

## Studies on Metal Complexes in Aqueous Solution by Infrared Spectrophotometry

### V. An Investigation of Some Glycolate Complexes

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Infrared spectra in the wave number range 1400–800  $\text{K}$  ( $\text{cm}^{-1}$ ) have been recorded for aqueous solutions of glycolate ( $\text{HOCH}_2\text{COO}^-$ ) complexes of the following metal ions:  $\text{UO}_2^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Nd}^{3+}$ . The extinction coefficients of the C–O stretching vibration of the C–OH group of the different systems have been determined.

Three types of bonding of the ligand have been deduced from these data.

- A. Pure chelates ( $\text{Cu}^{2+}$ , first  $\text{UO}_2^{2+}$  complex).
- B. Chelates formed *via* a water molecule bonded to the metal ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Nd}^{3+}$ , and the second and third  $\text{UO}_2^{2+}$ -complexes).
- C. The ligand is bonded through the carboxylate group only ( $\text{UO}_2^{2+}$ ). For the  $\text{UO}_2^{2+}$ -system the contribution of type C was estimated to be about 15 % of the total.

During the last few decades a great number of stability constants have been determined for metal complexes in aqueous solution. In principle, these "thermodynamic" quantities do not give any information on the structure of the complexes. It was remarked by Bjerrum,<sup>1</sup> however, that the quotient between the consecutive stability constants ( $K_n$ ) depended upon whether the ligand behaved as unidentate or multidentate. In the latter case  $K_n/K_{n+1}$  should be greater (about two times) than in the unidentate case. Hence by comparing  $K_n/K_{n+1}$  for similar systems, where electrostatic terms cancel, *e.g.* acetate and glycolate complexes, one may infer if any chelation occurs.

Some pertinent results<sup>2-7</sup> are collected in Table 1. They present a somewhat diffuse picture. The only case where chelation is indicated by greater values of  $K_1/K_2$  and  $K_2/K_3$  for glycolate is the copper system. The large increase of  $K_1$  when going from acetate to glycolate indicates that also the first americium glycolate complex is a chelate. In the case of  $\text{UO}_2^{2+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Gd}^{3+}$  the investigators have been very careful not to interpret their results in terms of an exclusive presence of chelate complexes.

Table 1. A survey of the stability constants of some acetate and glycolate systems.

Ionic strength M	Metal ion	Acetate			Glycolate			Ref.
		$K_1 M^{-1}$	$K_1/K_2$	$K_2/K_3$	$K_1 M^{-1}$	$K_1/K_2$	$K_2/K_3$	
1	$Cu^{2+}$	47	4.9	3.7	220	9.6	11.5	2
1	$UO_2^{2+}$	240	2.5	1.0	265	7.7	2.0	3
0.5	$Am^{3+}$	99	5.1	4.6	660	7.5	4.1	4,5
2.0	$Nd^{3+}$	80	6.3	4.6	320	4.6	4.1	6,7
2.0	$Gd^{3+}$	69	3.6	4.9	300	3.3	3.9	6,7

Ahrland,<sup>3</sup> *e.g.*, points out that "the chelate bond possibly formed is not very strong and it is certainly broken by the addition of the third ligand".

This situation illustrates the difficulty of using stability constants to solve the present problem. For this reason as well as others one has to turn to spectroscopy as in so many other cases dealing with molecular structure.

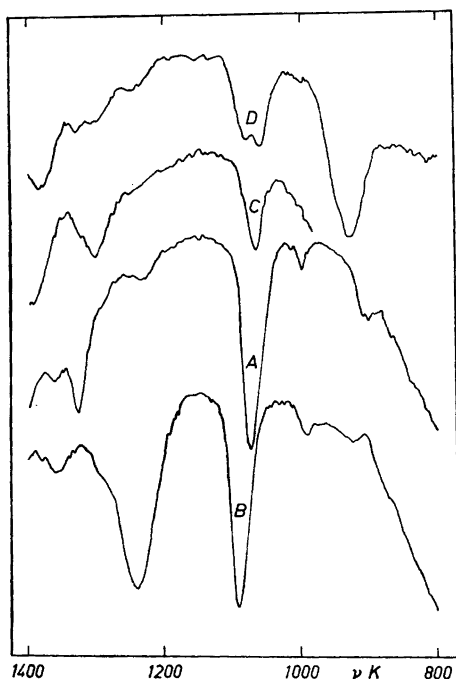


Fig. 1. Spectra of: A. Sodium glycolate 1 M (NaL). B. 1 M glycolic acid. C. 0.5 M NaL + 0.75 M  $NdCl_3$ . D. 0.5 M NaL + 0.5 M  $UO_2Cl_2$ .

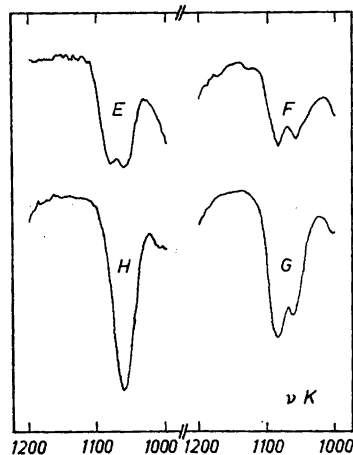


Fig. 2. The C—OH vibration absorption for some of the investigated systems. E. 0.67 M NaL + 0.67 M  $UO_2Cl_2$  (+ 10 % HCl). F. 0.4 M NaL + 0.4 M  $UO_2(NO_3)_2$ . G. 0.8 M NaL + 0.4 M  $UO_2(NO_3)_2$ . H. 1.33 M NaL + 1.33 M  $NiCl_2$ .

Goulden<sup>8</sup> has presented some interesting results in this field. He finds that the infrared spectra of glycolate complexes are distinctly different when the ligand is chelated and unidentate. The different absorption peaks in the region 1400–800 K of the free ion recorded in this laboratory is presented in Fig. 1. Following the assignments of Goulden<sup>8</sup> the 1235 K peak corresponds to the in-plane bending vibration of the OH group, and the 1074 K peak corresponds to C—O stretching vibration of the C—OH group. The most obvious spectral change caused by the formation of a chelate bond is, according to Goulden, that the OH in-plane bending absorption is moved to about 1390 K and increases in intensity. As this absorption is rather difficult to observe because of the near-lying absorption of the carboxylate group (about 1400 K) attention has been focused on the shifts of the C—OH stretching vibration in the present work. These shifts are not so drastic as those discussed by Goulden, but as there is no other absorption in the neighbourhood it is easier to observe the peak and to calculate its intensity.

This latter quantity is of even greater diagnostic value than the frequency shift. The interpretation of the intensity of the 1390 K peak may be difficult as there will probably be some coupling with the near-lying absorption of the CH<sub>2</sub> group and possibly also with that of the carboxylate group.

## RESULTS AND DISCUSSION

*Experimental details:* All measurements were made with the same technique as used in an earlier investigation.<sup>9</sup> Each solution had such a composition that the first complex should dominate *i.e.* the total concentrations  $C_M = C_L$  were so large that  $[ML] \gg [L]$ . Thus the spectra can be regarded as those of the first complex ML. pH was the one that results from mixing of the pure reagents specified.

In Fig. 1 spectra of some metal glycolate systems are presented and Fig. 2 shows some details of the C—OH absorption.

The most striking results are those of the uranyl system. Here two peaks in the region of the C—OH vibration are observed, different from that of the free ligand. Both of these must correspond to molecular entities that are uranyl glycolate complexes for the following reasons: Solids precipitated slowly from some of the solutions investigated. These solids gave spectra with an absorption at 1085 K, so the species absorbing at 1084 K in solution is most probably an uranyl complex. The only reasonable alternative to a uranyl-glycolate complex for the molecular species giving rise to spectra different from that of the free glycolate ion should be glycolic acid, formed by protons set free from the hydrolysed uranyl ion. However, one argument against this is that the peak in question is clearly observed at 1084 K and not at 1090 K as it should be for glycolic acid. Furthermore, the strong absorption at 1240 K characteristic for glycolic acid is not observed.

As the total concentration of uranyl ions is quite high in the investigated solutions, it is possible that there is some polymerisation caused by hydrolysis of  $UO_2^{2+}$ . However, from the above-mentioned absence of absorption due to glycolic acid it seems that the glycolate ions have greater affinity to the uranyl groups than to the protons set free at the hydrolysis. The remarkable

Table 2. Absorption data for solutions of uranyl nitrate and sodium glycolate,  $C_M = C_L$ .

$C_M$ M	Band I			Band II		
	$\nu$ K	$A$	$AC_L^{-1}d^{-1}$ $M^{-1}cm^{-1}$	$\nu$ K	$A$	$AC_L^{-1}d^{-1}$ $M^{-1}cm^{-1}$
0.25	1057	0.0530	106	1083	0.068	136
0.33	1056	0.0550	84	1084	0.070	106
0.40	1057	0.0884	111	1083	0.1176	147
0.50	1057	0.1040	104	1084	0.1340	134
0.67	1058	0.1293	97	1085	0.1684	126
1.00	1058	0.228	114	1085	0.287	143
Mean	1057		103	1084		132

Before introduction of these values of  $AC_L^{-1}d^{-1}$  into Table 3 they have been reduced with 6 % to account for the overlapping of the two nearlying bands. For this reduction the formula  $\varepsilon = \varepsilon_0 \times 2 \exp[-(\nu - \nu_0)^2 / (\Delta\nu)^2]$  (Ref. 15), was used with the estimation  $\nu - \nu_0 = 2(\Delta\nu)^{1/2}$ .

constancy (Table 2) of both the relative and the absolute intensities of the two peaks when the total concentration increases from 0.25 M to 1.0 M also indicates that the binding conditions of the glycolate ion is the same in all solutions. Hence one is justified in considering both species absorbing at 1084 and 1057 K, respectively as uranyl-glycolate complexes, irrespective of whether they have a polynuclear uranyl central group or not.

Solutions of uranyl chloride (with some excess of hydrochloric acid) and sodium glycolate had almost the same spectral pattern (*cf.* Fig. 2) as solutions containing uranyl nitrate.

The intensities of the C—OH absorptions for the various systems are presented in Table 3.

Table 3. Absorption data of the C—O vibration of the C—OH group for the different systems investigated under such conditions that the first complex is the dominating species.

	$\nu_{C-OH}$ (K)	$AC_L^{-1}d^{-1}$ $M^{-1}cm^{-1}$	$(\Delta\nu)^{1/2}$ K
Na <sup>+</sup>	1074	250 ± 5	25
H <sup>+</sup>	1090	270 ± 10	25
Co <sup>2+</sup>	1060	150 ± 10	25
Ni <sup>2+</sup>	1060	145 ± 5	25
Cu <sup>2+</sup>	1055	85 ± 2	30
Gd <sup>3+</sup>	1067	155 ± 10	25
Nd <sup>3+</sup>	1068	145 ± 10	25
UO <sub>2</sub> <sup>2+</sup>	1057	97 ± 10	30
	1084	124 ± 10	25

As it is most probable (Ref. 2) that the copper system presents a case of chelated ligands it can be inferred from the  $\text{Cu}^{2+}$  data of Table 2 that for ligands bonded as chelates the intensity as well as the frequency of the C—OH vibration decreases. This generalisation is in accordance with the observations made by Goulden<sup>8</sup> for lactate systems. Hence it can be concluded that the uranyl complex absorbing at 1057 K is a chelate. This conclusion in its turn means that the glycolate ion is not bonded as a chelate in the above-mentioned precipitate ( $\nu = 1085$  K). (Solid copper glycolate gives an absorption at 1055 K, *i.e.* no solid state effects seem to shift the C—OH absorption, and hence the solid state effects are probably very small also in the uranyl system). It seems plausible that the bonding is of the type



which has been established<sup>10</sup> for sodium uranyl acetate. Another

possibility for the bonding of the solid compound may be one of the type found by Jelenic *et al.*<sup>11</sup> for uranium(IV) acetate, *i.e.* the uranium atoms are kept together with carboxylate bridges.

For the complex absorbing at 1084 K in solution it seems most reasonable to assume a structure of the sodium uranyl acetate type. This yields a strong positive charge placed in line with the C—C bond. It may then be interesting to compare the effects of such a charge on the C—OH vibration with those of the proton in glycolic acid. In the latter case the charge is smaller and is by necessity not situated in line with the C—C bond.

Denoting as  $x$  the fraction of the uranyl glycolate complex which is chelated the following relations can be formulated for the absorbance  $A$ :

$$A_{1057} = C_L \cdot x \cdot \epsilon_{1057} \cdot d \quad (1)$$

$$A_{1084} = C_L(1-x) \epsilon_{1084} \cdot d \quad (2)$$

Now, from Table 2 it holds, that  $A_{1057}/C_L d = 97 \text{ M}^{-1} \text{ cm}^{-1}$ , and  $A_{1084}/C_L d = 125 \text{ M}^{-1} \text{ cm}^{-1}$  which gives the equations:

$$97 = x \epsilon_{1057} \quad (3)$$

$$125 = (1-x) \epsilon_{1084} \quad (4)$$

To solve these equations some additional information is needed. Some of this may be obtained from spectra of solutions with  $C_L > C_M$  (Table 4). In such solutions hydrolysis is probably quite negligible. The data of Ahrland<sup>3</sup> also indicate that for the values of  $C_L$  and  $C_M$  used here the complexes  $\text{ML}_2$  and  $\text{ML}_3$  will be the dominating species. At least this holds if one uses the complex formation function obtained by Ahrland for those solutions that had the smallest excess of glycolic acid, thus comparable to the solutions of the present investigation with no such excess.

Then, assuming that the concentration of species absorbing at 1061 K is  $C_L \cdot y$  M and that the extinction coefficient of the other species (absorbing at 1084 K) is equal to that of the corresponding species of the first complex, the following equations are obtained:

$$122 = y \epsilon_{1061} \quad (5)$$

$$160 = (1-y) \epsilon_{1084} \quad (6)$$

Table 4. The uranyl system,  $C_L > C_M$ .

	$\nu$ K	$A \cdot d^{-1} C_L^{-1} *$ $M^{-1} cm^{-1}$	$(\Delta\nu)_{\frac{1}{2}}$ K
$C_M = 0.4 \text{ M}$ $C_L = 0.8 \text{ M}$	1062 1085	119 157	25 25
$C_M = 0.4 \text{ M}$ $C_L = 1.2 \text{ M}$	1062 1083	124 164	25 25
Mean	1062 1084	122 160	25 25

\* These values are corrected for overlapping as before (Table 2).

As there is still one unknown quantity too much, an assumption has to be made. The most reasonable one seems to be that  $\epsilon_{1061}$  is equal to the almost constant value found for the extinction coefficients of all the other systems absorbing in the spectral range 1060–1070 K (Table 2). Thus, assuming that  $\epsilon_{1061} = 145 \text{ M}^{-1} \text{ cm}^{-1}$ , eqns. (3)–(6) give:

$$x = 0.87_5; y = 0.84 \text{ and } \epsilon_{1084} = 1000 \text{ M}^{-1} \text{ cm}^{-1}; \epsilon_{1057} = 110 \text{ M}^{-1} \text{ cm}^{-1}.$$

The predominant species of the uranyl complex ML is thus the one absorbing at 1057 K. As it has almost as low an extinction coefficient as the copper complex the attribution of a chelate character to the ligand in this case seems justified. The species of the second and third uranyl complexes,  $ML_2$  and  $ML_3$ , which absorb at 1061 K are obviously different from the chelate absorbing at 1057 K. Probably they are of the kind with the OH group bonded to a water ligand of the metal ion *via* a hydrogen bond. The same must then hold true for the other systems with that remarkable constancy of extinction coefficients that has already been used in the calculation presented above.

Had, *e.g.*, the gadolinium ion been bonded to the OH group directly, one should expect a greater decrease of the absorption to be caused by this tripositively charged ion than by the copper ion. On the other hand, had there been a purely unidentate ligand in the complexes, bonded only through the carboxylate group, one should by analogy with the glycolic acid expect an increased frequency as well as a greater absorption intensity than for the free ligand.

If the bonding takes place via a water molecule as indicated above one should expect much the same spectral change irrespective of whether the water molecule is bonded to a tri- or a bivalent metal ion. From these conclusions the following generalisations are made:

## A. Species with pure chelated ligand:

$$\nu < 1058 \text{ K} \quad (\Delta\nu)_{1/2} \approx 30 \text{ K} \quad \varepsilon < 120 \text{ M}^{-1} \text{ cm}^{-1}$$

B. Species with ligand chelated *via* a water molecule:

$$1060 \text{ K} \leq \nu < 1070 \text{ K} \quad (\Delta\nu)_{1/2} \approx 25 \text{ K} \quad \varepsilon = 150 \pm 10 \text{ M}^{-1} \text{ cm}^{-1}$$

## C. Species with ligand bonded through the carboxylate group only:

$$\nu > 1080 \text{ K} \quad (\Delta\nu)_{1/2} \approx 25 \text{ K} \quad \varepsilon \gg 250 \text{ M}^{-1} \text{ cm}^{-1}$$

It is interesting to note that the species of type C are more abundant among the second and third uranyl complexes than among the first,  $1-y/1-x = 160/125$ , and that the large part of the first complex is of type A. This is in accordance with the data of Ahrlund.<sup>3</sup> Also it is interesting to note that Grenthe<sup>12</sup> finds it probable from enthalpy measurements, that the lanthanide complexes are of type B. If the interpretation given above is correct, it follows that whereas  $\text{Cu}^{2+}$  forms complexes of type A,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  form complexes of type B. This illustrates the delicate balance between the affinities of the ligand and of the water molecules towards the metal ion which governs the composition of the mixed  $\text{ML}_n(\text{H}_2\text{O})_m$  complexes in aqueous solution.

In this context it may be worth remarking that in principle one may expect complexes of a fourth type, call it D, of an outer-sphere kind. In such complexes all positions in the inner coordination sphere of the metal are occupied by water molecules, the ligands L occupying positions in the outer sphere of coordination only. Ligands bonded in this way can be expected to have vibration spectra very similar to that of the free ions. As absorption at 1074 K corresponding to the free glycolate ion does not seem to be present to any great extent it can be inferred that complexes of type D are not dominating in any of the glycolate systems investigated.

It can be asked why the different species have so different band intensities as they have. In the case of types A and B it is reasonable that a positive charge in close proximity to the oxygen atom in the C—OH group will tend to decrease the polarity of the  $\text{C}^+—\text{O}^-$  bond. Hence both frequency and above all intensity will decrease. This decrease will be greater if the charge is a metal ion capable of forming a covalent bond (type A) than if it is a proton in a water molecule forming a hydrogen bond only. The great increase of intensity of the type C complexes, however, is more difficult to explain. It is possible that the difference between the effect of the uranyl group ( $\varepsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and that of the proton ( $\varepsilon = 270 \text{ M}^{-1} \text{ cm}^{-1}$ ) depends upon the more central attachment of the positive ion in the former case which was discussed above. By inductive effects there may then be an increase of positive charge on the carbon atom in the COH group which increases the polarity of the  $\text{C}^+—\text{O}^-$  bond. This increase of charge will obviously be greater in the case of the  $\text{UO}_2^{2+}$  ion attached in direct line with the C—C bond.

A contribution to the solution of the question of whether a bidentate ligand is actually chelated in complexes or not can thus be offered by infrared spectroscopy (*cf.* Ref. 13). As the interpretations suggested here are very tentative, it is to be hoped that other spectroscopic techniques will also be

applied to solve this problem. The investigation of Larsen and Olsen<sup>14</sup> involving measurements of circular dichroism of optically active ligands seems very fruitful in this connection.

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