Studies on Uranyl Complexes : Part III—Potentiometric Investigation of Uranyl-Amino Acid Complexes

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Uranyl complexes with some α-, β- and γ-amino acids have been studied potentiometrically to determine the nature of coordination sites in these complexes. The amino group is not involved in coordination. Relative stabilities of the complexes are discussed.

Much of the stability constant data on uranyl-amino acid complexes are not consistent with respect to ionic medium, anion associated with the uranyl ion and the pH at which the constants have been calculated. Chelation of uranyl ion by amino acids itself appears to be uncertain. Many workers have reported that amino acids are bidentate chelating ligands for the uranyl ion, the chelation being effected through the carboxyl oxygen and amino nitrogen. The present authors have also reported data on uranyl complexes on the above basis. 

Further work in our laboratory, particularly polarography of uranyl-amino acid complexes has led us to believe that amino acids behave as monodentate ligands towards the uranyl ion. The present investigation was undertaken to establish the nature of binding of simple amino acids with the uranyl ion. If chelation does occur, study of complexes with ligands such as α-, β- and γ-amino acids should show the effect of the variation of ring size on the stability of the chelate. On the other hand, if the carboxyl group alone is involved in coordination, variation in complex stabilities should reflect changes in the basicity of the donor group with the structure of the ligand. The present results support the view that amino acids are only monodentate in their complexes with the uranyl ion.

Uranyl perchlorate, prepared from uranyl nitrate (AR BDH) by the standard procedure, was assayed by the zone's reductor method for uranyl content and by cation resin exchange for free acid. Standard carbonate-free sodium hydroxide (1 M) was used in all the titrations. The ligand acids (BDH or Fluka) were used as such. Sodium perchlorate was used to provide constant ionic strength at \( \mu = 0.1 \text{ M} \).

Procedure — An E.C.I.L. digital pH meter (accuracy, ± 0.01 pH unit) was used after standardising with potassium hydrogen phthalate buffer (0.05 \( M \); pH 4.01 at 30°) for pH titrations. All the titrations were carried out in a thermostated titration cell (30°). The cell was covered with a black paper during titration to eliminate any photochemical reaction of the photosensitive uranyl ion. After each addition of the titrant alkali the solution was stirred well by a magnetic stirrer and allowed to stand for 5 min for attainment of equilibrium.

The acidity constants of the acid and basic functions of the amino acids were determined by the method of Albert.

The lowering of the initial pH observed in the titration curves of the metal-amino acid mixtures (1:1) or higher against sodium hydroxide relative to the free ligand curve shows that complex formation occurs in all the cases. In all the cases an inflection occurs at one mole of base per mole of ligand followed by a buffer region. Precipitation was observed to occur in the neighbourhood of pH 5.4, at all metal-ligand ratios. To understand the nature of binding in these complexes, it is essential to know (a) whether the inflection in the titration curve below pH 3.5 is due to the neutralization of the COOH or the NH\(_2\) group of the acid which exists as H\(_2\)N—C\(_6\)H\(_4\)—COOH in the presence of perchloric acid and (b) the nature of the reaction occurring in the buffer region—whether it is hydrolysis or complexation.

According to Ahrlan et al., the hydrolysis of the uranyl ion follows a mechanism typified as 'mechanism IIIa'. The number of protons (Z) coming off per UO\(_2^{2+}\) during the reaction is given by:

\[
Z = \frac{[\text{NaOH}]-[\text{HClO}_4]+[\text{H}^+]-[\text{OH}^-]}{T_m}
\]

where [NaOH] and [HClO\(_4\)] are experimental concentrations and \( T_m \) is the total concentration of the metal ion used in the titration. A plot of \( Z/2 \) against \( (\log T_m + 2\phi ) \) for the various points in the titration curve using the hydrolysis constant \( \log k = -6.35 \) (ref. 13) should be a smooth curve if the reaction occurs according to mechanism IIIa.

In the present work, similar titrations of metal salt + HClO\(_4\) vs alkali were performed in the presence and in the absence of the ligand. The \( Z/2 \) values calculated for the metal + ligand titrations beyond the inflection point were found to be very similar to those calculated in the case of metal alone titration leading to the conclusion that the reaction occurring in the buffer region is hydrolysis. And since, in the titration of the metal in presence of the protonated ligand, the inflection occurs below pH 3.5, it is reasonable to infer that the carboxyl group gets deprotonated and complexes with the uranyl ion. The overall inference then is that only the carboxyl oxygen interacts with the metal ion and that there is no chelation. The plots of \( Z/2 \) vs \( (\log T_m + 2\phi) \) for various amino acids which fall on a line similar to that for the metal are shown in Fig. 1.

The \( \alpha \)-amino acids, DL-\( \alpha \)-alanine, DL-\( \beta \)-phenylalanine, DL-\( \alpha \)-amino-\( n \)-butyric acid, DL-\( \alpha \)-aminoisobutyric acid, DL-valine and DL-tryptophan con-
tain the glycine moiety $H_2N^+ - RC{{R}'} - COO^-$ with different substituents $R$ and $R'$ on the $\alpha$-carbon atom. The dissociation constant of the COOH group and hence the coordinating ability of the resulting COO$^-$ in these amino acids is low with $pK$ values in the range 2.3-2.5 due to the presence of the basic $-NH_2$ group on the adjacent carbon atom. Complexes formed by such ligands would be of low stability unless chelation through the amino nitrogen enhances it.

Titrations were performed with metal-ligand ratios 1:1, 1:2, and 1:5. In all the cases an inflection was observed corresponding to one mole of base per mole of ligand. The region of minimum hydrolysis and maximum complexation was selected from the $Z/2$ and $n$ values. Log $K_{ML}$ values were calculated at a few selected $pH$ values within this region using Irving and Rossotti equation\(^1\) and the mean taken (Table 1). Formation of higher (1:2) complexes is also indicated since the $n$ values exceed 1.5 in the 1:5 titration. However, since this happens at a higher $pH$, complexation and hydrolysis should be taken to occur simultaneously and hence the value of $K_{ML}$ obtained cannot be relied upon. The reported log $K_{ML}$ values for complexes of these ligands are consistent with their basicites.

In the case of $\beta$-alanine and DL-$\beta$-aminoisobutyric acid, the amino group is further away from the carboxyl compared to its position in $\alpha$-amino acids and the basicity of the ligands is therefore higher. More stable complexes resistant to hydrolysis at relatively higher $pH$ values can be expected with $\beta$-amino acids. Though $n$ values were found to increase to 1.5 at higher $pH$ values, calculations were however restricted to the 1:1 species only because of hydrolysis to some extent at higher $pH$ values. The log $K_{ML}$ values were 2.44 and 2.39 (Table 1) for $\beta$-alaninete and $\beta$-aminoisobutyrate complexes respectively ($pK_{COOH} = 3.6$ and 3.5).

In the $\gamma$-amino acids the amino group is still further away from COOH group and as a result the basicity of the ligands increases further to values near those for unsubstituted acids. It is found that the

### Table 1 - Stability Constant Data of Uranyl-Amino Acid Complexes

Temp. = 30°; $\mu = 0.1 \text{ M (NaClO)}_4$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\log K_{ML}$ COOH</th>
<th>$\log K_{ML}$ $-NH_2$ group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Alanine</td>
<td>2.48</td>
<td>9.67</td>
</tr>
<tr>
<td>DL-$\alpha$-Amino-$n$-butyric acid</td>
<td>2.36</td>
<td>9.60</td>
</tr>
<tr>
<td>$\alpha$-Aminoisobutyric acid</td>
<td>2.35</td>
<td>10.08</td>
</tr>
<tr>
<td>DL-Valine</td>
<td>2.41</td>
<td>9.49</td>
</tr>
<tr>
<td>DL-$\beta$-Phenylalanine</td>
<td>2.36</td>
<td>8.97</td>
</tr>
<tr>
<td>DL-$\gamma$-Tryptophan</td>
<td>2.33</td>
<td>9.40</td>
</tr>
<tr>
<td>$\beta$-Alanine</td>
<td>3.61</td>
<td>10.07</td>
</tr>
<tr>
<td>DL-$\beta$-Aminoisobutyric acid</td>
<td>3.53</td>
<td>9.91</td>
</tr>
<tr>
<td>$\gamma$-Aminoisobutyric acid</td>
<td>4.04</td>
<td>10.26</td>
</tr>
<tr>
<td>Isobutyric acid</td>
<td>4.76</td>
<td>10.26</td>
</tr>
</tbody>
</table>

References

The observed chemical shifts (\(\sigma\)) for azido-ammine cobalt(III) complexes are given in Table 1. The values are negative and the shifts are quite large, about 7500 to 9500 ppm relative to the reference complex \([K_3[Co(CN)_6]]\).

The paramagnetic contribution to the shielding tensor (\(\sigma_{\text{para}}\)) which dominates the \(^{59}\text{Co}\) chemical shifts has been calculated for these five complexes (Table 1) using the equation of Griffith and Orgel\(^7\). The data in column 3 can be compared with those of column 2 in which the observed values of relative chemical shifts are converted to the absolute values by adding \(\sigma_{\text{para}}\) for \([K_3[Co(CN)_6]\times 1.53\)

It is seen from Table 1, that successive replacement of \(\text{NH}_3\) ligand by \(\text{N}_3^-\) ion in the complexes results in an increase in the \(\sigma\) values which is also observed in the case of \(\text{aqo}\), oxalato\(^2\), cyano\(^3\), and carbonato\(^4\), series of Co(III)-ammine complexes. These shifts have also been associated with an increase in covalency\(^8\). Further, the increase in \(\sigma\) with successive increase in the number of azide groups in the complex means that the shielding decreases with the substitution of the electronegative group \(\text{N}_3\) in the coordination sphere of hexammine Co(III) complex.

To compare the above order with that obtained on the basis of the electronic spectral data, the electronic spectra of these complexes were recorded and a weak \(d-d\) absorption was observed in the visible region which may be assigned to the transition \(1A_1g \rightarrow 1T_2g\) of \(d^8\) configuration. The successive replacement of ammonia by azide decreases the energy separation between the ground and excited states.

In the case of the octahedral complexes of Co(III) of the type \([\text{Co(NH}_3]_6\)\(^{2+}\), two absorption bands are observed in the visible and near UV regions. These bands should be assigned to the transitions \(1A_1g \rightarrow 1T_g\) and \(1A_1g \rightarrow 1T_2g\) ref. (13, 14). When one of the ammonia molecules in the hexammine cobalt(III) is replaced by azide group, distortion of octahedral symmetry takes place due to ligand inequivalence.

It is seen from Table 1 that the band I (\(1A_1g \rightarrow 1T_g\)) is not split. Splitting has never been observed for band II because it is obscured by the tail of the intense charge-transfer absorption in the UV region. It is also interesting to note that the \(D'\) values calculated using Wentworth and Piper's relation\(^9\) go on increasing as more and more ammonia molecules are replaced by azide groups in the inner sphere of hexamminecobalt(III) complex. The increase in \(D'\) values can be correlated with increase in the covalency in the complexes of azido-amminecobalt(III) since the \(D'\) values depend upon \(r^3/R^2\), where \(r\) is the average radius of \(d\) shell in complex and \(R\) is the average radius of Co-ligand distance. Increase in \(D'\) values indicates either expansion of \(d\) orbitals or shortening of Co-azide distance. Either of these would be consistent with increased covalency in Co-ligand bond in the complexes under study. This is also supported by our NMR results.

Theory\(^7\) predicts a linear relation between the \(\lambda_{\text{max}}\) of the longest wave length \(d-d\) band and the applied field used for \(^{59}\text{Co}\) NMR in six-coordinated Co(III) complexes. A linear plot is observed when