Isatin-3-imine Complexes of Co(II) & Zn(II)

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Complexation behaviour of a new series of ligands, isatin-3-imines, towards Co(II) and Zn(II) has been studied. The resulting complexes are characterized on the basis of analytical, infrared and electronic spectral and magnetic susceptibility data. Isatin-3-imines act as neutral bidentate ligands, Co(II) and Zn(II) form bis and mono complexes respectively with coordinated halide ions.

A large variety of aromatic and aliphatic primary amines react with isatin and substituted isatins to give isatin-3-imines (I). While the reactions of aromatic amines are facile, the aliphatic amines sometimes give undesirable side products. (I) may coordinate with metal ions either as a neutral bidentate or as a monovalent bidentate ligand in the enolized form (II).

![Diagram of Isatin-3-imine structures](image)

However, it would be interesting to study whether enolized form (II) is stabilized as a result of coordinating with metal ions (coordination selectivity). It has been observed that complexation of the Schiff base derived from isatin and o-aminophenol takes place via the enolized form of the ligand system. It seems to be the only report in this area and it was thought worth while to study the generality of the systems by studying the behaviour of various isatin-3-imines (both aliphatic and aromatic) towards metal ions. We wish to report our results here.

Isatin (Sigma Chemicals) was used as such. Metals and halogens were estimated according to published procedures. All the isatin-3-imines were prepared similar to the procedure described earlier.

Preparation of metal complexes—A methanolic solution of metal halide and isatin-3-imine in 1:2 molar ratio for Co(II) and 1:1 for Zn(II) was stirred for 30 min. On cooling yellowish brown crystals were obtained in good yields. They were washed thoroughly with hot methanol.

These complexes are sparingly soluble in common organic solvents and they do not have sharp melting points. Use of metal acetates instead of metal halides give products on refluxing which are always contaminated with metal isatin complexes and decomposed ligand. Analytical data are given in Table 1.

Co(II) forms complexes of the type ML₂X₂ and Zn(II) forms MLX₂ where L stands for isatin-3-imine and X for halogen. The IR spectrum of the ligand exhibits ν(NH), ν(C=O) and ν(С=N) at 3230, 1750 and 1720 cm⁻¹ respectively. The positions of these bands remain fairly unaffected when the substituent R group is changed. In the IR spectra (nujol) of Co(II) and Zn(II) complexes the ν(C=O) and ν(C=N) are shifted to lower frequencies, the shift in ν(C=O) being of the order of 30 cm⁻¹ and in ν(C=N) it is of the order of 40-80 cm⁻¹, suggesting that oxygen and nitrogen of the imine form are involved in coordination. In the series of isatin-3-imine complexes where R is alkyl group, the lowering of ν(C=O) and ν(C=N) is not significantly different from one amine to another, whereas in going from aliphatic to aromatic amines the lowering of ν(C=O) and ν(C=N) as a result of complexation is significant. Thus in the case of Co(II) complexes when R is alkyl group the lowering of both ν(C=O) and ν(C=N) is about 30 cm⁻¹, while the corresponding shift is about 70 cm⁻¹ in the case of aromatic amines. This can be attributed to the delocalization of the lone pair electrons of imine nitrogen with the π-system of the aromatic group.

In Co(II) complexes the strong ring vibration of the ligand at 1678 cm⁻¹ overlaps with ν(C=N) of the complexes when R = alkyl group and appears as a shoulder when R = aryl. The other ring vibration at 1615 cm⁻¹ of the ligand occurs as a shoulder in the complexes where R = alkyl and as a split band where R = aryl.

The position of δ(N-H) remains unaltered in the complexes showing that nitrogen at position-I does not participate in the bonding process. However, the δ(N-H) occurs at 1350 cm⁻¹ in the free ligand similar to that in dimethylurea and this shows a marginal shift towards higher frequencies in the complexes.

The μeff for Co(II) complexes calculated from room temperature magnetic susceptibility studies (Gouy method, Hg[Co(SCN)₄] as calibrant) vary from 4.8 to 5.05 BM. This clearly shows that the complexes have octahedral geometry with high-spin Co(II) as central metal ion. The electronic spectrum of the ligand shows a band around 24390 cm⁻¹, suggesting that oxygen and nitrogen of the imine form are involved in coordination. In the case of Co(II) complexes, the strong ring vibration of the ligand at 1678 cm⁻¹ overlaps with ν(C=N) of the complexes when R = alkyl group and appears as a shoulder when R = aryl. The other ring vibration at 1615 cm⁻¹ of the ligand occurs as a shoulder in the complexes where R = alkyl and as a split band where R = aryl.

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the Zn(II) complexes due probably to chelation. Similar observation has been made in the case of isatin.8 No well-defined bands appear in the solid spectra of Co(II) complexes, instead a shoulder is observed. The position of this absorption corresponds to octahedral Co(II) ion. Lack of resolution in this region makes proper assignments difficult. From the present results we conclude that Co(II) and Zn(II) complexes adopt octahedral and tetrahedral geometries respectively.

It may be pointed out here that the ligands act as neutral bidentate in both Co(II) and Zn(II) complexes, contrary to the earlier observation.6

References

Reactions of Silicon(IV) Tetraacetate with Bifunctional Tridentate & Tetradentate Schiff Bases
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Bifunctional tridentate Schiff bases (SBH) having the donor system HO-N-OH and the general formula C8H8O2N2C(CH3)=N(phenyl)-N(OH)R (where R = -(CH2)2- or -(CH2)2CH-) of n-C3H7 or o-C3H7 react with silicon tetraacetate in the molar ratio 1:1 and 1:2 to give monomeric penta- and hexa-coordinated complexes of the type Si(OAc)2(SB) and Si(SB)2 respectively. On the other hand, bifunctional tetradentate Schiff bases (S'B'H)C8H8N2O2C(CH3)=N(CH2)2N-CH3 (where n = 2 or 3), having the donor system HO-N-OH yield only monomeric hexa-coordinated complexes of the type Si(OAc)2(S'B') (where S'B'H represents the bifunctional tetradentate Schiff base). The bisacetoxydimethylsilicon-Schiff base complexes are highly susceptible to moisture and undergo replacement reactions with 2-methylpentane-2,4-diol. The resulting Si(OAc)2(SB), Si(OAc)2(S'B) and Si(SB)2 type of complexes are stable.

In view of the commercial importance of the nitrogenous compounds of silicon, a number of silicon complexes with bifunctional tridentate and tetradentate Schiff bases (I and II) have now been prepared and characterized on the basis of elemental analyses, conductance and IR data.

Schiff bases of 1-phenylbutane-1,3-dione with 2-hydroxyethylamine, 2-hydroxy-1-propylamine and 3-hydroxy-1-propylamine were prepared by taking equimolar amounts of hydroxyalkylamine and 1-phenylbutane-1,3-dione in benzene and refluxing for several hours, followed by the removal of water-benzene azeotrope and recrystallization in absolute ethyl alcohol. Schiff base of 1-phenylbutane-1,3-dione with 2-hydroxyaniline was prepared by heating equimolar amounts of both in absolute ethyl alcohol for 1 hr and then recrystallized by the same solvent before use. Schiff bases of 1-phenylbutane-1,3-dione with ethylenediamine and 1,3-propylenediamine were prepared by heating equimolar amounts of the reactants in absolute ethyl alcohol and recrystallized with the same solvent. The analysis and physical characteristics of these Schiff bases are reported in Table 1.

Silicon-Schiff base complexes — Silicon tetraacetate was dissolved in dry benzene (40 ml) and the calculated amount of the Schiff base was added. The contents were refluxed over a rathiohead for 8-10 hr in the case of 1:1 molar ratio and for 14-16 hr in the case of 1:2 molar reactions respectively. The excess of the solvent was removed over rathiohead and the product then dried under vacuum. The details of their synthesis, analysis and physical properties are recorded in Table 2.

Table 1 — Analysis and Characteristics of Schiff Bases

<table>
<thead>
<tr>
<th>Si No.</th>
<th>Schiff base</th>
<th>Physical characteristics</th>
<th>Analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>State</td>
<td>m.p. (°C)</td>
</tr>
<tr>
<td>1</td>
<td>=-CH2CH2=</td>
<td>Light yellow</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>=-CH2CH-</td>
<td>solid</td>
<td>do 111</td>
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<tr>
<td>3</td>
<td>=-CH2CH2CH2=</td>
<td>Colourless</td>
<td>78-79</td>
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<tr>
<td>4</td>
<td>=-O-C3H7</td>
<td>Orange-yellow</td>
<td>164</td>
</tr>
<tr>
<td>5</td>
<td>=-CH2CH-</td>
<td>Colourless</td>
<td>181</td>
</tr>
<tr>
<td>6</td>
<td>=-CH2CH2CH2=</td>
<td>solid</td>
<td>do 112</td>
</tr>
</tbody>
</table>

*has been used to distinguish the compounds of the same molecular formula. For R and R' see structures I and II.