R E S U M E

1. Studies on the complexes of amino acids with chromium(II)
   chloride, titanium(III) chloride, oxovanadium(IV) sulphate
   and oxouranium(VI) sulphate:

   The complex formation between Cr\(^{2+}\), Ti\(^{3+}\), VO\(^{2+}\) and
   UO\(_2\)^{2+} with various amino acids has been studied in solution.
   The composition of the complex species formed in solution
   was determined by potentiometry and conductometry. With
   chromium (II) chloride both sulphur containing amino acids
   viz., cysteine, taurine and methionine, and non sulphur
   containing amino acids such as glycine, DL-\(\alpha\)-alanine,
   \(\beta\)-alanine, DL-serine, DL-valine, L-proline, DL-leucine and
   L-asparagine were used. With other metal ions only non
   sulphur containing amino acids were employed. A combining
   ratio of 1:1 for the metal and amino acids was obtained in
   each of the complexes.

   The stability constants of the amino acid complexes
   were determined by conducting pH-metric titrations. The
   titrations were performed by employing mixtures containing
   (a) amino acid (b) metal and (c) amino acid + metal, using
   standard KOH as a titrant. The formation constants of the
   complex species were calculated applying Bjerrum's method
   simplified by Albert for amino acid system. By titrating
each aminoacid in the presence of various metallic ions, the pH-values were obtained after each addition of alkali. The values of \([\text{sc}]\), the concentration of free aminoacid and \(\bar{n}\) the average number of molecules of aminoacid bound by one atom of the metal were determined from the equations (IV) and (V) (Chapter I, page 153).

The formation curves (plots of \(\bar{n}\) versus \(-\log [\text{sc}]\)) are given in figures 2C to 35C in chapter I. From these curves the values of \(-\log [\text{sc}]\) were evaluated at \(\bar{n} = 1\) and subsequently the values of \(\log K_s\) by applying the relation, \(\log K_s = -2\log [\text{sc}]\) (Chapter I, page 154). The calculated values of \(\log K_s\) were determined by the addition of average values of \(\log K'_s\) and \(\log K''_s\). The values of overall stability constant, \(\log K_s\) obtained from the formation curves were found to be in good agreement with those calculated (table No. 36, Chapter I).

Various qualitative correlations may be obtained from the study of \(\log K_s\) values (summarised in the table No. 36, Chapter I) and comparing them with \(pK_s\)'s values of the corresponding aminoacids. The order of stabilities of aminoacid complexes can be classified into three categories namely, (I) aminoacid complexes containing \(\beta\)-alanine, DL-\(\alpha\)-alanine and L-proline, where the order of stability is:
$UO_2^{2+} \approx Cr^{2+} > Ti^{3+} > VO^{2+}$ (II) L-asparagine and DL-serine complexes where metals follow the order: $Ti^{3+} > Cr^{2+} \approx VO^{2+}$ $UO_2^{2+}$ and (III) in which metals fall in between the groups (I) and (II) e.g., $VO^{2+}$ $Cr^{2+}$ $UO_2^{2+}$ $Ti^{3+}$ and includes the aminoacids L-leucine and DL-valine. The aminoacids belonging to the first category have highest $pK_a$'s values e.g., L-proline (10.68), $\beta$-alanine (10.66) and DL-$\alpha$-alanine (9.97) whereas the two aminoacids, L-asparagine and DL-serine belonging to second category have the lowest $pK_a$'s values. The rest of the aminoacids have $pK_a$'s values in between (I) and (II).

The order of stability constants in the metal complexes, in general, is: L-proline $> \beta$-alanine $> DL-\alpha$-alanine $> \gamma$-alanine $> LD$-valine $> DL$-serine $> L$-asparagine, which is roughly the same as that of the $pK_a$'s order of the aminoacids e.g., L-proline (10.68), the highest and L-asparagine the lowest (8.85).

In case of $Cr^{2+}$ complexes with sulphur containing aminoacids, the order of stability constants is: Cysteine $> \text{methionine} > \text{taurine}$ (table No. 36, Chapter I), which runs parallel to the order of $pK_a$'s values of cysteine (10.28), methionine (9.34) and taurine (9.08). By comparing the log $K'$ and log $K_a$ values of cysteine complex with those of
corresponding glycine and DL-α-alanine complexes, the
higher stability of cysteine complex is attributed to the
involvement of sulphur in coordination. This view is
further strengthened by the fact that besides -NH₂ and
COO⁻ groups, the log K¹ and log K₂ values of taurine were
much lower than that for cysteine. On the basis of these
comparisons, the coordination through COO⁻, NH₂ and S-
has been suggested in the cysteine complex. In Cr²⁺-
methionine complex, only two coordination sites viz., COO⁻
and -NH₂ are involved as may be concluded on the basis of
similar comparisons.

CONCLUSION:-

Chromium (II) chloride, titanium(III) chloride,
oxovanadium(IV) sulphate and oxouranium(VI) sulphate form
(1:1) complexes with aminoacids namely, glycine, L-asparagine,
DL-valine, DL-serine, DL-proline, DL-leucine, L-leucine,
DL-methionine, cysteine and taurine. The stability of
aminoacid complexes increases with increase in pKₐ's values
viz., L-proline being the highest and L-asparagine the
lowest. Uranyl complexes have the highest log K₃ values
for the aminoacids with largest dissociation constants e.g.,
β-alanine, DL-α-alanine and L-proline against Ti³⁺ complexes
having highest log K₃ values with aminoacids of lowest
dissociation constants e.g., L-asparagine and DL-serine. Cr^{2+} and WO^{2+} complexes have almost the same stabilities and give highest values with amino acids having pK_a's value in the middle of the amino acid series. In general, the stability of the amino acid complexes decreases with increase in the chain length of the carbon atoms and the distance between amino and carboxylic groups. The coordination in the Cr^{2+}-cysteine complex takes place through COO^-, -NH_2 and -SH groups, whereas in the methionine complex it occurs only through -NH_2 and COO^- groups.

2. Behaviour of Copper(I) iodide in aqueous potassium iodide containing amino acids:

Evidence for the complex formation between insoluble copper(I) ion and amino acids has been obtained on the basis of solubility studies. The studies consist of the determination of copper(I) in two sets of solution, the one without and the other with amino acid. From the solubility data, there is an appreciable difference in Cu^+ contents of the two sets (table 2A, 2B and 2C, Chapter II). This is an indirect evidence for the complex formation in the amino acid system consisting of Cu_2I_2, KI and amino acid in aqueous medium.

The concentration of Cu_2I_2 combined with amino acid was determined by subtracting the concentration of Cu_2I_2 in
aqueous potassium iodide without aminoacid from that of Cu₂I₂ with the same concentration of KI but in the presence of aminoacid. The concentration of aminoacid consumed in complex formation was calculated by the difference of the concentration of aminoacid added initially and that of estimated from the Cu₂I₂ solution colorimetrically.

From the solubility data there is evidence for the formation of 1:1 complex species with L-leucine and L-proline, and 1:2 complex in case of glycine. The coordination in 1:1 species occur through amino and carboxylic groups with the subsequent replacement of one proton from the latter. In 1:2 complex the mechanism consists of the formation of 1:1 complex with copper(I) in the initial stage and subsequent formation of 1:2 chelate due to the oxidation of copper(I) to copper(II).

The plot of free aminoacid concentration [L] and Ksp, the solubility product of the aminoacid complex gives straight lines with slopes of 1:1 for L-leucine and L-proline, and 1:2 for glycine supporting thereby the results of solubility measurements (figure No.2, Chapter II).

Conclusion:

The composition of the complexes formed by the interaction of copper(I) and aminoacid has been determined
on the basis of solubility measurements. The concentration of copper(I) varies significantly when aminoacid is added to the solution of Cu$_2$I$_2$ in aqueous potassium iodide. The difference in copper(I) contents gives the actual concentration of copper(I) combined with aminoacid in complex formation. A ratio of 1:1 is obtained for L-leucine and L-proline complexes and 1:2 for glycine complex. From the slopes of the linear plots of solubility product of aminoacid complex, $K_{sp}$ and $[L]$; the free aminoacid concentration, same combining ratios for metal aminoacid complexes are obtained, thus confirming the results of solubility measurements.

3. **Substitution reactions of square planar tetra Kis (thiourea) palladium(II) chloride with some aminoacids:**

The kinetic of the substitution reactions of square planar tetra Kis (thiourea) palladium(II) chloride, Pd(tu)$_4$Cl$_2$ with various aminoacids viz., glycine, DL-$\alpha$-alanine, threonine, L-asparagine, DL-valine, DL-serine and L-proline have been studied by spectrophotometric method. The studies showed that these reactions proceed by a displacement mechanism following a two term rate law. The applicability of two term rate law in the substitution reaction of Pd(II) complexes is demonstrated by the linear plots obtained by
plotting $K_{\text{obsd.}}$, the first order rate constant determined experimentally versus $[Y]$, the concentration of aminoacid (figure No. 8, Chapter III). The values of $K_1$ and $K_2$, the first and second order rate constants, respectively, were determined from the intercepts and slopes of the linear plots (table No.8., Chapter III). Following Basolo, the rate constant $K_1$ represents the slow displacement of thiourea molecule by the solvent $H_2O$ which is then readily displaced by the aminoacid. A direct nucleophilic displacement of thiourea by aminoacid is responsible for $K_2$. The mechanistic path for such type of substitution reaction may be represented as

$$tu \rightleftharpoons Pd \rightleftharpoons tu \quad 2H_2O \quad tu \rightleftharpoons Pd \rightleftharpoons H_2O \quad 2tu \quad tu \rightleftharpoons Pd \rightleftharpoons H_2O$$

As a typical example, the $K_{\text{obsd.}}$ values at 35°C for the various aminoacids of 0.1M concentrations follow the order: glycine (8.625) > DL-valine (5.75) > DL-serine (4.876).
L-proline (4.10) > DL-threonine (3.63) > DL-\(\alpha\)-alanine (3.03) > L-asparagine (2.99). The order of increasing ionization constants of \(\alpha\)-amino carboxylic group is: DL-valine > glycine > DL-serine > threonine > L-asparagine > L-proline. A comparison of the two series indicate the increase in \(K_{\text{obsd.}}\) values with increase in ionization constants of \(\alpha\)-amino carboxylic group and consequently the influence of ionization constant on the extent of substitution of aminoacid in the complex.

**Conclusion:** The mechanism of substitution reactions of square planar \(\text{Pd(tu)}_4\text{Cl}_2\) with various aminoacids have been investigated, spectrophotometrically. The kinetics found to follow the two term rate law expressed as \(K_{\text{obsd.}} = K_1 + K_2[Y]\) where \(K_{\text{obsd.}}\) is the first order rate constant determined experimentally, and \(K_1\) and \(K_2\) from the intercept and slope of the linear plots of \(K_{\text{obsd.}}\) versus \([Y]\). \(K_1\) represents the slow displacement of thiourea molecule by the aminoacid whereas \(K_2\) is responsible for the direct nucleophilic displacement of thiourea by aminoacid. The influence of ionization of carboxylic group on the extent of substitution of aminoacid in the complex, \(\text{Pd(tu)}_4\text{Cl}_2\) is obvious on comparing the order of \(K_{\text{obsd.}}\) values for various aminoacid complexes and the corresponding ionization constant values for each aminoacid. With the exceptions of DL-\(\alpha\)-alanine and L-proline, there is an increase in \(K_{\text{obsd.}}\) values of
aminocacid complexes with an increase in the ionization constant of the corresponding \(-\)aminocarbonylic group in the aminocacid series.

4. **Metal complexes of alkaloids**

The complexes of alkaloids with some transition metal ions such as Ti\(^{3+}\), VO\(^{2+}\), UO\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\) and Cr\(^{3+}\) have been synthesised. The complexes with codeine were synthesised with a large group of metal ions namely, VO\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\), Ti\(^{3+}\) and Cr\(^{3+}\). Unlike alkaloids, their complexes are in general, highly soluble in water but insoluble in common organic solvents such as alcohol, acetone, ether, chloroform, tetrahydrofuran etc. The results of chemical analyses indicate a ratio of 1:2 (metal:ligand) for quinaldine and codeine complexes, and 1:1 for brucine and quinine complexes.

Infra red spectra of the complexes were studied in order to determine the possible coordination sites in the metal-alkaloid complexes. Useful informations were obtained regarding the nature of coordination on comparing the spectra of the complexes with those of the respective alkaloids and correlating the major changes or shifts occurring in the bands assigned to donor groups pertinent to coordination.
Due to the presence of various functional groups, spectra of the alkaloids consist of numerous bands and it is a remote possibility to give specific assignments to every band. But some of them may be definitely assigned on the basis of spectral data available in literature.

The infra red spectra of quinaldine and its complexes with TiCl₃, VOCl₂ and UO₂SO₄ give some useful information regarding the bonding in these complexes. The main information is obtained from the changes occurring in the regions ca. 1000 cm⁻¹ and 850 - 700 cm⁻¹ assigned to the ring skeletal and CH out of plane deformation vibrations, respectively. The bands arising from ring skeletal vibrations and those from CH out of plane deformation modes are shifted to higher wave numbers together with increase in intensities (table 1, Chapter IV). The changes in the above mentioned regions are more pronounced in the VO²⁺ complex and may be explained in terms of σ-bonding through vacant d orbital of the metal, and delocalized σ orbital of the heterocyclic nitrogen. The Ti³⁺ complex also shows similar changes, but to a lesser extent. However, in the UO₂²⁺-quinaldine complex the changes are least pronounced.

On the basis of the changes in the spectra of quinaldine complexes, the coordination through heterocyclic
nitrogen is inferred, although the bond strength decreases from \( \text{VO}^{2+} \) to \( \text{VO}_2^{2+} \).

In quinine alkaloid, there are three pertinent coordination sites namely, the nitrogen atoms of 6-methoxyquinoline and quinuclidine rings, and a secondary hydroxyl group. The infra red spectra of \( \text{Ti}^{3+} \) and \( \text{VO}^{2+} \) complexes give some definite information regarding the bonding in these complexes at one of the possible sites.

The secondary hydroxyl stretching vibrations appeared at 3650 cm\(^{-1}\) in the quinine alkaloid are shifted to lower frequencies on coordination and the CH stretching vibrations appearing near 3000 cm\(^{-1}\) show the same behaviour. A possible consequence from the shifts in CH and CH stretching vibrations is the involvement of heteroatomic nuclues of the substituted quinoline in coordination. Further evidence in favour of coordination through heterocyclic nitrogen is obtained on considering the changes occurring in the regions of ring CC, CN stretching vibrations of 6-methoxy quinoline, ring skeletal vibrations of heterocyclic aromatic ring and CH out of plane vibrations. The bands in these regions are usually shifted to higher frequency side with an increase in the number of bands.

There is not much evidence for the coordination through nitrogen of quinuclidine ring in the complexes of quinine.
The spectrum of the quinine shows a medium intensity band at 1040 cm\(^{-1}\) and is assigned to CN stretching modes of heteroparaffinic ring. This band shifts to lower frequency side in the spectra of the complexes viz., Ti\(^{3+}\) (1010 cm\(^{-1}\)) and V\(^{2+}\)(1020 cm\(^{-1}\)). Besides the slight shifts in CN stretching modes, there is a paucity of information in favour of the coordination through more basic and reactive nitrogen of quinuclidine ring.

Brucine is a complex alkaloid belonging to indole group, containing several ring systems, e.g., pyrrocoline, tetrahydroindole, keto-piperazine and 1-oxa \(\Delta\)-3-cycloheptane together with various functional groups such as CH\(_3\)O, -NHCO, CH\(_2\) - N= CH\(_2\) etc. The infra red spectral studies were carried out to ascertain the possible coordination sites in the complexes of brucine with VOCl\(_2\), TiCl\(_3\) and UO\(_2\)SO\(_4\).

In the alkaloid, brucine, there are three positions susceptible to coordination namely, -NHCO, acylazole group, the oxygen of a 7-membered oxepine ring and the tertiary nitrogen of CH\(_2\) - N - CH\(_2\) present in the 5/6 pyrrocoline ring. In the spectrum of brucine, the CO and CN stretching modes of n-acylazole group, belonging to keto-piperazine ring system occurred at 1626 cm\(^{-1}\) and 1335 cm\(^{-1}\), respectively. However, no such bands appeared at these positions in the
complexes. The bands arising from CC, CO stretching vibrations of the oxepine ring, and CN stretching of the tertiary bridge head nitrogen present in the 5/6 pyrrocoline ring, appeared at 1450 cm$^{-1}$ and 1090 cm$^{-1}$, do not show any shift on coordination. Summarising the available information from the infra red spectra of the brucine and its complexes, there is ample evidence for the coordination through nitrogen of acylazole group.

The infra red spectra of codeine and its complexes with Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, VO$^{2+}$, Mn$^{2+}$, Ti$^{3+}$ and Cr$^{3+}$ give some reliable information regarding the bonding in these complexes. There are three possible coordination sites in the codeine namely, the secondary/hydroxyl group, tertiary nitrogen attached to methyl group and the oxygen of the furan ring.

The medium intensity band at 3600 cm$^{-1}$ in the spectrum of the codeine is assigned to secondary OH group stretching vibrations. However, in the complexes no such band appeared at this frequency. In the Ni$^{2+}$, Co$^{2+}$ and Cu$^{2+}$ complexes, this band is shifted to much lower frequency whereas in the spectra of Mn$^{2+}$, VO$^{2+}$, Ti$^{3+}$ and Cr$^{3+}$ complexes, there is no band in the region ca.3500-3600 cm$^{-1}$ or in the vicinity. The absence of the bands at this frequency e.g., 3600 cm$^{-1}$ or in the neighbouring region is a clear indication of the coordination of the metal through hydroxyl group. The band
at 2710 cm\(^{-1}\) arising from N-CH\(_3\) stretching in the codeine and those from ring CC, CO stretching, CH in and out of plane, and ring skeletal vibrations of dihydrofuran ring system remain almost unaltered in the complex (table No. 4, page 235). This clearly indicates the very remote possibility of coordination through these two coordination sites viz., -NCH\(_3\) and oxygen of the dihydrofuran ring.

**Conclusion:**

The main evidence in favour of the coordination through heterocyclic nitrogen in the quinaldine complexes with Ti\(^{3+}\), VO\(^{2+}\) and UO\(_2\)^{2+} is the exhibition of some marked changes usually associated with the spectra of coordinated heterocyclic amines e.g., shifting of the bands to the higher wave numbers together with increase in their numbers. In quinaldine this phenomenon is specially observed in the regions of ring CC, CN stretching vibration (Ca. 1600 cm\(^{-1}\)) and CH out of plane deformations (Ca. 800 cm\(^{-1}\)).

On the basis of studies on the infra red spectra of Ti\(^{3+}\) and VO\(^{2+}\) complexes with quinines, there is a sufficient evidence for coordination through the heterocyclic nitrogen of 6-methoxyquinoline. This conclusion is derived on the basis of the observed shifts to higher frequencies in the regions of ring CC, CN stretching, ring skeletal and CH out of plane vibrations of substituted quinoline ring on
coordination together with increase in the number of bands. Although the nitrogen of the quinuclidine ring is more basic and electrons are readily available due to reduced "F-strain," but there is little evidence of coordination as indicated by the infra red spectra of the complexes.

The possibility of coordination in brucine arises due to the presence of three important donor groups e.g., -NCO group, a part of keto-piperazine ring, the oxygen of the seven membered oxapine ring, and the tertiary bridge head nitrogen present in the 5/6 pyrrocoline ring. The infra red spectra of the alkaloid and its complexes with VOCl₂, TiCl₃ and UO₂SO₄ indicate coordination through nitrogen of acylazole group as revealed by the disappearance of CO and CN stretching vibrations in the complex. These modes occur at 1625 cm⁻¹ and 1335 cm⁻¹, respectively. The position of the other bands arising from CC, CO stretching vibrations of the oxapine and those from CN stretching of the tertiary nitrogen present in the 5/6 pyrrocoline ring remains almost constant on coordination.

The information obtained from the spectra of the codeine and its complexes with Cu²⁺, Cd²⁺, Ni²⁺, Mn²⁺, V⁰²⁺, Ti³⁺ and Cr³⁺ reveals the possibility of coordination through secondary OH group. The main evidence in favour of coordination through
OH is the absence of any band at 3600 cm\(^{-1}\) (OH stretching) or in the vicinity in the spectra of the complexes. The evidence is further supported by the non-shifting of the bands arising from \(\text{NCH}_3\) stretching modes, and ring CC, CO stretching, ring skeletal, and CH in and out of plane vibrations of dihydrosubstituted furan ring present in the alkaloid on complexation.
Studies on the complexes of chromium(II) chloride with some amino acids

Introduction

The complexes of transition metals with amino acids are of interest because of the biological importance of this family of compounds, and the presence of potential coordinating amino and carboxylic groups. Albert has carried out a detailed study on the stability constants of various amino acid complexes, based upon pH and potentiometric measurements. He showed that the reactivities of various amino acids towards a metal ion were dependent on the stability of the resulting complexes and ionization constants. However, no attempt has been made so far to study the amino acid complexes with unstable oxidation states. The present communication reports on the composition and stabilities of chromium(II) chloride complexes of some amino acids.

Experimental

The amino acids, glycine, L-proline, DL-serine, β-alanine, DL-α-alanine, L-asparagine, L-leucine and DL-valine (B.D.H. biologically pure products) were used.

and 0.01 M solutions were prepared in doubly-distilled, air-free water.

Chromous chloride was prepared by the method of Bathis and Baier. Chromic chloride was first reduced to chromous chloride with zinc–hydrochloric acid, and then precipitated as chromous acetate by adding ammonium acetate. The red precipitate of chromous acetate was dissolved in a minimum quantity of hydrochloric acid. The chromous chloride formed was precipitated with absolute alcohol, separated, and washed several times with small aliquots of ice-cold, air-free, doubly-distilled water. It was then dissolved in doubly-distilled water and the solution kept in an air-tight storage vessel in an atmosphere of nitrogen (pH of solution, 3.5). The solution was standardized potentiometrically by titrating with standard copper sulphate.

Carbonate-free KOH was used for preparing the aqueous solution of KOH which was stored in a Pyrex bottle fitted with a tube containing KOH for protection against atmospheric carbon dioxide. The solution was standardized by titrating with standard oxalic acid, and checked periodically before carrying out the pH-metric titrations.

The potentiometric titrations were carried out using a Tinsley potentiometer with lamp and scale arrangements using platinum and calomel as indicator and reference electrodes, respectively. The pH-metric titrations were made with a direct reading EIL pH-meter, model 23A (England), using glass and calomel electrodes. All titrations were carried out in a specially designed cell with provision for transferring the chromous chloride solution from the storage vessel and for passing oxygen-free nitrogen in order to stir the solutions. The concentration of the chromous chloride solution was checked before the study of each system.

Result and discussion

The composition of the complexes with amino acids was determined potentiometrically by titrating with standard copper sulphate.

Fig 1 Potentiometric titrations (A) 10 ml 0.666 × 10⁻¹ M CrCl₂ (in cell) to 0.666 × 10⁻¹ M DL-serine (from burette), (B) 10 ml 0.50 × 10⁻¹ M CrCl₂ (in cell) to 0.50 × 10⁻¹ M DL-serine (from burette), (C) 10 ml 0.44 × 10⁻¹ M CrCl₂ (in cell) to 0.44 × 10⁻¹ M DL-serine (from burette).

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metrically by taking various concentrations of chromous chloride (in the cell), and equimolar solutions of amino acids (from the burette). In all cases a ratio of 1:1 (chromium(II) amino acid) was obtained from the potential concentration curves (Fig 1 for DL-serine). Information concerning complex formation was obtained from pH-metric titration curves. For each amino acid, three sets of pH metric titrations were carried out in the order: (a) amino acid (0.01 M), (b) chromous chloride (0.005 M), and (c) a mixture of chromous chloride and amino acid having a total concentration of 0.005 M and 0.01 M respectively, using 0.1 N KOH as titrant. The pH curves of all the amino acids show a definite shift indicating the formation of complexes of chromous chloride with amino acids (Fig. 2 for DL-serine).

The complex formation constant $K_c$ was evaluated following the method of Albert. The values of $\log K_c$ at $n = 1$ (where $n$ is the average number of molecules of amino acid bound by one atom of the metal) for various amino acids were calculated from the values of $-\log [Sc]$ obtained by the plot of $n$ against $-\log [Sc]$ (Fig. 3) ($[Sc]$ is the concentration of free amino acid). By application of relation (xii) of ref. 4.

![Graphical representation](image)

**Fig. 2** pH metric titrations (A) 50 ml 0.01 M DL-serine (in cell) (B) 25 ml 0.02 M DL-serine + 25 ml 0.01 M CrCl$_2$ (in cell) (C) 50 ml 0.005 M CrCl$_2$ (in cell)

**Fig. 3** Formation curves (A) DL-serine chromium(II) complex (B) DL-valine chromium(II) complex (C) DL-proline chromium(II) complex

**Table 1**

<table>
<thead>
<tr>
<th></th>
<th>Graphically</th>
<th>Calculated</th>
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<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>DL α-Alanine</td>
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</tr>
<tr>
<td>3</td>
<td>β-Alanine</td>
<td>9.86</td>
</tr>
<tr>
<td>4</td>
<td>Glycine</td>
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<tr>
<td>6</td>
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</tr>
<tr>
<td>8</td>
<td>DL-Valine</td>
<td>8.70</td>
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the values of \( \log K \), for various amino acids were evaluated. The values obtained graphically and by calculation are given in Table 1.

The values of overall stability constants obtained from the formation curve (Fig. 3) are in good agreement with those calculated.

There does not seem to be any definite correlation between the nature of the amino acid and the \( K \) value; however, with a few exceptions the value of \( K \) decreases with increase in chain length of carbon atoms and also seems to decrease as the distance between amino and carboxylic groups increases. These observations could not be quantitatively substantiated as no information could be obtained as to the nature of the bounding because the complexes could not be isolated. The present studies are the first to report on the chemical reaction of unstable chromium(II) ions with amino acids, and the stabilities of the resulting complexes.

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Studies on the composition and stability of uranyl, vanadyl and titanous complexes with some amino acids

A number of papers on the metal complexes of amino acids have appeared in the literature in recent years. These studies are mainly concerned with the determination of the stability constant of a complex by various electrometric methods, viz. potentiometry, pH-metry, polarography, etc. References to studies on the complexes of Cu, Zn, Fe, Ni, Co, Mn, Cd and other transition metals are available but no attempt has yet been made to investigate possible complex formation between VO$^{2+}$, UO$^{2+}_2$ and Ti$^{3+}$ ions with amino acids.

The present communication deals with the behaviour of these ions towards some amino acids. Formation of 1:1 complexes has been indicated by conductometric titrations, and the stability constants of the complexes have been computed from the results of pH-metric titrations.

Experimental

Amino acids such as glycine, β-alanine, DL-α-alanine, L-asparagine, DL-serine, L-leucine, DL-valine and L-proline (BDH biologically pure) were used for the experiments and their solutions (0.01 M) were prepared in doubly-distilled water.

Uranyl sulphate (BDH AnalaR), and vanadyl sulphate (BDH) were employed and solutions of these salts were analysed gravimetrically as the metal oxides$^5$$^6$. An aqueous solution of titanium(III) chloride was prepared by dissolving crystals$^7$ of TiCl$_3$  6 H$_2$O in air-free doubly-distilled water, and the solution standardized$^8$. Fresh solutions were always prepared before use and kept covered with a layer of kerosene oil or toluene throughout the investigations to avoid oxidation.

Carbonate-free KOH solution was used for pH-metric titrations. It was stored in a Pyrex bottle fitted with a KOH tube for protection against atmospheric CO$_2$. The solution was standardized by titrating with standard oxalic acid solution, and the strength was checked periodically before carrying out pH-metric titrations.

The conductometric titrations were performed using a Philips conductivity bridge model PR 9500/90 and a dip type conductivity cell (cell constant 1.48). The pH-metric titrations were carried out with a direct reading EIL pH-meter model 23A using glass and calomel electrodes. All the titrations were carried out in a specially designed cell, with provision for adding metal salt solutions from a burette, to a stirred oxygen-free system.

Results and discussion

The composition of the vanadyl, uranyl and titanous complexes with various amino acids was determined conductometrically. The conductometric titrations were reversible. In all cases a ratio of 1:1 (metal:amino acid) was established. Typical curves are given in Fig. 1. The pH-metric titrations were performed in triplicate for each amino acid. The titrations were carried out in the order (a) amino acid (0.01 M),
Fig. 1 Reverse conductometric titrations (1) M/15 TiCl₃ added to 40 ml of M/300 DL-serine, (2) M/12 UO₂SO₄ added to 40 ml of M/240 DL-α-alanine, (3) M/15 VOSO₄ added to 40 ml of M/300 DL-valine.

Fig. 2 Formation curves (A) DL-valine-VOSO₄ complex, (B) DL-α-alanine-UO₂SO₄ complex, (C) DL-serine-TiCl₃ complex.

Table 1

<table>
<thead>
<tr>
<th>Amino acids</th>
<th>Vanadyl sulphate</th>
<th>Uranyl sulphate</th>
<th>Titanous chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Graphical</td>
<td>Theoretical</td>
</tr>
<tr>
<td>L-Asparagine</td>
<td>6.95</td>
<td>6.90</td>
<td>6.88</td>
</tr>
<tr>
<td>DL-α-Alanine</td>
<td>8.75</td>
<td>8.70</td>
<td>9.00</td>
</tr>
<tr>
<td>Glycine</td>
<td>× ×</td>
<td>8.62</td>
<td>8.65</td>
</tr>
<tr>
<td>L-Leucine</td>
<td>9.08</td>
<td>9.10</td>
<td>8.61</td>
</tr>
<tr>
<td>L-Proline</td>
<td>10.33</td>
<td>10.30</td>
<td>10.46</td>
</tr>
<tr>
<td>DL-Serine</td>
<td>7.54</td>
<td>7.50</td>
<td>6.86</td>
</tr>
<tr>
<td>DL-Valine</td>
<td>8.65</td>
<td>8.65</td>
<td>8.59</td>
</tr>
</tbody>
</table>

(b) metal salt (0.005 M) and (c) metal salt and amino acid (total concentration 0.005 M and 0.01 M, respectively), employing 0.1 N KOH as titrant. The pH-titration curves show appreciable shifts, indicating the formation of complexes with the amino acid (Fig. 3). The complex formation constant $K_c$ was evaluated by the method modified by Albert^4. The values of log $K_c$ at $\bar{n} = 1$, where $\bar{n}$ is the average number of molecules of

amino acid bound by one atom of the metal ion, were calculated from the values of $-\log [\text{Sc}]$ obtained by plotting $n$ vs. $-\log [\text{Sc}]$ (Fig. 2). $[\text{Sc}]$ is the concentration of the free amino acid. The values of $\log K^\alpha$ for various amino acids evaluated from the formation curves, and those calculated are given in Table 1.

The values of the overall stability constants $\log K^\alpha$, obtained from the formation curves (Fig. 2), are in good agreement with those calculated.

Uranyl sulphate, vanadyl sulphate and titanous chloride form 1:1 complexes with various amino acids (L-asparagine, $\beta$-alanine, DL-$\alpha$-alanine, glycine, L-leucine, L-proline, L-serine and DL-valine). In the vanadyl and titanous complexes the values of $\log K^\alpha$ vary from L-asparagine (6.95, 7.25) to L-proline (10.33, 10.08), whereas in uranyl complexes the variation is from DL-serine (6.86) to L-proline (10.46). There does not seem to be any correlation between the nature of the aminoacids and the $K^\alpha$ values although, with a few exceptions, the latter decreases with increase in chain length of carbon atoms. The real nature of bonding in these complexes is a matter of speculation as no complex could be isolated in a sufficiently pure form.

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Complexes of chromium(II) chloride with some sulphur-containing amino acids

The interaction of transition metal ions with amino acids covers a vast area of research because of its biological importance, and the coordinating ability of amino and carboxylic groups. However, very few papers deal with the interaction of amino acids with transition metals having abnormal oxidation states. Recently a systematic study on this aspect of the problem was undertaken by the authors and the complexes of Cr$^{2+}$, UO$_2$$^{2+}$, VO$^{2+}$ and Ti$^{3+}$ with non-sulphur containing amino acids were studied. The present communication deals with the composition of various sulphur-containing amino acid complexes, based upon pH-metric and potentiometric measurements.

Experimental

The amino acids, DL-methionine, taurine and cysteine (B.D.H. Biologically pure products) were used and 0.01 M solutions were prepared in doubly distilled air-free water. Chromous chloride was prepared by the method of Bathis and Bailer. The aqueous solution of chromous chloride was prepared as described previously, and stored in an air-tight storage vessel under an atmosphere of oxygen-free nitrogen (pH 3.5). The solution was standardized potentiometrically by titration with standard copper sulphate. Carbonate-free KOH was used to prepare an aqueous solution of KOH and the solution was kept in a Pyrex bottle fitted with a guard tube containing KOH for protection against atmospheric carbon dioxide. The solution was standard-

ized by titrating with standard oxalic acid and checked periodically before carrying out the pH-metric titrations.

The potentiometric titrations were carried out with a Tinsley potentiometer having a lamp and scale arrangement and employing platinum and calomel electrodes. The pH-metric titrations were performed with a direct reading EIL pH-meter model 23A (England). All the titrations were carried out in a specially designed cell described previously. The concentration of chromous chloride was checked before studying each system. All investigations were carried out at 25°C.

Results and discussion

Chromous chloride forms 1:1 complexes with DL-methionine, taurine and cysteine as determined from potentiometric curves (Fig. 1). The titrations were carried out using various concentrations of chromous chloride in the cell and equimolar solution of amino acids. The information regarding complex formation was obtained by noting the shifts in the pH-titration curves.

For each amino acid three sets of pH-metric titrations using 0.1 N KOH as a titrant were carried out in the order: (a) amino acid 0.01 M, (b) chromous chloride 0.005 M and (c) a mixture of chromous chloride and amino acid having a total concentration of 0.005 M and 0.01 M, respectively, (Fig. 2).

The values of the logarithm of the formation constant, log $K_n$ at $n = 1$ (where $n$ is the average number of molecules of amino acid bound by one atom of the metal) for the amino acids were calculated from the values of $-\log [S_c]$ obtained by the plot of $n$ vs. $-\log [S_c]$, where $[S_c]$ is the concentration of free amino acid (Fig. 3). By applying the relation $\log K_n = -2 \log [S_c]$, values of the formation constants for all three amino acids were evaluated. The values obtained graphically and by calculation
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Fig. 2 pH-metric titrations. (A) 50 ml 0.01 M DL-methionine (in cell), (B) 50 ml 0.005 M CrCl₂ (in cell), (C) 25 ml 0.02 M DL-methionine + 25 ml of 0.01 M CrCl₂ (in cell).

Fig. 3 Formation curves. (A) DL-methionine-chromium(II) complex, (B) taurine-chromium(II) complex, (C) cysteine-chromium(II) complex.

The values of overall stability constants obtained from the formation curves are given in Table 1.

The values of overall stability constants obtained from the formation curves are in good agreement with those calculated. The values of log Kₙ given in Table 1 are given as an indication of the possible correlation between the nature of the amino acids and overall stability constants. The value of log Kₙ decreases as the distance between amino and carboxylic group increases (between NH₂ and −SO₂OH in the case of taurine). The present studies do not clarify the part played by sulphur atoms.

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