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

The complexes of chromium (II) chloride, titanium(III) chloride, oxovanadium(IV) sulphate and oxouranium(VI)sulphate with various amino acids such as glycine, L-asparagine, DL-valine, DL-serine, DL-leucine, L-leucine, L-proline, DL-α- alanine and β-alanine have been studied in solution. With chromium(II) chloride, the interaction with sulphur containing amino acids such as cysteine, methionine and taurine has also been studied. The studies are mainly concerned with the composition and stability of metal aminoacid complexes formed in solution by employing electrometric techniques of potentiometry and conductometry.

A combining ratio of 1:1 for the metal and aminoacid was obtained in each of the complexes as is evident from the results, of electrometric titrations. The stability constants of the aminoacid complexes were determined by performing pH-metric titrations with the mixtures containing (a) aminoacid, (b) metal and (c) aminoacid + metal, using standard KOH as a titrant. The value of formation constant was evaluated by applying Bjerrum's method, simplified by Albert for aminoacid system.
The observed and the calculated values of the stability constants for the various metal aminoacid complexes are given in table 36, chapter I. It appears that the observed values were in good agreement with those calculated from the equations IV, V, VI, VII and IX, chapter I.

For β-alanine, DL-α-alanine and L-proline complexes, the order of stability is: UO$_2$$^{2+} \approx$ Cr$^{2+} >$ Ti$^{3+} >$ VO$^{2+}$. In case of L-asparagine and DL-serine complexes, the metals follow the order: Ti$^{3+} >$ Cr$^{2+} \approx$ VC$^{2+} >$ UO$_2$$^{2+}$. The order of stability of L-leucine and DL-valine complexes is: VO$^{2+} \approx$ Cr$^{2+} >$ UO$_2$$^{2+} >$ Ti$^{3+}$. In general, the order of stability constants in metal complexes is: L-proline > β-alanine > DL-α-alanine > glycine > L-leucine > DL-valine > DL-serine > L-asparagine, which with a few exceptions is the same as that of increasing pK$_a$ order of aminoacids.

The Cr$^{2+}$ complexes with sulphur containing aminoacids follow the stability order: cysteine > methionine > taurine. On the basis of the comparison of log K' and log K$_a$ values for cysteine and those for glycine, and DL-α-alanine complexes, the coordination through COO$^-$, NH$_2$ and S$-$ has been suggested. The bonding through NH$_2$ and COO$^-$ in methionine complexes has been inferred on the basis of similar comparative study.
Behaviour of copper(I) iodide in aqueous potassium iodide containing aminoacids:

The possibility of complex formation between copper(I) and aminoacids has been investigated on the basis of the characteristic of copper(I) halide to become soluble in aqueous alkali halide solution. Evidence for the complex formation between copper(I) iodide and aminoacid such as L-leucine, L-proline and glycine has been obtained from the results of solubility data. The copper contents in two sets of solutions, the one without and the other with aminoacid differ considerably (table 2A, 2B and 2C, chapter II). The concentration of aminoacid consumed in complex formation was calculated by the difference of the concentration of aminoacid added initially to that estimated from the cuprous solutions, colorimetrically. From the solubility data, there is an indication of 1:1 complex formation with L-leucine and L-proline, and 1:2 complex species in case of glycine. The results are further substantiated from the slopes of the plots between free aminoacid concentration [L] and the solubility product of the aminoacid complex, K_sp (Fig.2, chapter II).

Substitution reactions of tetrakis (thiourea) palladium(II) chloride with some aminoacids:

The kinetics of the substitution reactions of square planar complex, Pd(tu)_4Cl_2 with some aminoacids such as
glycine, DL-α-alanine, threonine, L-asparagine, DL-valine, DL-serine and L-proline has been studied, spectrophotometrically. The first order rate constant, $K_{\text{obsd}}$, was evaluated from the slope of the linear plots between time, $t$ and $\log \frac{(O.D)_t - (O.D)_0}{(O.D)_0 - (O.D)_t}$ (Fig. 1 to 7, chapter III).

Linear plots were also obtained by plotting $K_{\text{obsd}}$ and $[Y]$, the concentration of aminoacid (Fig. 8, chapter III). These results indicate that the substitution reaction proceed by a displacement mechanism following the famous two term rate law, suggested by Basolo. The rates of $K_1$ and $K_2$, the first and second order rate constant, respectively, were determined from the intercept and slope of the linear plot. The values of $K_{\text{obsd}}, K_1$ and $K_2$ are given in table No.8, chapter III. The rate constant $K_1$ represents the slow displacement of thiourea molecules by the solvent, $H_2O$ which is then readily displaced by the aminoacids. However, the second order constant, $K_2$ is responsible for the direct nucleophilic displacement by the aminoacid.

**Transition metal complexes of the alkaloids:**

The interaction of alkaloids such as quinaldine, quinine, brucine and codeine with transition metal ions results in the formation of stable complexes. In general, the complexes are highly soluble in water and insoluble in alcohol,
acetone, ether, chloroform etc. With quinaldine and codeine, there is formation of 1:2 complexes whereas with quinine and brucine 1:1 complex species are formed. The nature of the coordination in the solid complexes has been investigated on the basis of infra red spectral studies. The site of coordination in the metal - alkaloid complexes was located by comparing the spectra of the complexes with those of the respective alkaloid and studying the major changes or shifts occurred on coordination.

From the studies of the infra red spectra of quinaldine and its complexes with TiCl$_3$, VOCl$_2$ and UO$_2$SO$_4$, coordination through heterocyclic nitrogen is suggested. The conclusion is mainly based upon the changes took place in the regions of ring CC, CN stretching, ring skeletal and CH out of plane vibrations. The changes in these regions are depicted by the increase in the wave number and increase in number of bands on coordination. The changes are most marked in the vanadyl and least in the case of titanous chloride complex (table I, chapter IV).

Out of these possible coordination sites namely, heterocyclic nitrogen of 6-methoxy quinoline, nitrogen of the paraffinic quinuclidine, and secondary OH group present at the junction of two ring systems. The infra red spectra of the
quinine and its complexes with $\text{VOCl}_2$, $\text{TiCl}_3$ and $\text{UO}_2\text{SO}_4$
give considerable evidence of coordination through heterocyclic
nitrogen of the substituted quinoline. The evidence is based
upon the changes occurred 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
deformation vibrations. The bands in these regions are
shifted to higher frequency side with increase in the number
of the bands. There are no noticeable changes in the positions
of the bands arising from the secondary hydroxy stretching
vibrations and CN stretching vibrations of quinuclidine ring
(table 2, chapter IV).

There are three pertinent sites for coordination in the
brucine namely, $\equiv\text{NCO}$ (acylazole group), the oxygen of the 7-
membered oxepine ring and the tertiary bridge head nitrogen
present in the 5/6 pyrrocoline ring. Sufficient evidence for
the coordination through nitrogen of the acylazole group has
been obtained on comparing the spectrum with those of its
complexes with $\text{VOCl}_2$, $\text{TiCl}_3$ and $\text{UO}_2\text{SO}_4$. The CO, CN stretching
modes of n-acylazole system belonging to keto-piperazine ring
system occurred at 1626 and 1335$\text{cm}^{-1}$, respectively. The spectra
of the complexes are devoid of these bands. There are no
appreciable changes in the positions of the bands arising from
CC stretching of the 7-membered oxepine ring and CN stretching of bridge head tertiary nitrogen of the 5/6 pyrrocoline ring. This excludes the possibilities of coordination through these sites (table 3, chapter IV).

The infrared spectra of codeine and its complexes with Cu²⁺, Co²⁺, Ni²⁺, VO²⁺, Mn²⁺, Cr³⁺ and Ti³⁺ give some important clues regarding the bonding in these complexes. The alkaloid, codeine has three sites susceptible to coordination: namely, the secondary hydroxy group, tertiary nitrogen attached to methyl group and oxygen of the furan ring. The fact that secondary OH stretching vibrations occurring at 3600 cm⁻¹ in the codeine, do not appear in the complexes at this frequency or near by regions, is a conclusive evidence for coordination through secondary OH group in metal–codeine complexes. The possibilities of coordination through CH₃–N or oxygen of the dihydrofuran ring are quite remote. No appreciable shifts are noted in the CH₃–N stretching, and CC, CO ring stretching, CH in and out of plane, and ring skeletal vibrations of dihydrofuran ring (table 4, chapter IV).