plexes of La, Pr and Nd were precipitated by this
method. In the case of Sm, Gd and Tb, a little
benzene had to be added with stirring to precipitate
the complexes. The complexes of Y, Er and Yb
did not precipitate even after adding benzene.
Hence, for their preparation the solutions were kept
on a water-bath for 30 min during which time the
solvent evaporated completely and the complexes
began to crystalize out. Acetone was added and
the contents stirred well to obtain the crystalline
complexes. All the complexes were filtered through
a sintered crucible and washed with cold acetone, and
dried over calcium chloride under reduced pressure.
The analytical data (Table I) show that the
complexes have the general formulae, Ln(DMA)₆I₃·
3H₂O, where Ln = La, Pr, Nd, Sm, Gd and Tb,
and Ln(DMA)₄I₃·3H₂O, where Ln = Y, Er and Yb.
The complexes are hygroscopic and resemble their
parent salts in their colour. They, however, turn
yellow after several days. They are soluble in
polar solvents and insoluble in non-polar solvents.
The composition of the complexes prepared is
different from that reported for the corresponding
rare-earth perchlorate complexes and contrary to
our previous observations on the complexes of
dimethyl- and diphenyl-sulphoxides with the rare-
earth iodides and perchlorates. This may be due
to the fact that the method used for the preparation
of the iodide complexes is different from the one
used for the preparation of the perchlorate com-
plexes.

The IR spectra of all the complexes are similar
in their major details. The spectra of the com-
plexes are characterized by a displacement of vC═O
of the ligand at 1660 cm⁻¹ to lower frequencies
(≈1600 cm⁻¹) and a small shift of vC—N of the ligand
at 1500 cm⁻¹ to higher frequencies (≈1520 cm⁻¹)
suggesting the coordination of the ligand to the
metal through the carbonyl oxygen.

A broad band in the region of 3150-3450 cm⁻¹
for the complexes of La, Pr and Nd suggests the
presence of both coordinated and lattice held water
molecules. A band around 670 cm⁻¹ attributable
to the rocking mode of coordinated water is also
observed for these complexes. However, in the
Sm, Gd and Tb complexes, this band is not observed
suggesting that the water molecules in these com-
plexes are not coordinated. This decrease in the
coordination number is due to the decrease in the
cationic size along the lanthanide series. In the
complexes of Y, Er and Yb, the appearance of the
H₂O stretching modes at lower frequencies
(≈3300 and ≈3180 cm⁻¹) and of the rocking mode
of water around 690 cm⁻¹ suggest that the water
molecules are coordinated. The thermal behaviour
was also studied for determining the number of
coordinated water molecules, but the technique
failed because the complexes decomposed when
heated to 100°.

The stoichiometries of these complexes show
that the number of ligand molecules attached to
the metal ion decreases from six for the complexes
of La-Tb to four for the complexes of Y, Er and Yb.
Normally one would expect the number of ligand
molecules attached to the metal to decrease from
to five. The anomalous behaviour in the present
complexes may be due to the presence of water
molecules in the coordination sphere, at the expense
of a DMA molecule, in the complexes of Y, Er and Yb.

The molar conductance values (Table I) in acetone
show that all the complexes behave as 1:1 electrolytes
in this solvent. This suggests that two of the
iodide ions are coordinated to the metal in all
the complexes. Thus, the coordination number
for Sm, Gd and Tb in these complexes becomes
eight, and for Y, Er and Yb it becomes nine. The
coordination number for La, Pr and Nd is nine
or ten depending on whether one or two molecules
of water are coordinated. The complexes, however,
have as 1:2 electrolytes in acetonitrile (Table I)
probably due to the displacement of an iodide ion
from the coordination sphere by the solvent.

The molecular weight determinations of the com-
plexes in water show the presence of ten and eight
species in solution for the two sets of complexes,
suggesting complete dissociation of the complexes
in water.

One of the authors (D.K.K.) thanks the UGC,
New Delhi, for the award of a fellowship.

References
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Ni(II) Complexes with Salicylideneaminoguanidine
& o-Hydroxyaceto phenoneaminoguanidine

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Received 12 March 1976; revised 23 November 1976; accepted 6 June 1977

Complexes of Ni(II) with Schiff bases derived from
aminoguanidine and salicylaldelyde or o-hydroxy-
on the basis of analytical, UV and IR data. Complexes of the type \([\text{Ni(L)(Py)}]X\), where \(LH = \text{Schiff base, Py = pyridine and } X = \text{NO}_3, \text{Cl}, \text{Br} \) or \(I \) are assigned square planar structure while complexes of the type \([\text{Ni(L)(Py)}]\text{ClO}_4\) are assigned octahedral structure.

OVORKA et al. have recently suggested\(^1\) the use of salicyldieneaminoguanidine (LH) as a reagent for the estimation of Ni(II). In this note the preparation and characterization of Ni(II) complexes of the type \([\text{Ni(L)(Py)}]X\), where \(L = \text{Schiff base Py = pyridine and } X = \text{NO}_3, \text{Cl}, \text{Br} \) or \(I \) are reported. The Schiff bases used have been derived from aminoguanidine and salicylaldehyde (LH) or o-hydroxyacetophenone.

Aminoguanidine bicarbonate was obtained by the action of sodium bicarbonate on aminoguanidine in ammoniacal acid. It is also substantiated by the presence of \(\text{NH}_2\) group. In the cases of nitrate and perchlorate complexes, the IR data of inorganic and coordination compounds show bands at 3430, 3300 cm\(^{-1}\) which may be assigned to \(\text{NH}_2\). The position of the N-H frequency is unchanged from that of ligands, hence \(\text{NH}_2\) and \(\text{NH}_2\) do not take part in the coordination.

The diamagnetic properties and the magnetic properties of the hexaordinated complex suggest that they are octahedral.

The author is thankful to Prof. S. P. Ghosh, Patna University, Patna, for useful discussions and to Shri R. N. Thakur, Bihar University, for recording IR spectra.

References
Mixed Ligand Complexes of Ni(II), Zn(II) & Cd(II) with 2,2'-Bipyridyl as a Primary Ligand & α-Amino Acids as Secondary Ligands

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Received 21 April 1976; accepted 3 March 1977

Solution equilibria of the systems Ni(II), Zn(II) or Cd(II)-2,2'-bipyridyl(bipy)-α-amino acids [glycine (gly), α-alanine (ala) or norleucine (norleu)] have been studied. The pH-metric titration of the reaction mixture containing equimolar solutions of metal ion, bipy and one of the secondary ligands (gly, ala and norleu) have shown the formation of 1:1:1 mixed ligand complexes and their monohydroxo derivatives. The formation constants of the resulting complexes have been determined at 30±1° (μ=0·1, KNO₃) and in terms of the secondary ligands: gly>ala>norleu.

The equilibria involved in the mixed ligand chelate formation in the above systems may be expressed as:

\[ \text{MA}^{2+} + \text{L}^\equiv \text{MAL}^+ \quad \text{or} \quad \text{MA}^{2+} + \text{L}^\equiv \text{MAL}^+ \quad \text{or} \quad \text{MAL}^+ \]

where \( M^{2+} \) stands for metal ion, \( A \) for bipy and \( L^\equiv \) for the secondary ligand anion. The formation constant \( K_{\text{MAL}} \) of the 1:1 mixed ligand chelate may then be given by the relation (2)

\[ K_{\text{MAL}} = \frac{[\text{MAL}^+]^2}{[\text{MA}^{2+}][\text{L}^\equiv]} \]

The dissociation constant \( \phi K_i \) of norleucine (9·60±0·06) was determined by Chaberek and Martell's method and that of glycine (9·69), α-alanine (9·86) and 2,2'-bipyridyl (4·44) has been taken from the literature. The dissociation constant \( \phi K_i \) of norleucine (9·60±0·06) was determined by Chaberek and Martell's method and that of glycine (9·69), α-alanine (9·86) and 2,2'-bipyridyl (4·44) has been taken from the literature. The pH titration curves of solutions containing equimolar quantities of nickel, zinc or cadmium nitrate and 2,2'-bipyridyl respectively exhibit a sharp inflection at \( m=1 \) (where \( m = \text{noles of base added per mole of the metal ion} \) indicating the formation of 1:1 binary complex in the lower buffer region.

The \( \phi H \) titration curves of solutions containing nickel, zinc and cadmium nitrate in the presence of equimolar concentration of 2,2'-bipyridyl (HA⁻) and one of the secondary ligands (HL) exhibit only one sharp inflection at \( m=1 \), followed by buffer regions. In the initial stage, all these curves run slightly above the corresponding 1:1, M(II)-bipy titration curves and superimpose over these at \( m=1 \). This may be due to the zwitterion formation tendency of the α-amino acids and it indicates that initially M(II)-bipy complex is formed in the above systems. The mixed ligand chelate formation occurs after \( m=1 \) and this indicates that the chelation of the secondary ligand starts after the complete chelation of 2,2'-bipyridyl with the metal ion. It may be inferred from a similar comparison of titration curves with the corresponding composite curves which can be drawn by adding the horizontal distance of the secondary ligand curve to the horizontal distance of the M(II)-bipy curve at the same \( \phi H \).

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