount of NaOH 2.5 M and reprecipitating the acid with dilute HCl.

Purity of the final product was of the order of 99.6%, as determined by potentiometric titration.

Uranyl nitrate

The salt used was of analytical grade (Merck); solutions were standardized gravimetrically by ignition of suitable aliquots to $U_3 O_8$.

Carbonate-free KOH

A solution of carbonate-free KOH, whose concentration is denoted by C_B, was prepared according to the instructions of SCHWARZENBACH and BIEDERMAN (5). Its ionic strength was made up to 0.100 M with potassium nitrate taking into account the neutralization of the hydroxyl ion in the titrations.

Water

All the water used in this work was de-ionized, e. g. distilled water which was passed through a mixed-bed ion-exchange resin.

All other chemicals used were of analytical grade.

2.2 — Synthesis of the complexes

The species Na (UO_2) (H_2O) HY and $(UO_2)_2$ $(H_2O)_2$ Y, where Y stands for the completely ionised form of EGTA, were crystalized from aqueous-solution at pH ~ 4.

Both are sparingly soluble but some difficulty was experimented in obtaining pure sample of the first; $(UO_2)_2$ $(H_2O)_2$ Y formed easily as a vitreous like sheet on the surface of its solutions.

Analysis:

Na (UO_2) (H_2O) HY

Calc.   C — 24.4   H — 3.3 U_3O_8 — 40.8 %
Found   C — 24.4   H — 3.3 U_3O_8 — 40.5 %

$(UO_2)_2$ $(H_2O)_2$ Y

Calc.   C — 17.7   H — 2.5   N — 2.9 U_3O_8 — 59,0%
Found   C — 17.8   H — 3.2   N — 3.0 U_3O_8 — 58,6%

The uranium contents of the complexes were determined after decomposition of organic matter, precipitation of ammonium di-uranate and ignition to the oxide $U_3 O_8$.

2.3 — Instruments

pH measurements and titrations were made with the radiometer pHM4 instrument, using a radiometer type G2025B glass electrode and a saturated calomel reference.

IR spectra were obtained in a Perkin-Elmer model 21 recording spectrophotometer equipped with a sodium chloride prism. The solid chelates were pressed into KBr disks using about 1-2 mg of the chelate to 500 mg of the diluent.

2.4 — Technique

The technique used for the calibration of the pH meter and for the titration was described in a previous paper (4).

Measurements were now conducted at 25.0±0.1° C and the value of K_W used was 1.68×10^{-14}.

The experimental data obtained in the titrations are

summarized below — tables 1, 2, 3. In these tables, C_M is the total concentration of metal, and C_L is the total concentration of ligand.

Table 1

Titration of EGTA alone. $T = 25.0^\circ C$ $\mu = 0.100$ M (KNO$_3$)
$C_L = 1.038 \times 10^{-3}$ M $C_B = 0.100$ M

KOH v ml	pH	v	pH	v	pH
0.00	2.906	2.00	4.400	3.10	9.018
0.20	2.948	2.20	7.680	3.20	9.093
0.40	3.003	2.30	7.992	3.30	9.170
0.60	3.061	2.40	8.239	3.40	9.249
0.80	3.118	2.50	8.410	3.50	9.328
1.00	3.199	2.60	8.546	3.60	9.409
1.20	3.292	2.70	8.662	3.70	9.488
1.40	3.422	2.80	8.764	3.80	9.575
1.60	3.576	2.90	8.854	3.90	9.670
1.80	3.810	3.00	8.940	4.00	9.761

3 — COMPUTATION OF THE STABILITY CONSTANTS

The mass balances for the ligand and the metal are as follows:

$$C_L = [H_4L]+[H_3L]+[H_2L]+[HL]+[MHL] \qquad (1)$$
$$C_M = [M]+[MHL] \qquad (2)$$

Charges are ommited for the sake of simplicity, except when necessary.

The electroneutrality condition gives

$$[K^+]+[H^+]+_2[M^{2+}] = [H_3L^-]+_2[H_2L^{2-}]+ \\ +_3[HL^{3-}]+[MHL^-]+[NO_3^-]+[OH^-] \qquad (3)$$

where $[K^+]$ is the concentration of potassium ions introduced during the titration and $[NO_3^-] = _2C_M$ is the concentration of nitrate ions added as uranyl nitrate. From equations 1, 2 and 3 it may be derived

$$(3-a)\,C_L -[H]+[OH] = _3[H_4L]+_2[H_3L]+[H_2L]. \qquad (4)$$

and

$$[M] = C_M - C_L + \alpha_H\,[HL] \qquad (5)$$

In these equation a is the «degree of neutralization», defined as the number of equivalents of base added *per* mole of ligand;
Hence

$$[HL] = \frac{(3-a)\,C_L -[H]+[OH]}{\beta_H} \qquad (6)$$

Table 2

Titrations of EGTA in the presence of the uranyl ion
$T = 25.0^\circ C$ $\mu = 0.1$ M (KNO_3)
$C_L = 1.038 \times 10^{-3}$ M $C_B = 0.100$ M
$C_M = 0,010$ M (a) and $0,020$ M (b)

KOH v ml	(a)	pH	(b)
0.00	2.813		2.742
1.00	3.012		2.909
1.20	3.065		2.950
1.40	3.116		2.993
1.60	3.178		3.041
1.80	3.243		3.098
2.00	3.331		3.145
2.10	3.382		....
2.20	3.441		3.213
2.30	3.504		....
2.40	3.579		3.290
2.50	3.664		....
2.60	3.767		....
2.80	4.049		3.480
3.00	4.593		3.597
3.20	5.180		3.736
3.40	5.551		3.908
3.60	5.870		4.109
3.80	6.227		4.333
4.00	6.844		4.558

α_H and β_H are given by

$$\alpha_H = 1 + \frac{[H]}{k_3} + \frac{[H]^2}{k_2 k_3} + \frac{[H]^3}{k_1 k_2 k_3}$$

$$\beta_H = \frac{[H]}{k_3} + 2 \frac{[H]^2}{k_2 k_3} + 3 \frac{[H]^3}{k_1 k_2 k_3} \qquad (7)$$

where the k_i are the ionization constants of the complexone.

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Table 3

Titration of the complex $(UO_2)_2 (H_2O)_2 Y$

$T = 25.0°C \qquad \mu = 0.1 \text{ M } (KNO_3)$

$C_L = 1.030 \times 10^{-3} \text{ M} \qquad C_B = 0.100 \text{ M}$

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KOH v ml	pH	KOH v ml	pH
0.00	4.542	1.10	5.770
0.10	4.650	1.20	5.875
0.20	4.766	1.30	5.978
0.30	4.871	1.40	6.072
0.40	4.982	1.50	6.178
0.50	5.096	1.70	6.404
0.60	5.212	1.90	6.732
0.70	5.336	2.10	7.388
0.80	5.439	2.30	7.955
0.90	5.547	2.50	8.381
1.00	5.658	2.70	8.641

The stability constant of the complex $(UO_2) (H_2O) HY$, here denoted by MHL, is calculated from the definition:

$$K_{MHL} = \frac{C_M - [M]}{[M] [HL]} \qquad (8)$$

For the 2 : 1 complex $(UO_2)_2 (H_2O)_2 Y$, here denoted by $M_2 L$, the following mass balances have to be considered

$$C_L = [H_4L] + [H_3L] + [H_2L] + [HL] + [L] + [MHL] + [M_2L] \qquad (9)$$

$$C_M = [M] + [MHL] + 2[M_2L] \qquad (10)$$

And the electroneutrality condition takes the form:

$$[K^+] + [H^+] + 2[M^{2+}] = [H_3L^-] + 2[H_2L^{2-}] + {} + 3[HL^{3-}] + 4[L^{4-}] + [MHL^-] + [NO_3^-] + [OH^-] \qquad (11)$$

From equations 9, 10 and 11 it may be derived

$$[L] = \frac{(4 - a) C_L - [H] + [OH]}{\beta_H + K_{MHL} \cdot \dfrac{[H]}{k_4} [M]} \qquad (12)$$

and

$$C_M - 2C_L = [M] - 2\alpha_H [L] - [MHL] \qquad (13)$$

Hence

$$[M] = \frac{C_M - 2C_L + 2\alpha_H [L]}{1 - K_{MHL} \cdot \dfrac{[H]}{k_4} [L]} \qquad (14)$$

Equations 12 and 14 are solved simultaneously by an iterative procedure; then β_{M_2L} may be calculated. From the definition

$$\beta_{M_2L} = \frac{[M_2L]}{[M]^2 [L]} = \frac{C_M - [M] - K_{MHL} \dfrac{[H]}{k_4} [M] [L]}{2[M]^2 [L]}$$

Or:

$$\beta_{M_2L} = \frac{C_M - [M] \left\{ 1 - K_{MHL} \cdot \dfrac{[H]}{k_4} [L] \right\}}{2[M]^2 [L]} \qquad (15)$$

4 — RESULTS AND DISCUSSION

The titration curves of EGTA alone and in presence of the equivalent and twice the equivalent amount of uranyl ion are shown in fig. 1, corresponding to the data in tables 1 and 2.

The trend of the 1 : 1 titration curve is analogous to that of other cases when protonated complexes are formed; the branch of the curve between $a = 3$ and

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$a = 4$ should then correspond to the neutralization of the last proton of the complexone.

The values of the dissociation constants computed from data in table 1 ($pK_1 = 1.85$, $pK_2 = 2.86$, $pK_3 = 8.73$ and $pK_4 = 9.38$) were used to calculate the formation constant of the 1 : 1 complex formulated as $UO_2 Y^{2-}$, but no consistent results could be obtained.
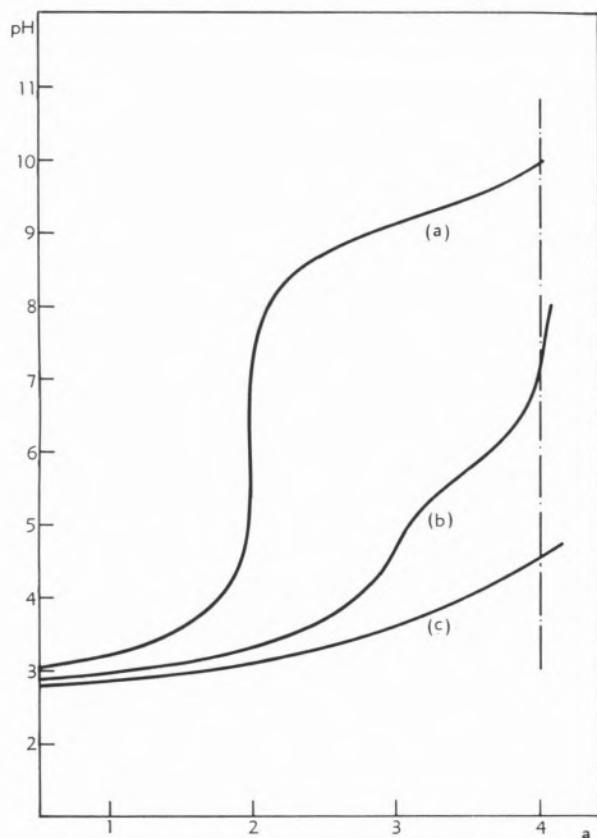

Fig. 1 — Titration curve of EGTA alone (a) *and in the presence of the equivalent* (b) *and twice the equivalent* (c) *amount of* UO_2^{2+} *ions.*

It was then assumed that only the species UO_2HY^- was present and that the branch of the curve between $a = 3$ and $a = 4$ was due to the ionization of a proton from a coordinated water molecule. This would give a value of $pKa^{H_2O} = 5.74 \pm 0.02$, which is exactly of the order found in other cases when a molecule of water coordinated to the uranyl ion ionizes at low pH (1, 3). The increased acidity of water is certainly due to the weakening of the O - H bond by the effect of the electron affinity of the uranyl group.

The calculation of the formation constant of the protonated complex gave also consistent results (^{1}) —

table 4 — thus adding further support to our hypothesis. The first species is consequently formulated as $(UO_2)(H_2O) HY^-$; by ionizing a proton from the water molecule the hydroxo-complex $(UO_2)(HO) HY^{2-}$ is obtained.

Table 4

Formation constants of proton and uranyl complexes of EGTA

$$T = 25.0^\circ C \qquad \mu = 0.1 \text{ M (KNO}_3)$$

| Species	Constant	Values
H_iL	pk_1	1.85 ± 0.05
	pk_2	2.86 ± 0.02
	pk_3	8.73 ± 0.02
	pk_4	9.38 ± 0.03
$(UO_2)(H_2O) HL^-$	$\log K^M_{MHL}$	9.14 ± 0.02
	pk^H_{MHL}	5.74 ± 0.02
$(HO_2)_2 (H_2O)_2 L$	$\log \beta_{M_2 L}$	17.66 ± 0.03
	$pk^H_{M_2} (H_2O)_2 L$	5.21 ± 0.02
	$pk^H_{M_2} (OH)(H_2O) L$	6.13 ± 0.02

In this table the symbols have the folowing meaning:

$$K^M_{MHL} = \frac{[MHL]}{[M][HL]} \quad \beta_{M_2L} = \frac{[M_2L]}{[M]^2[L]} \quad K^H_{M_2(H_2O)(HO)L} = \frac{[H][M_2(OH)_2L]}{[M_2(H_2O)(OH)L]}$$

$$K^H_{MHL} = \frac{[H][ML]}{[MHL]} \quad K^H_{M_2(H_2O)_2L} = \frac{[H][M_2(H_2O)(HO)L]}{[M_2(H_2O)_2L]}$$

The 2 : 1 titration was used to calculate the formation constant of the species containing two uranyl groups *per* molecule of the complexone. The formation of this complex is now apparent from the trend of the 1 : 1 and 2 : 1 curves and, of course, from the results obtained above. Consistent values were obtained and other titrations repeated over a ten-fold range of concentration of the uranyl ion gave only small admissible

(^{1}) The hydrolisis of the uranyl ion was taken into account; however, the correction based on a value (6) of $K = 1.0 \times 10^{-6}$ for the reaction

$$_2UO_2^{2+} + H_2O = U_2O_5^{2+} + _2H^+$$
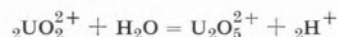
was found to be negligible.

deviations, showing that no other polymeric forms exist in appreciable amounts, under the conditions of work.

The titration curve shows a tendency for an inflexion at $a = 6$ which suggests again that two coordinated water molecules are loosing their protons, similarly to what happens with the 1 : 1 complex. The species formed in solution are accordingly formulated as

$$(UO_2)_2 (H_2O)_2 Y, (UO_2)_2 (HO) (H_2O) Y^-$$
$$\text{and } (UO_2)_2 (HO)_2 Y^{2-}$$
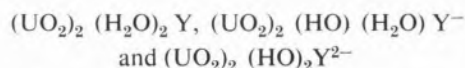
and their respective formation constant and dissociation constants are summarized in table 4.

Olation of these species does not seem likely as titrations at varied concentrations of the complexes gave only negligible deviations for the constants.

The results obtained allow some predictions to be made on the possible structure of all the species formed. Indeed, the 1 : 1 complex seems to involve only part of the EGTA skeleton and one of the nitrogen atoms of this ligand is certainly not coordinated; in the 2 : 1 complex both uranyl groups seem to be equivalent, since the free energy change in the formation of this complex almost doubles that of the 1 : 1 complex. It is also clear that in either case there exists a molecule of water coordinated to each uranium atom.

The doubts at this stage are whether the ether oxygen atoms of EGTA are also coordinated or whether there are free carboxylate groups. This will, of course, affect the distribution of the donor atoms in the equatorial plane of the cation.

Infra-red spectra could help in deciding some of these points, so we isolated in solid form the species Na (UO_2) (H_2O) HY and $(UO_2)_2$ $(H_2O)_2$ Y, as described under «Experimental»; analysis and titration both agreed well with the formulae above.

The IR spectra of these substances in KBr pellets were recorded (fig. 2); some of the peaks in the spectra are not very well defined, but several bands of interest can be assigned (table 5).

The bands at 1560 (shoulder) and 1630 cm^{-1} are of considerable interest; indeed they seem to correspond both to the carbonyl group in the carboxylate (7). This problem was discussed by several authors (7, 8, 9) who found that the antisymmetric stretching frequency of the carbonyl group in — COOM varies as M is changed and suggested that these variations could be due to the nature of the O — M bond.

Thus, if this bond is primarily ionic, the resonance in the carboxylate group is favoured and this decreases the double bond character of the CO group; its stretching frequency will then shift to lower values. If the O — M bond is primarily covalent, resonance is blocked and the opposite effect will be observed.

In addition, the frequency for the — COOH group is located at higher values and it is sometimes possible to differenciate a coordinated carboxylate, a free carboxyl and a free carboxylate. This will be likely to be found in complexes with primarily covalent O — M bonds; for ionic — O — M bonds no distinction of free — COO⁻ groups is possible.

Table 5

Bands of interest in the IR spectra of uranyl complexes of EGTA

Na $(UO_2)(H_2O)HY$	$(UO_2)_2 (H_2O)_2 Y$	Assignement
908 cm^{-1}	920 cm^{-1}	UO_2^{2+}
1562 »	1560 »	free — COO⁻
1630 »	1630 »	covalently bound — COO⁻
2425 »		— N⁺ — H
2925 »	2905 »	— CH₂ in chelate rings
3360 »	3400 »	— O — H

Thus, in IR spectra of several complexes formed by EDTA and other complexones, peaks are observed in some characteristic regions and assigned as follows (7, 8, 9):

1700 cm^{-1}	....	free — COOH
1590-1615 cm^{-1}	....	free — COO⁻ or ionic — COOM
1625-1650 cm^{-1}	....	covalent — COOM

Following these conclusions we may also assign the shoulder at 1560 cm^{-1} to free carboxylate groups in both the 1 : 1 and 2 : 1 uranyl complexes of EGTA; the band at 1630 cm^{-1} will then be due to coordinated carboxylate groups, and it may be inferred that the uranium-oxygen bonds have considerable covalent character.

The absence of bands near 1740 cm^{-1} and 1220 cm^{-1},

which correspond to the groupings — COOH and presumably to — CH_2 COOH in the free ligand(7), confirms that the remaining proton in $Na(UO_2)(H_2O)HY$ is bonded to an uncoordinated nitrogen atom.

The vibrations found at 2905 and 2925 cm^{-1} are of the order of those found for — CH_2 — when this group is part of a moderately strong chelate ring like those of the complexes of transition metals with EDTA (7).

The band at 2740 cm^{-1} in the spectrum of $Na(UO_2)(H_2O)HY$ may be due to — CH_2 — not included in chelate rings, and it is perhaps significant the fact that this band is much weaker in the spectrum of $(UO_2)_2(H_2O)_2 Y$ where less methylenic groups are free in this connection.

The band at 2425 cm^{-1} in the spectrum of the 1 : 1 complex may be due to the stretching vibration
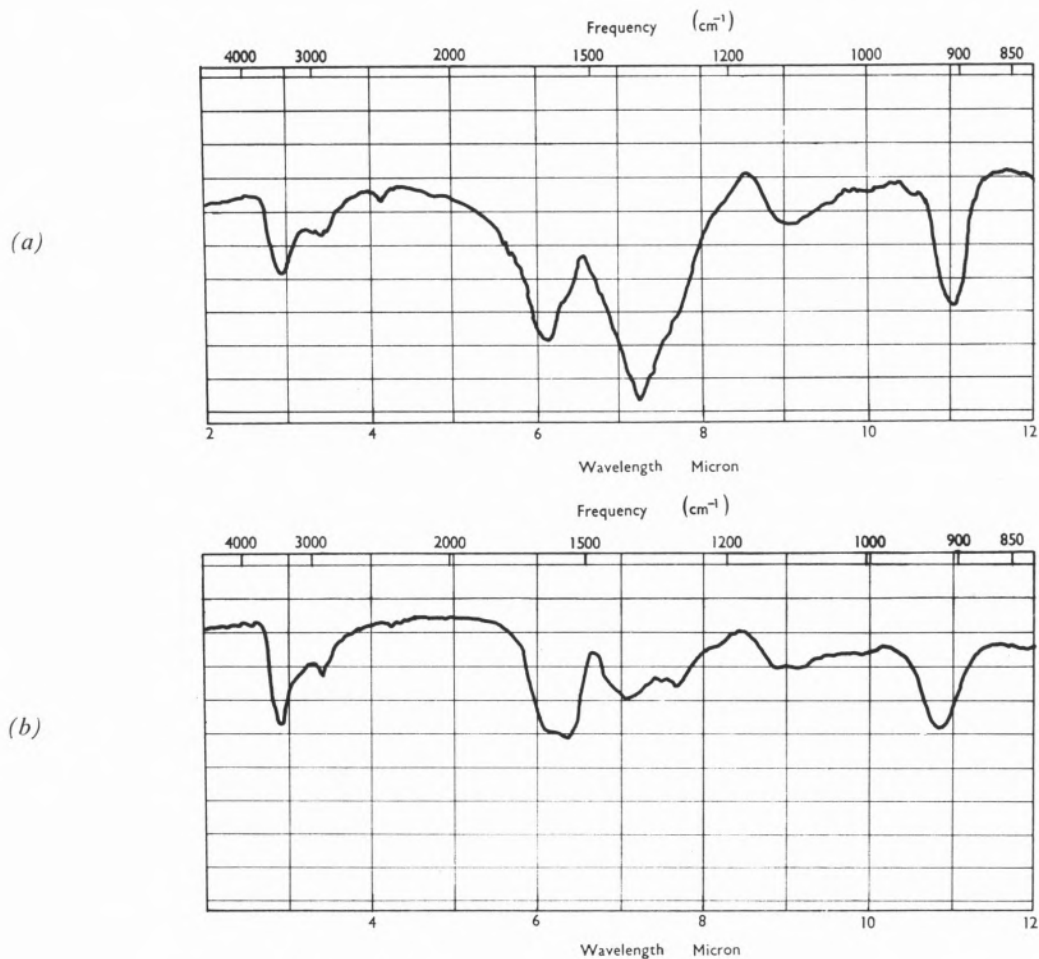
Fig. 2 — IR spectra of
(a) $Na(UO_2)(H_2O)HY$
(b) $(UO_2)_2(H_2O)_2 Y$
where Y stands for the completely ionised form of EGTA

In weaker complexes (such as those of the alkaline-earth ions) the frequency is lower, of the order of 2830 cm^{-1}, and even lower for the potassium and sodium salts (2800 cm^{-1}).

On the other hand, for strongly bound chelates, the frequency is of the order of 3000 cm^{-1} (EDTA chelates of Co (III), Fe (III), Cr (III), etc.).

of N — H, which occurs in the range 2425-2680 cm^{-1} in several trimethylamine hydrochlorides (10). This band is absent in the spectrum of the 2 : 1 complex as it should be if the assignement is correct.

The spectra and the constants determined in this work are of some interest for the understanding of the structures of the species studied.

For the 2 : 1 complex which has free carboxylate groups, few free methylenic groups, two coordinated water molecules and equivalent uranyl-complexone bonds, the structure proposed is as follows:

II
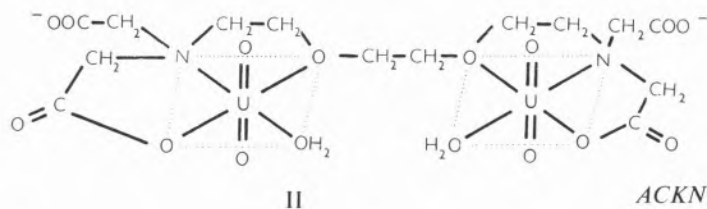
For the 1 : 1 complex either III or IV are possible:

III

IV
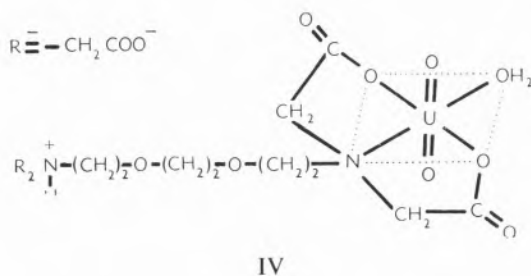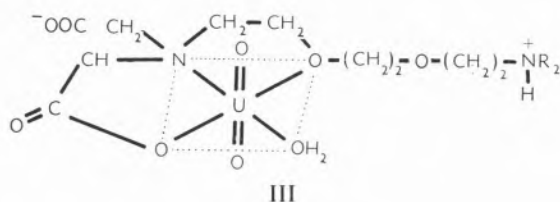
The data available is not sufficiently conclusive to decide which of these structures is correct, but, in both cases, uranium has a coordination number (6).

This is not the general situation, since 4,5 or 6 single ligands may be bonded to the uranyl group, a total coordination number 8 being currently accepted for the uranium atom (11); however, in the present system, the existence of the 2 : 1 complex, analysis, symmetry and bonding considerations support the hypothesis of the existence of only four coordinating atoms in the equatorial plane of the uranyl group. The possibility of bidentate carboxylate, found to occur in some uranyl compounds (12), is not likely in this case since it does not agree with the spectra.

Comparison with complexes of similar ligands, like EDTA, HIMDA and others, may throw some more light on this problem, which will be discussed again in a future paper of the present series.

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RESUMO

Os complexos formados pelo catião UO_2^{2+} com o ácido etilenoglicol-bis-(aminoetiléter)-tetracético foram estudados por técnicas potenciométricas e absorsiométricas. Os resultados obtidos demonstram que podem existir em solução as espécies $UO_2 (H_2O) HY^-$, $(UO_2)_2 (H_2O)_2 Y$, $(UO_2) (HO) HY^{2-}$, $(UO_2)_2 (HO) (H_2O) Y^-$ e $(UO_2)_2 (HO)_2 Y^{2-}$; as constantes de formação destas espécies foram determinadas potenciomètricamente. Isolaram-se compostos no estado sólido correspondendo às fórmulas Na $(UO_2) (H_2O) HY$ e $(UO_2)_2 (HO)_2 Y$; os espectros no infravermelho destes compostos dão considerável apoio à formulação com moléculas de água coordenadas e grupos carboxilato livres e sugerem que as ligações urânio-oxigénio possuem um carácter covalente pronunciado.