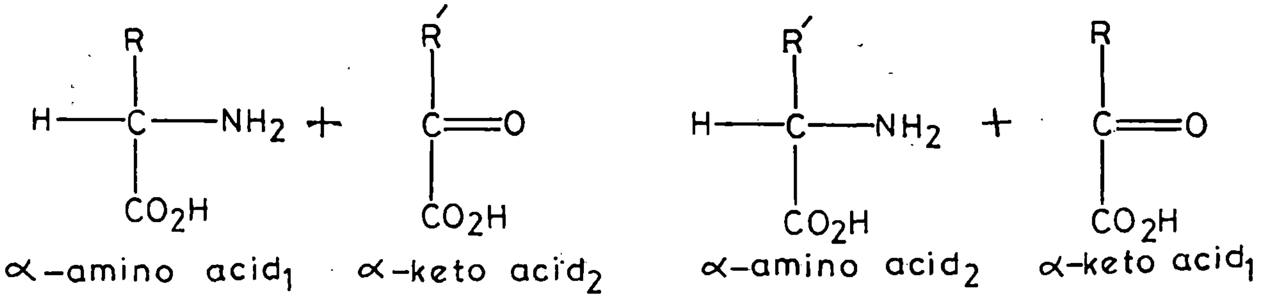
Chapter-I

Introduction

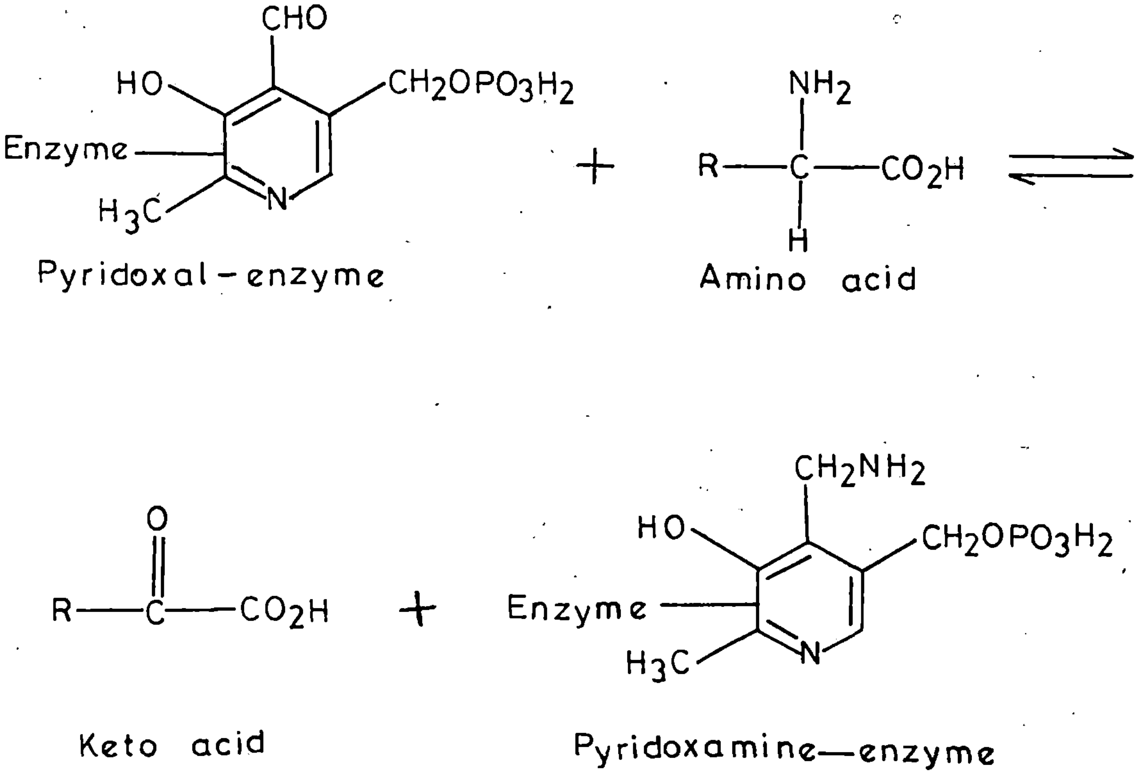
Aims and objectives of the work :

Main theme of the research work embodied in this treatise is the study of new chiral coordination compounds of UO_2^{2+} entity and Ln^{3+} ions using chiroptical methods with a view to establish their absolute configurations/conformations. Such studies for determining absolute configurations/conformations of metal complexes in solution are quite important because of their bio-inorganic relevance, e.g., in understanding mechanisms of reactions of amino acids like transamination, racemization, decarboxylation, etc. Metabolic reactions of amino acids i.e., non-oxidative enzymatic transformation of amino acids like transamination, decarboxylation, racemization, α, β-elimination, etc. are catalyzed by various enzymes in which pyridoxal acts as the coenzyme; all these reactions proceed through the Schiff base of pyridoxal 5'-phosphate (PLP) and amino acid. Pyridoxal 5'-phosphate (vitamin B_6) catalyzed reactions of amino acids can be duplicated in part in model systems mostly with the aid of certain metal ions. Practically all the amino acids perticipate in transamination reactions. After feeding rats with N^{15}-labelled amino acids, almost all the amino acids (except lysine and threonine) contained the N^{15} isotope but glutamic and aspartic acid and also glutamine had the highest contain suggesting a key role for these amino acids in amino-group transfer.[1-4]

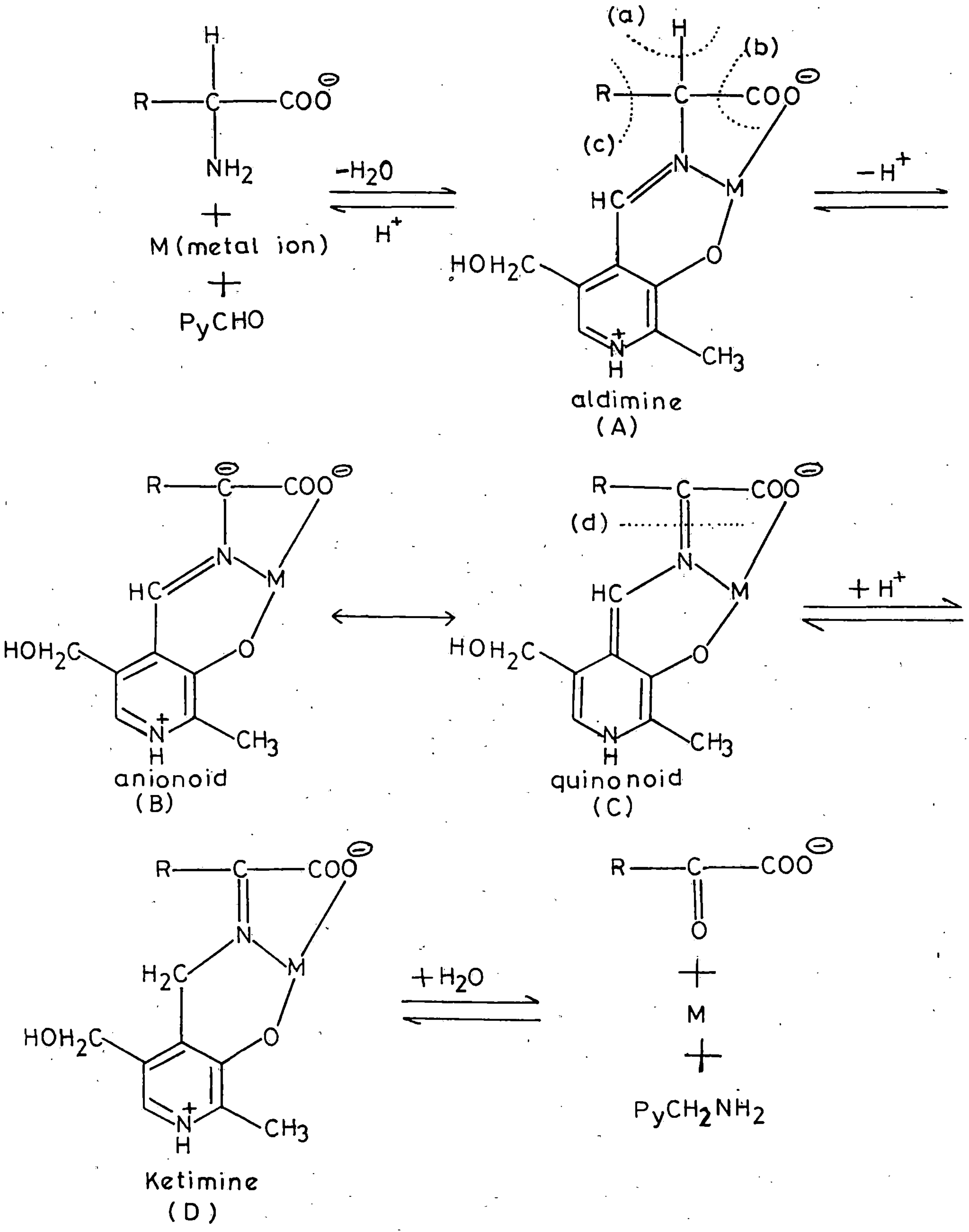
Transamination is an important reaction which provides a link between the carbohydrate and protein metabolism through the transference of amino groups from amino acids to keto-acids.



These reactions are catalyzed by transaminase enzymes and the most abundant of these are the glutamate-oxaloacetate and glutamate-pyruvate transaminase :-



The first indication that metal ions might be involved in enzymatic and non-enzymatic pyridoxal catalyzed reactions was found by Metzler and Snell (1952)[5,6] who succeeded in reproducing some of these reactions by incubating pyridoxal and a metal salt (Cu^{2+}, Co^{2+}, Fe^{2+}) with the amino acid, and have suggested a general mechanism for non-enzymatic transamination between an amino acid and a keto-acid by metal-activated pyridoxal and other related reactions. This remarkable work of Snell and his group (1952 onwards)[5,6] must be considered as one of the principal starting point in the development of "inorganic biochemistry". Work on such model systems is significant for several reasons. There is no other group of metal complexes which manifest as great a diversity of reactions of coordinated ligands, whether of biological significance or not, as do pyridoxylidene and pyridoxylimino chelates. Studies of reactions of coordinated ligands is an important area of research in coordination chemistry and catalysis.[15-17] In order to have a clear understanding of such reactivities, it is essential to know the absolute configurations/conformations of such complexes in solution. Actually there remains much to be understood about this aspect using chiroptical methods like CD spectra supported by other evidences especially ^1H NMR spectra.


M (metal ion)
PyCHO
-H2O
H+
(a)
(b)
(c)
−H+
aldimine
(A)
anionoid
(B)
(d)
quinonoid
(C)
+H+
Ketimine
(D)
+H2O
PyCH2NH2

Despite the lack of proof that these enzymes function as metalloenzymes, the metal complex (A) may simulate certain of the features of enzymatic active sites in the sense of facilitating Schiff base formation and of labilizing bonds formed by the α-carbon in the condensed amino acid portion in such a complex. The formation of aldimine or ketimine Schiff base is an essential feature of all currently accepted mechanisms of vitamin B_6 catalysis, many of which also require lability of the α-hydrogen in those reactions proceeding to products through an intermediate aldimine.[5-14]

Hydrolysis of intermediate (C) at (D) gives pyridoxamine and a keto-acid, that is, interchange of amino group between molecules of two amino acids, leads to a process called transamination. The overall transamination reaction (3) results from the coupling of the sequential reactions (1) and (2) :-

$$\mathrm{RCH(NH_2)COOH} + \mathrm{Pyridoxal} \rightleftharpoons \mathrm{RCOCOOH} + \mathrm{Pyridoxamine} \qquad \ldots(1)$$

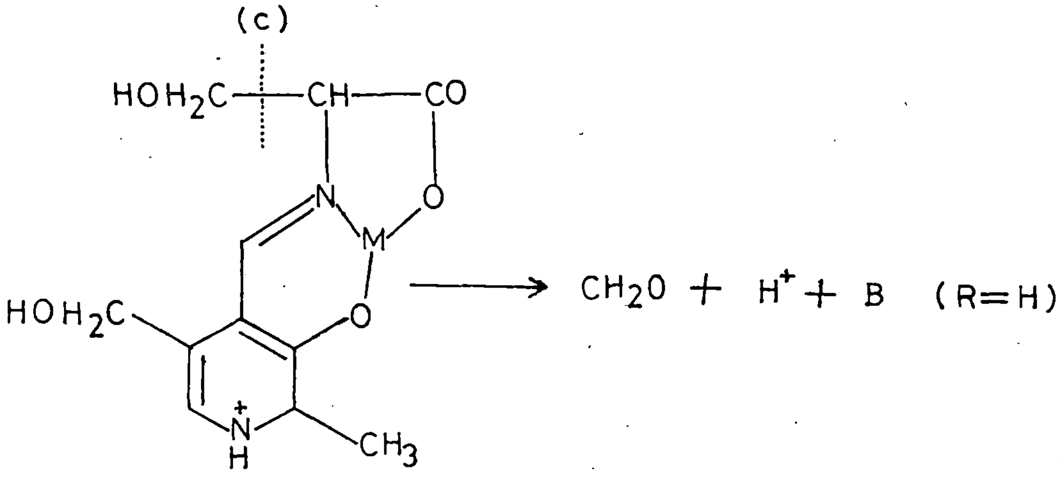
$$\mathrm{Pyridoxamine} + \mathrm{R'COCOOH} \rightleftharpoons \mathrm{R'CH(NH_2)COOH} + \mathrm{Pyridoxal} \qquad \ldots(2)$$

$$\mathrm{RCH(NH_2)COOH} + \mathrm{R'COCOOH} \rightleftharpoons \mathrm{R'CH(NH_2)COOH} + \mathrm{RCOCOOH} \qquad \ldots(3)$$

Ionization of a hydrogen atom by the breaking of bond (a) to give (C) followed by recombination to (A) and hydrolysis gives the original amino acid racemized.

A decomposition, leading to pyridoxal, CO_2 and the amine corresponding to the amino acid could occur by scission of bond (b) of (A) : enzymic decarboxylations of α-amino acids usually require pyridoxal.

There are other ways in which a complex of type (B)-(C) can break up if the substituent (R) permits. One example is the complex (E) derived from serine. The bond (C) can break giving (B)-(C) (R=H), a proton and formaldehyde. Subsequently (B)-(C) (R=H) hydrolyses to glycine and pyridoxal.

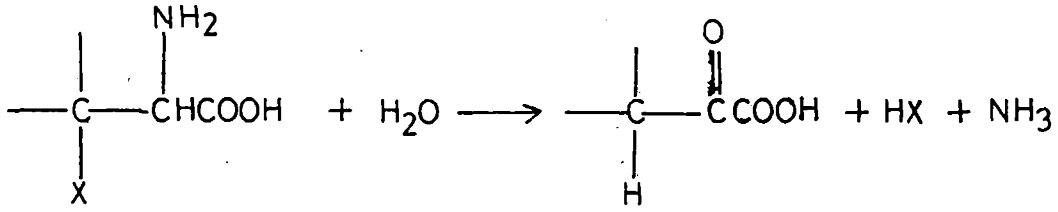


(E)

The overall reaction is :-

$$HOCH_2CH_2(NH_2)(CO_2H) \longrightarrow CH_2O + H_2NCH_2CO_2H$$

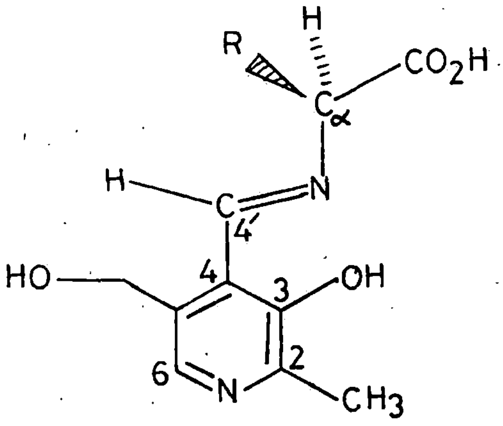
There are many pyridoxal dependent enzymes that catalyze α,β-elimination of the following type.



$$-\overset{|}{\underset{X}{\underset{|}{C}}}-\overset{NH_2}{\overset{|}{C}}HCOOH + H_2O \longrightarrow -\overset{|}{\underset{H}{\underset{|}{C}}}-\overset{O}{\overset{\|}{C}}COOH + HX + NH_3$$

They include serine dehydratase, threonine dehydratase, homocysteinine desulphhydratase, cystathionine β-lyase and cystathionine γ-lyase. Other examples include phenylserine aldolase, cysteine synthetase and tryptophan synthetase.

The above-mentioned reactions of Schiff bases involve a number of electron and hydrogen shifts and presumably are controlled by subtle conformational effects. It has been suggested that the bond perpendicular to the π system of the Schiff base is most easily broken, and that the enzymes govern reaction specificity by controlling the conformation of the N-C_α bond.



Another important structural feature is the conformation of the C_4-C_4' bond, which is predominantly cis.

A general theory on the mechanism of these non-enzymatic reactions involves four stages :

(1) Formation of a Schiff base with subsequent electron displacement from the α-carbon atom to the electronegative ring nitrogen through a conjugated system of double bonds. Weakening of the bonds to the α-carbon atom thus results.

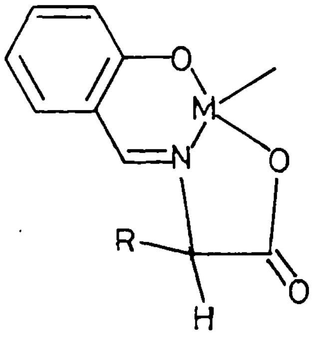
(2) Release of H^+, $COOH^+$ or R^+ from the α-carbon to produce a transitional Schiff base.

(3) Localization of the lone pair of electrons of the heterocyclic nitrogen either onto the α-carbon for racimization and decarboxylation or onto the formyl carbon for transamination. Protonation at the α-carbon then occurs for all reactions except that involving initial labilization of a α-hydrogen. In this instance subsequent protonation can occur either at the α-carbon or at the formyl carbon (transamination).

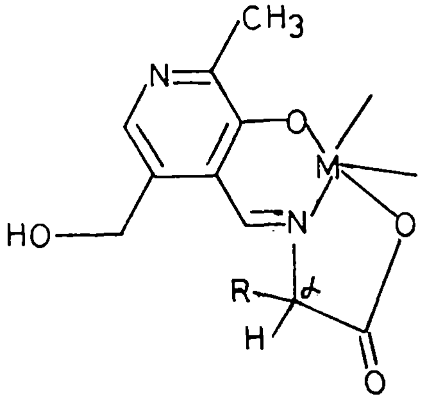
(4) Hydrolysis of the carbon-nitrogen bond to give the products.

The fundamental factors are variations in resonance energy and electronic distribution among the possible states.

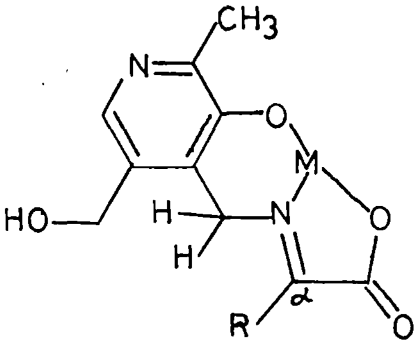
The modern picture of enzyme transamination is therefore to a great extent based on the work with chemical model ("biomimetic") reactions rather than an experiment with enzyme-catalysed reaction. In such model studies the salicylaldimine complexes are also considered whose structural and electronic properties are similar in several respects to those of the



pyridoxylidene (aldimine) and pyridoxylimino (ketimine) Schiff base complexes postulated to have the basic structural features shown below :



Aldimine



Ketimine

However salicylaldehyde does not possess the catalytic properties of pyridoxal or the simpler hydoxy pyridine aldehyde in amino acid transformation.

In such model studies several metal ions have been used extensively, e.g., Cu^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}; in case of Cu^{2+} the M^{n+} : aldehyde : amino acid is 1:1:1. But for other metal ions it is usually 1:2:2; stoichiometries like 2:3:3 are seldom observed in such systems. Apart from physico-chemical studies on such complexes, several of them have been isolated in the solid state and their structures determined through X-ray crystallography. Although the existence of both aldimine and ketimine complexes in solution is now well documented, there exist only several reports of presumed isolation of ketimine species.

Brief mention may be made here about the highlights of different earlier studies of various workers. X-ray crystallographic studies on such model systems involving mainly Cu^{2+} complexes indicate that the N-(salicylaldimine) residues are coordinated to the metal atoms using the phenolic oxygen atom, azomethine nitrogen atom and one of the oxygen atom of the carboxylate group i.e., tridentate ligand coordination. Most of these complexes are of mononuclear type. However in a number of cases like L-tyrosine, L-valine derivatives, the oxygen atom of the carboxylate group can act as a bridging atom between two copper atoms.[18-25] These conclusions are based on X-ray crystallographic studies on the following systems —N-(salicylidene)-glycinatoaquocopper (II) tetrahydrate; N-(salicylidene) α-aminoisobutyratoaquo copper (II); diaquo (N-salicylidene-L-threoninato) copper (II); acetato (N-methyl-N'-salicylidene-1,3-propanediaminato) copper (II) dimer; N-(salicylidene)-glycinatoaquo copper (II) hemihydrate; bis-N-phenylethyl-salicylaldiminato copper (II); μ-(N-salicylidene-L-valinato-O)-N-(salicylidene)-L-valinatodiaquodicopper (II); catenatetraqua-di- μ_3-(N-salicylidene-DL-glutamato)-tri copper (II) heptahydrate; N-(pyridoxylidene)-DL-valinato copper (II); N-(salicylidene)-L-phenylalaninatoaqua copper (II) dimer and catena- μ-(N-salicylidene-L-tyrosinato-O, O') copper (II). Valuable data like X-ray crystallographic studies, magnetic properties etc. have been gathered on transition metal dimers with different types of Schiff bases including those derived from alanine, valine, leucine, methionine etc. Considerable works have been done on the NMR studies of conformations in solution of pyridoxal Schiff base derivatives of amino acids by Gansow, Holm, Chang and others.[11-13] Preparative aspects of Schiff base derivatives of pyridoxal, salicylaldehyde, related aldehydes, their metal chelates have been studied in great details; .their IR and other spectroscopic data have been published.[1,7-9] In some cases mechanisms of unusual reactions of some amino acids have been studied which have no enzymatic counterpart; for example the cyclization of histidine Schiff base.[14] Measurement of temperature dependence of magnetic susceptibility of several

Schiff base complexes of first transition metals have also been reported.[10,26-28]

Optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of a considerable number of Cu^{2+} complexes of Schiff base derivatives of L-amino acids have been reported.[1,29-31] However, no detailed interpretation of CD spectral curves of such complexes have yet been undertaken. CD spectra of some Mn(III), Eu(III) and UO_2^{2+} Schiff base complexes have also been reported.[32-34] From 1962 onwards a brilliant series of works have been published by H.E.Smith and his group on the interpretation of CD spectra of chiral Schiff bases derived from different types of chiral amines, amino acids and related derivatives. A salicylideneimino chirality rule has been developed (using the coupled oscillator model for the generation of Cotton effects) which correlates unambiguously the sign of the relevant CD bands with the absolute configurations/conformations of the chiral Schiff base derivatives. Actually in recent years chiroptical methods have been developed considerably for determining absolute configurations of in situ transition metal complexes of ligating natural products from circular dichroism spectra.[35-46] Natural products whose stereo chemistry can be investigated in this way are e.g., acids glycols, amines, aminoalcohols, diamines, peptides and nucleoside derivatives.[47] Reports on ORD curves of some N-salicylidene aminosugars are also exist.[48] It is evident that comprehensive studies on metal complexes of imine acids, involving detailed interpretation of CD spectra supported by NMR evidence are yet to be placed on a firm basis.

The present work is an attempt in that direction involving mainly oxometal ions and trivalent lanthanides as even preparative works are scarce in this field. Here a large number of new optically active metal complexes of imine acids (i.e., Schiff bases derived from amino acids) have been isolated in the solid state and the recently developed salicylideneimino chirality rule[46] has been used extensively to determine their absolute configurations/conformations from their CD spectra; these studies have been substantiated by their NMR spectral data. In such studies it has been possible to carry out stereospecific reactions even in alkaline medium.

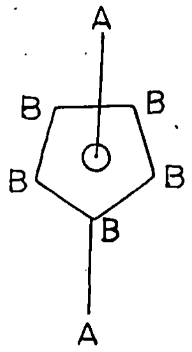
At this stage it may be convenient to have a brief overview of the pertinent aspects of the chemistries of UO_2^{2+} entity and Ln^{3+} ions.

Of the more than fifty mononuclear oxoions known (general formula MO_x^{n+}, where x = 1,2,3 and n = 1,2,3,4 and 5), the uranyl ion, UO_2^{2+} is remarkably stable with respect to the strength of the U-O bond.[49-51] It can persist through a variety of chemical changes, and it behaves like other cations whose properties are intermediate between those of M^+ or M^{2+} ions and those of ions of similar size but greater change. The stability of UO_2^{2+} ions in aqueous solution is shown by the very long half life for exchange with $H_2O^{18} > 10^4$ hours. Here the metal atom is in its highest oxidation states and the two metal-oxygen bonds in UO_2^{2+} are definitely covalent in nature.[58] The Molecular Orbital picture of the UO_2^{2+} entity indicates that the metal-oxygen axial bond is a triple bond consisting of one σ - and two π - linkages.[52-57] This triple bond picture is essential to spectroscopic interpretation and it explains very naturally the special stability which seems associated with the UO_2^{2+} entity.

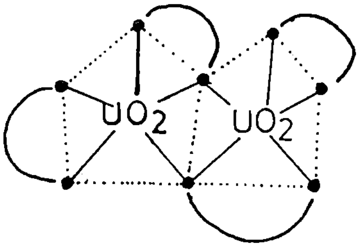
Crystallographic data show that four, five or six ligand atoms can lie in the equatorial plane of the axial O-U-O group; the ligand atoms may or may not be entirely coplanar depending on circumstances. Planar five and six coordination in the equatorial plane is commonest and appears to give geometry more stable than the puckered hexagonal configuration. An example is the structure of the anion in the complex salt sodium uranyl acetate where the O-U-O axis is perpendicular to the equatorial plane; the carboxylate groups are bidentate and equivalent so that the equatorial coordination number of uranyl entity is six. Similar structures have been found in other species such as $[UO_2(NO_3)_2(H_2O)_2]$, $UO_2(NO_3)_2[OP(OEt_3)]_2$ and $Rb[UO_2(NO_3)_3]$.[59,60] The type of coordination polyhedron obtainable is influenced by the nature of the ligands; for bi- or polydentate ligands with O or N donor atoms, the type of polyhedron generated depends on rigidity, coplanarity and distance of the donor atoms (bite) of the ligand. The more compact the ligand and the smaller the bite, the more effective is the ligand in generating high coordination structures.[62,63] Very compact ligands are the peroxo group (bite 1.5 Å) and nitrato group (2.1 Å). In the 8-quinolinolato (bite 2.6 Å) and tropolonato (bite 2.6 Å) ligands the more compact planar conformation and the minor intraligand repulsion factor allow a high coordination number (hexacoordination in the equatorial plane). With β-diketonato-(bite 2.7 Å) and salicylaldiminato-(bite 2.9 Å) adducts, the uranyl ion reaches the maximum values of 7 (including the axial oxygens) coordination. Two common geometries for UO_2^{2+} complexes involved seven and eight coordination.[61]

Seven coordination

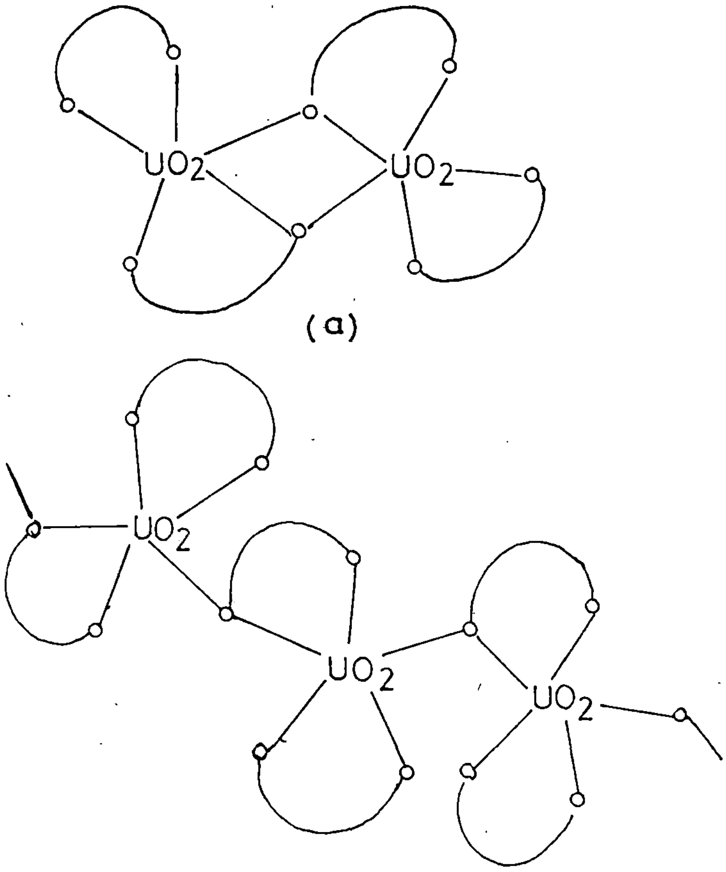
For the UO_2^{2+} ion one polyhedron must be taken into account and it is given by the pentagonal bipyramid which only allows the trans O-U-O group to be linear.



Most complexes exhibit a mononuclear pentagonal bipyramidal geometry but polynuclear configurations have also been found; in this case the ligand oxygens bridge two metals. Typical examples are given by $UO_2(acac)_2$, $UO_2(trop)_2$[63-65]



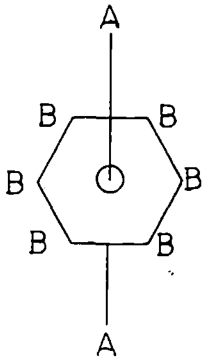
$UO_2(acac)_2$



Two forms of $UO_2(trop)_2$

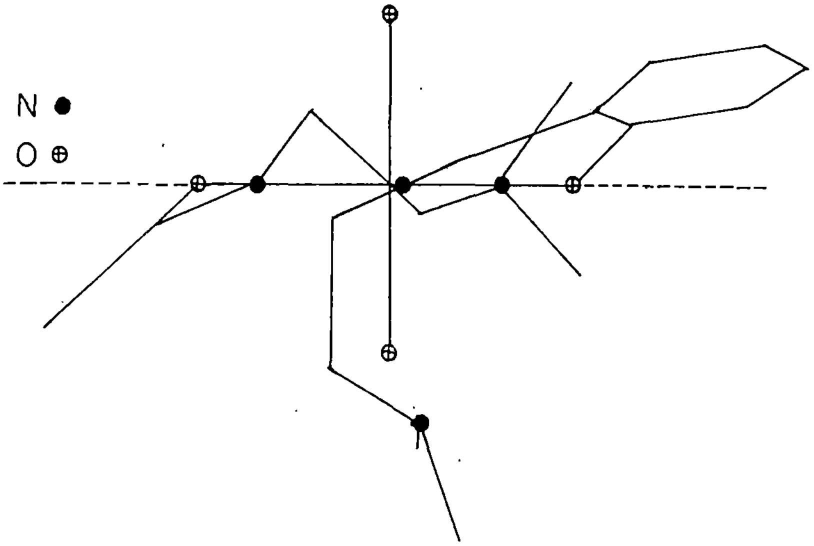
Eight coordination :

The hexagonal bipyramid is charactèristic of uranyl complexes where the apical positions are occupied by oxygen atoms. The hexagonal bipyramid has two sets of nonequivalent ligand sites



A and B and its shape is specified by the ratio of bond lengths r_A/r_B. This polyhedron is not energetically favoured and has been found only when a linear O-U-O group is present; X-ray crystallographic data has proved this idea.

Over these years a number of good reviews on various aspects of the coordination chemistry of the actinides and of UO_2^{2+} entity in particular have been published.[61,68-76,81] Some interesting results on the X-ray crystallographic studies on Schiff base derivatives of UO_2^{2+} entity as well as some bridged uranyl complexes may be mentioned here.[69,70,74,77-79] In case of bis (N-ethylenedimethylaminesalicylaldiminato) dioxouranium (VI) each uranium atom is in a pentagonal-bipyramidal environment. Two oxygen and three nitrogen atoms form the base of the pyramid and the uranyl oxygens occupy the apical positions; the structure provides a clear illustration of the two different modes of ligand coordination within the same molecule. A projection of the molecule down a direction perpendicular to the uranyl group is shown in the following figure and it may be seen that the complex exhibits on overall 'stepped' geometry with the $-CH_2-CH_2-$ carbon atoms out from the equatorial plane by 0.24 and -0.53 Å.



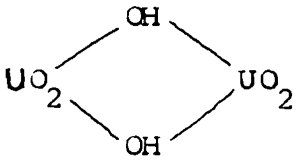
In UO_2(salen) MeOH [where H_2 salen = N,N'-ethylenebis (salicylaldimine)] the chelating ligands are bent away in opposite direction with respect to the equatorial plane. The N-C-C-N group is in a near gauche conformation and its torsion angle is 51.8°. This conformation and the maintanance of the trigonal nature of the nitrogen cause the salicylaldehyde group to adopt a 'stepped' geometry. Most likely the larger ligand bite (2.9 Å) of salicylaldiminato derivatives is responsible for the fact that in the corresponding uranyl complexes an equatorial coordination number not exceeding 5 is attained and this coupled with flexibility of the ligand skeleton allows distortion of the chelated ligands from the equatorial plane.

The UO_2^{2+} entity being a typical hard acid, the following ligand displacement series has been obtained through studies on its complex forming properties :-

$CO_3^{2-} \geqslant OO^{2-} > OH^- > F^- > CH_3COO^- \geqslant C_2O_4'' > SO_4^{2-} > Cl^- \geqslant NO_3^- > \text{amines} > Br^- > I^-$.

Most of these ligands can act as bridges between two UO_2^{2+} entities as indicated by X-ray crystallographic studies on the following compounds :-

$[UO_2(CH_3COO)_2(Ph_3PO)]_2$, anhydrous UO_2CO_3, $(NH_4)_2[(UO_2)_2(C_2O_4)_3]$ etc.

In case of $[(UO_2)_2(OH)_2Cl_2(H_2O)_4]$ the  bridge is not symmetric.

Various spectroscopic studies have been done on uranyl compounds e.g., electronic, IR, Raman, ^1H NMR, circular dichroism and photoelectron spectra as well as other properties of the uranyl entity like polarisability and magnetic susceptibility.[52-57,61,80-92]

For the UO_2^{2+} entity the U-O distance is not constant in different compounds, the range appears to be from ~1.6 Å to ~2.0 Å. Accordingly there has been extensive use of infrared data for correlating bond lengths, R_{UO}(Å) and force constants, F_{UO} (millidynes/Å), using the Jone's equation

$$R_{UO} = 1.08\ F_{UO}^{-\frac{1}{3}} + 1.17.$$

Where comparison is possible, the rule generally agrees with X-ray data.[80]

^{1}H NMR studies on uranyl complexes indicate that deshielding of ligand protons on coordination to UO_2^{2+} entity is a combined effect of several factors, e.g., drainage of electron density towards the UO_2^{2+} entity, magnetic anisotropy of the uranyl entity and several other factors related to the overall geometry of the complex molecule; sometimes intraligand effects may cause shielding or deshielding of some of the ligand protons.[82-86]

Although extensive theoretical works backed/up by experimental studies have been published to interpret the electronic spectrum of the UO_2^{2+} entity,[52-57] in actual UO_2^{2+} complexes with organic ligands, it has been observed that charge transfer transitions from equatorial ligand pπ orbital to the 5f and/or 6d orbital of the uranium atom usually completely cover the apical oxygen ⟶ 5f transition within the UO_2^{2+} entity.[61,82]

Some results have been published on other properties of the UO_2^{2+} entity like refraction, R_D cm^3 and magnetic susceptibility.[82,88-92] The UO_2^{2+} entity has a small intrinsic temperature independent paramagnetism, the molar susceptibility being 57×10^{-6}. This paramagnetism can be ascribed to what Van Vleck calls "high frequency terms", e.g., to the matrix element of the magnetic moment operator $\beta[L + 2S]$ between the ground state and higher state. Since all spins are paired off in a ground state, $S = 0$ and there is no contribution from the spin magnetic moment. The fact that the susceptibility of the uranyl ion is paramagnetic, is a strong support for the occurrence of 5f electrons in the bond. This paramagnetic susceptibility is expected to be markedly anisotropic being zero parallel to the O-U-O axis and maximum perpendicular to this axis. In actual practice in coordination compounds with large or medium organic ligands the diamagnetic contribution of the ligand atoms becomes considerable and calculation of a value of $\sim 60 \times 10^{-6}$ c.g.s. unit for the 'χ' value of the UO_2^{2+} entity in a diamagnetic compound, poses some problems and interpretations based on such 'χ' values are subject to ambiguity.

The coordination chemistry of the trivalent lanthanide ions has expanded rapidly over the last three and a half decades.[103-105] A majority of the complexes have been derived from strongly chelating anionic ligands with oxygen donor sites. Some neutral nitrogen donors have also been used for this purpose like

1,10-phenanthroline, 2,2′-bipyridyl, triazine derivatives, terpyridyl derivatives, various diamine derivatives, etc.

A significant difference in coordinating tendency of lanthanide ions and d-type transition metal ions result from effective shielding of the lanthanide 4f orbitals by the $5s^2$ $5p^6$ octet, precluding the existence of strongly covalent metal-ligand interaction. So metal-ligand bonding in lanthanide complexes is substantially electrostatic as corroborated by magnetic spectral and kinetic data.[105] Thus it is not surprising that the species isolable from aqueous media are derived from anionic donors in which strong electrostatic bonding with the metal ion is possible. The fact that complexes derived from neutral nitrogen donors could not be isolated, prompted the assumption that these species were thermodynamically unstable in aqueous solution. The ability of lanthanide ions to coordinate with neutral nitrogen donors could be best evaluated in non aqueous media of moderate polarity.[95]

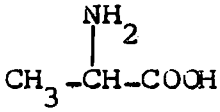
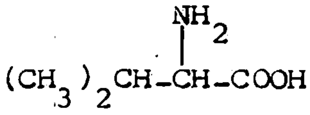
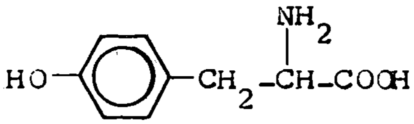
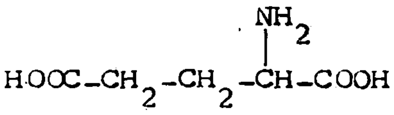
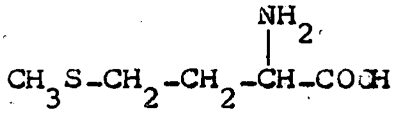
It is now well established that coordination numbers greater than six are favoured in lanthanide systems. The variation in coordination number (six to twelve) observed in lanthanide complexes may be attributed to steric factors and electrostatic forces of attraction and repulsion, rather than bond orientation by the well shielded 4f orbitals of the metal ion. Thus the relatively large size of the lanthanide ions (La^{3+} = 1.061 Å, Lu^{3+} = 0.848 Å) generally allow accommodation of more than six donor atoms in the coordination sphere. One important review[95] on lanthanide complexes with neutral nitrogen donors is concerned on different aspects ranging from coordination number, bonding, molecular geometry, thermodynamic and kinetic stability, fluorescence, NMR, IR and other spectroscopic data as well as X-ray crystal structure determinations of compounds like $La(bipy)_2(NO_3)_3$, $Eu(terpy)_3(ClO_4)_3$ etc. Another interesting review[96] has been published on lanthanide complexes with neutral macrocyclic ligands, e.g., crown ethers and cryptands. This is a logical extension of the work on alkali and alkaline earth metals with macrocyclic ligand systems.[96] For trivalent lanthanides such a study has additional specific motivations which include among others (1) the use of lanthanide ions as spectroscopic probes, (2) the stabilization of uncommon oxidation states and (3) the systematic study of lanthanide ion coordination properties. In this case as well a vast amount of physicochemical studies have been mentioned. Chiral lanthanide compounds as well as NMR studies of metal complexes using lanthanide shift reagents, have been the subject of important review articles.[97,98] While intense efforts have been made to detail the nature of d-d optical activity much less interest has been focused on analogous studies of the f-f optical activity associated with chiral lanthanide complexes. This situation has arisen partly from the difficulty of resolving the very labile lanthanide complexes, partly from a general lack of interest in lanthanide solution chemistry and partly from an ill-conceived concept of rarity of the members of the series. The information available from chiroptical methods has began to receive systematic attention from several groups, in-spite of the fact that chiral lanthanide compounds have been prepared in great numbers but rarely studied from that particular point of view. While early studies involving f-f optical activity attempted to use CD as a chiroptical probe, more recently it has been established that circularly polarised luminescence (CPL) studies of emissive compounds is a much more suitable tool for these studies.[106,107] Richardson and co-workers have developed a general theory of f-f optical activity of lanthanide ions in complexes having trigonal dihedral symmetry.[108] Brittain and his co-workers are working on CPL studies of chiral Schiff base complexes of lanthanides.[109] The corresponding Eu(III) derivatives are often highly luminescent and display very strong optical activity characteristic of a marged sum of vicinal, conformational and configurational effects. Chiral lanthanide compounds have been studied by NMR methods.[110] Direct determinations of enantiomeric purity via the NMR technique have been made by taking advantage of the fact that the spectra of enantiomers are nonequivalent in a dissymmetric environment. A general review of the bio-inorganic chemistry of lanthanide ions has been written by Reuben[111] and the use of lanthanide ions as NMR chemical shift probes in biological systems has been detailed by Glasel.[112] Lanthanide shift reagents (LSRs) [like various β-diketone derivatives] have been used to simplify the NMR spectra of organic compounds containing suitable heteroatoms.[97,113,114] The lanthanide ions in these reagents can readily expand their coordination number to seven, eight or nine by binding to the heteroatoms of one or more molecules of the substrate under study. The interaction between the paramagnetic lanthanide ion and the nuclei of the substrate causes alteration of the magnetic environment of each nucleus and changes in the corresponding NMR chemical shift result.

One small but informative review on acyclic and macrocyclic Schiff base complexes of lanthanides and actinides has been published.[73] Schiff base derivatives of lanthanides have been the subject of different types of studies including x-ray crystal structure determination.[99-102] Finally the review published by Sinha on the structure and bonding in highly coordinated lanthanide complexes may be mentioned here.[93] Available X-ray crystal structural data on different trivalent lanthanide complexes indicate octahedral or slightly distorted octahedral geometry for coordination number six and for coordination number seven it is usually either capped octahedron or capped trigonal prism.

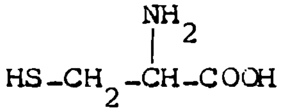
It may now be mentioned here that in-spite of all these studies systematic data on trivalent lanthanide complexes of chiral imine acids are still rare; use of chiroptical methods to establish absolute configurations/conformations in such cases is highly desirable. The present work is an attempt in this direction.

The present study :-

Here coordination compounds of UO_2^{2+} entity and trivalent lanthanides have been studied using ligands derived mostly from naturally occurring α-amino acids (classified below according to the nature of the R groups) as well as another amino acid (anthranilic acid).

Amino Acid	Formula	Number of ligands derived from the amino acid
Hydrophobic R		
Alanine	 $CH_3-\overset{NH_2}{\overset{\vert}{CH}}-COOH$	2
Valine	 $(CH_3)_2CH-\overset{NH_2}{\overset{\vert}{CH}}-COOH$	2
Hydroxylic R		
Tyrosine		2
Carboxylic R		
Glutamic acid	 $HOOC-CH_2-CH_2-\overset{NH_2}{\overset{\vert}{CH}}-COOH$	1
Sulphydryl and Thioether		
Methionine	 $CH_3S-CH_2-CH_2-\overset{NH_2}{\overset{\vert}{CH}}-COOH$	1

Cysteine

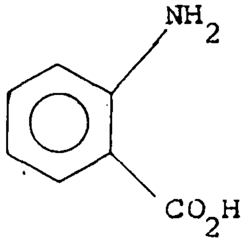


$HS-CH_2-CH(NH_2)-COOH$

1

Other amino acids

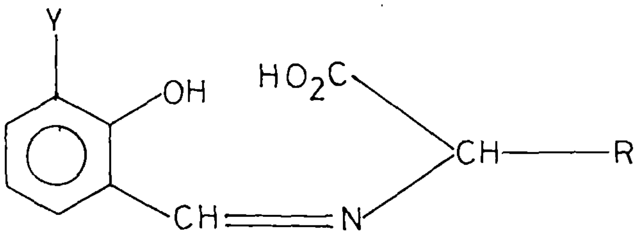
Anthranilic acid



2

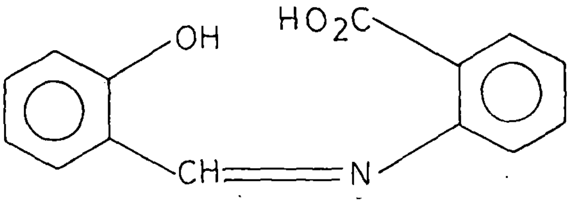
Most of the new complexes (UO_2^{2+}- more than sixty; Ln^{3+}- twenty) isolated here from imine acids involving naturally occurring α-amino acids (absolute configuration (L-/S-), are optically active. Although pKa values (alanine : pK_1-2.34, pK_2-9.37; valine : pK_1-2.32, pK_2-10.41; tyrosine : pK_1-2.18, pK_2-9.21, pK_3-10.47) of some of the amino acids used here are not much more different from each other, the behaviours of the corresponding imine acids with respect to alkali during complex formation with UO_2^{2+} are different, e.g., for these reaction mixtures pH was 9 in case of tyrosine, buffer solution of pH 5.5 was used in case of N-(salicylidene)-L-valine and no alkali was needed for N-(orthovanillidene)-L-valine. However, for the preparation of the Ln^{3+}- imine acid complexes one general method could be followed for all the imine acids. All these new compounds have been thoroughly characterized through physicochemical methods (TLC, elemental analyses, molar conductance in nonaqueous solvents, titration of complexes containing unneutralized ligand protons and calculations of the corresponding pKa values, TGA, μ_{eff} for Ln^{3+} complexes, UV-VIS, IR, low frequency IR, ^1H NMR and CD spectral studies).

The following ligand systems have been used in this study.

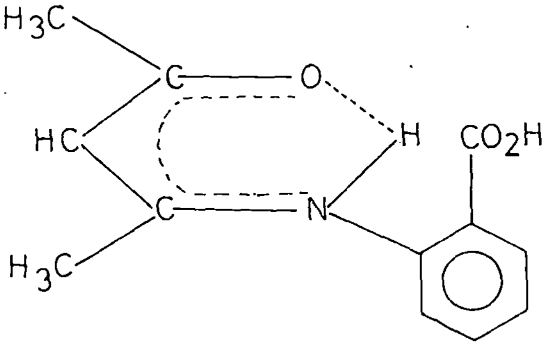


Y = H ;

Y = OCH_3 ;



N-(salicylidene)
anthranilic acid
($SAA-H_2$)



N-(acetylacetone)
anthranilic acid
($AAA-H_2$)

It has been observed that most of the ligands form complexes of different compositions (e.g., 1:1, 2:3, 1:2, etc.) with the UO_2^{2+} entity. In case of mixed ligand complexes with

2,2′-bipyridyl and 1,10-phenanthroline the UO_2^{2+} : imine acid ratio is usually 1:1; in such cases with $SAA-H_2$, N-(salicylidene) and N-(orthovanillidene) α-amino acids, the imine acid unit uses the azomethine group (-CH=N-), the phenolic -OH group and the carboxylic acid group $-CO_2H$ for coordination to the UO_2^{2+} entity. $AAA-H_2$ also exhibits comparable behaviour. For the bridged uranyl complexes (UO_2^{2+}:L-2:3) of these imine acids IR and ^1H NMR spectral data help considerably to distinguish between different modes of ligand coordination, i.e., normal tridentate and bridging ligands; the normal ligands as usual use the three above mentioned functional groups for the purpose of coordination in such cases but for the bridging ligands the azomethine group usually remains free, the other two functional groups being involved in coordination. Two types of -CH=N- stretching vibrations appear in the IR spectra for uncoordinated and coordinated azomethine -CH=N- groups; ^1H NMR spectra also show two types of signals (in the range 10.1-8.8 δ, ppm) for these different types of azomethine protons. For these UO_2^{2+}- imine acid systems it has been possible to block dimerization (i.e., formation of UO_2^{2+}: imine acid - 2:3 complexes) reaction through base adduct (1:1) formation this is very much vital for the interpretation of spectroscopic data of all these systems and to draw reasonable conclusions regarding their structures without recourse to X-ray structural studies.

For the Ln^{3+} complexes the metal-ligand ratio is almost exclusively 1:2, leading to an overall coordination number of six taking into account the tridentate nature of the imine acid.

Application of salicylideneimino chirality rule[46] to the CD spectra of optically active uranyl and trivalent lanthanide complexes of imine acids derived from α-amino acids helps to ascertain not only the absolute configurations/conformations of the assymmetric carbon atom of such chelated ligands but also the conformations of the complex molecule as a whole.

The thesis comprises of six chapters. In chapter I a brief review of different aspects of coordination chemistry of UO_2^{2+} entity and trivalent lanthanides along with the objectives of the present work has been presented. Chapters II-V deal with coordination chemistry of UO_2^{2+}- imine acid systems derived from different L-(S-) amino acids and anthranilic acid. Chapter VI is concerned with the trivalent lanthanide complexes of chiral imine acids.

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