2,4-diol — The above type of complexes were dissolved in anhydrous benzene (35 ml) and 2-methylpentane-2,4-diol added in equimolar ratio. The mixture was then refluxed for 8 hr and the excess of the solvent removed on the rotovap and then under reduced pressure. The details of synthesis, analysis and properties are recorded in Table 3.

Reactions of silicon tetraacetate with S'B'H₂ in 1:2 molar ratio were also attempted but in all the cases only 1:1 complexes were obtained.

The resulting derivatives are quite soluble in benzene except those derived from the Schiff bases 3-(2-hydroxyphenyl)-amino-1-phenyl-2-buten-1-one and bis(1-phenylbutane-1,3-dione)-1,3-propylenediamine, which are sparingly soluble. The diacetoxy derivatives are readily susceptible to moisture, whereas Si(SB)₂ type of derivatives appear to be quite stable. The ebullioscopic determinations of molecular weights in boiling benzene show them to be monomers indicating penta-coordinated (III) and hexa-coordinated (IV, V) environments for the central silicon atom in Si(OAc)₂(SB), Si(OAc)₂(S'B') and Si(SB)₂ type of derivatives respectively.

Further, replacement reactions of 2-methylpentane-2,4-diol (C₆H₁₄O₂) with Si(OAc)₂(SB) and Si(OAc)₂(S'B') type of derivatives can be represented as follows:

\[ \text{Si(OAc)}_2 \cdot \text{SB} + \text{C}_6\text{H}_{14}\text{O}_2 \rightarrow \text{Si(C}_6\text{H}_{18}\text{O}_2) \cdot \text{SB} + 2\text{AcOH} \]
\[ \text{Si(OAc)}_2 \cdot \text{S'B'} + \text{C}_6\text{H}_{14}\text{O}_2 \rightarrow \text{Si(C}_6\text{H}_{18}\text{O}_2) \cdot \text{S'B'} + 2\text{AcOH} \]

The resulting derivatives are yellow to brown in colour, soluble in benzene and monomeric in nature. However, as compared to bisacetoxy Schiff base derivatives, these are quite resistant to hydrolysis and melt/decompose comparatively at higher temperatures.

The conductivity measurements of some of the stable derivatives in dimethylformamide were carried out and found to be non-electrolytes.

The IR spectra of the Schiff bases exhibit vOH and vNH in the region 3320-3150 cm⁻¹. The shift to lower frequency region may be attributed to the presence of both types of hydrogen bonding — intermolecular (O-H...O) as well as intramolecular (O-H...N). These bands disappear in the silicon derivatives indicating chelation of the silicon atom to both oxygen and nitrogen.

![Diagram](image)

(Where HO - N - OH and HO - N - N - OH represent the bifunctional tridentate and bifunctional tetradentate Schiff base molecules respectively)

A strong band in the 1610-1590 cm⁻¹ region in the Schiff bases, characteristic of the azomethine (C=N—), remains unaltered or is slightly shifted towards lower side in the silicon derivatives on complexation.

A very strong band in the 1740-1710 cm⁻¹ region in the case of bisacetoxy Schiff base is assigned to vCO of the acetoxy group.

Several new bands in the silicon derivatives in the 760-615 cm⁻¹ region may probably be assigned to v(Si-O).

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**References**


**Co(II) Complexes of Benzoylhydrazones of Salicylaldehyde, o-Hydroxyacetophenone, o-Hydroxypropiophenone, o-Hydroxybutyrophenone & 2-Hydroxy-1-naphthaldehyde**

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Co(II) complexes of the general formulae [Co(L)₂] (type A) and [Co(L)] (type B) (L = ligand) with benzoylhydrazones derived from benzoylhydrazine and salicylaldehyde, o-hydroxyacetophenone, o-hydroxypropiophenone, o-hydroxybutyrophenone and 2-hydroxy-1-naphthaldehyde have been prepared and characterized on the basis of elemental analyses, magnetic moment, electronic and IR spectral data. In the case of Co(II) chloride, octahedral complexes are formed indicating the reaction of the ligands in the keto form, whereas in the case of Co(II) acetate tetrahedral complexes are obtained suggesting the coordination of benzoylhydrazones in the enolic form. IR spectral data suggest that the ligands are tridentate with a set of ONO donor atoms.

WITH a view to gaining information about keto-enol tautomerism in chelated benzoylhydrazones, we report here isolation and characterization of some new complexes of Co(II) with benzoylhydrazones derived from salicylaldehyde (BSH), o-hydroxyacetophenone (BAH), o-hydroxypropiophenone (BPp), o-hydroxybutyrophenone (BBH) and 2-hydroxy-1-naphthaldehyde (BNN).

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The benzoylhydrazones were prepared by the reaction of benzoylhydrazine (0·1M) with the corresponding aldehyde or ketone (0·1M) in ethanol following the method of Struve1. These were recrystallized from ethanol.

**Preparation of Co(II) complexes** — Dropwise addition of the solution of benzoylhydrazone (0·01M in 50 ml acetone) to a boiling ethanolic solution of cobalt(II) chloride or acetate (0·005M) and subsequent refluxing for 3-4 hr yielded, on cooling, two types of complexes, orange-brown [Co(L1)] (type A) and bluish [Co(L2)] (type B). These were filtered off, washed several times with ethanol and dried in vacuo. The complexes do not melt or decompose up to 300°. These are soluble in DMSO, DMF, partially soluble in acetone, ethyl methyl ketone, ethanol but insoluble in other common organic solvents. However, solubility of type B complexes is less than that of type A.

The magnetic moment and IR and electronic spectral measurements were made as reported previously2.

Analytical data (Table 1) reveal that A and B types of complexes have 1:2 and 1:1 (metal-ligand) ratio respectively. The molar conductance values for 10\(^{-4}\)M solutions in DMF or DMSO are very small and indicate non-ionic nature of the complexes. Efforts to determine molecular weights were not successful due to the limited solubility of the complexes.

Magnetic measurements show that complexes of the type [Co(L)] have \(\mu_{eff}\) values in the range 3·85-3·98 BM which is slightly lower than that for tetrahedral complexes3 (4·2-4·7 BM). This may be due to dimerization of the complexes. Oxygen bridged dimeric structure for Cu(II) complexes of benzoylhydrazones has been reported by Biradar et al.4. Magnetic moments for [Co(L)\(_2\)] complexes vary from 4·84 to 4·99 BM which are well within the range reported for high-spin pseudo-octahedral Co(II) chelates of aroylhydrazones5.

For Co(II) in tetrahedral field, three spin-allowed bands are expected, corresponding to the transitions \(4A_2(F)\rightarrow T_{2g}(F)(v_1)\), \(4A_2(F)\rightarrow T_{1g}(F)(v_2)\) and \(4A_2(F)\rightarrow T_{1u}(F)(v_3)\) whereas in the field of octahedral symmetry, the order of energy level splitting of the \(4F\) state is reversed.

**Table 1 — Analytical and Magnetic Moment Data of Co(II) Complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (calc.), %</th>
<th>(\mu_{eff}) (BM) at 300°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>9·50 (9·43)</td>
<td>20-02 (19·83)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>9·02 (9·00)</td>
<td>19-10 (18·93)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>8·57 (8·61)</td>
<td>17·98 (18·11)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>8·16 (8·26)</td>
<td>17·41 (17·37)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>8·08 (8·07)</td>
<td>17·04 (16·97)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>10·50 (10·42)</td>
<td>11·02 (10·96)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>9·79 (9·91)</td>
<td>10·51 (10·42)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>9·35 (9·42)</td>
<td>9·99 (9·91)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>8·95 (9·00)</td>
<td>9·38 (9·46)</td>
</tr>
<tr>
<td>[Co(C(_6)H(_4)NO(_2)]</td>
<td>8·82 (8·79)</td>
<td>9·22 (9·24)</td>
</tr>
</tbody>
</table>

Satisfactory C and H analyses were also obtained.

The electronic spectra of [Co(L)] complexes show only two bands in the region 7500-7650 and 16000-16190 cm\(^{-1}\) which may be attributed to \(v_8\) and \(v_9\) spin-allowed transitions respectively. Using the equations due to Carlin6 the theoretical value of the first spin-allowed band \(v_8\) is found to be in the range 3515-3580 cm\(^{-1}\) which is in fair agreement with the predicted value for tetrahedral complexes. In the tetrahedral environment, the first band \((10Dq)\) has been observed very rarely which should be found in the region 3000-5000 cm\(^{-1}\). In contrast, the spectrum of [Co(L)\(_2\)] is consistent with an octahedral environment. It exhibits two main bands appearing around 10000 and 20000 cm\(^{-1}\) and two shoulders around 18500 and 19400 cm\(^{-1}\). The first and the last bands can be assigned to \(v_1\) and \(v_2\) transitions respectively in idealized \(O_h\) symmetry and the shoulders may either be due to the appearance of \(v_3\) transition7 or they may be because of the splitting of \(v_2\) transition. It has been suggested8-10 that the energy of \(v_3\) transition should be approximately twice but not greater than 2·2 times that of the \(v_3\) transition. In the present complexes, the ratio of \(v_3/ v_2\) comes out to be \(\sim 1·95\) suggesting the shoulders around 19400 cm\(^{-1}\) to be due to \(v_2\) transition. Further, the ratio \(Dq(tetra)/Dq(octa)\) comes out to be 0·43, which is in agreement with the predicted value 4/9, thereby supporting the assigned geometry to the complexes.

In the IR spectra of the benzoylhydrazones and their complexes, [Co(L)\(_2\)], bands characteristic of \(\nu_{N\cdot H}\) (3000-3050 cm\(^{-1}\)) along with those due to other amide group vibrations are observed, suggesting that the ligand residue exists in keto form in the complexes. The free ligand exhibits characteristic bands around 1675 (\(\nu_{C\cdot O}\)) and 1250 cm\(^{-1}\) (\(\delta N\cdot H\)), assignable to amide I, II and III bands respectively11-13. In the spectra of complexes, amide-I band shifts to lower frequencies (1628-1637 cm\(^{-1}\)), while the amide-II band increases in frequency (1522-1529 cm\(^{-1}\)) and amide-III band splits into two components appearing in the ranges 1206-1215 and 1360-1380 cm\(^{-1}\) respectively. The position of amide-IV band remains unchanged while amide-VI band shows an upward shift. These changes in amide group vibrations indicate the coordination of amide oxygen to the metal ion14-16.

The \(\nu_{C\cdot N}\) of the ligand occurring in the region 1615-1625 cm\(^{-1}\) is lowered by 12-16 cm\(^{-1}\) in the chelates with slight loss in intensity of the band, suggesting that the nitrogen of the azomethine group is coordinated to Co(II).

The bands occurring in the regions 3200-3250 and 2700-2775 cm\(^{-1}\) due to \(\nu\)OH vibrations (involving intramolecular hydrogen bonding) in the free ligands are not observed in the complexes and the phenolic \(\delta\)CO around 1280 cm\(^{-1}\) in the ligands is shifted to the region 1298-1318 cm\(^{-1}\). This suggests that the \(\nu\)hydroxy group of the ligand is involved in coordination.

As compared to the octahedral Co(II) complexes, the IR spectra of complexes of the type [Co(L)] lack absorptions due to \(\nu\)NH and amide group vibrations but show strong bands around 1595 cm\(^{-1}\) due to \(\nu\)C=N—N=C\> residue confirming deproto-
nation of amino proton. It seems that the liberated protons are continuously removed from the reaction medium through the formation of weakly ionized acetic acid.

The authors are thankful to the UGC and CSIR, New Delhi, for financial support.

References

Ionization Constants & Thermodynamic Parameters of Salicylaldehyde & o-Hydroxyacetophenone, o-Hydroxypropio- & o-Hydroxy-5-methylbenzo-phenones

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The values of the thermodynamic ionization constants (pK) and the thermodynamic functions $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ associated with the ionization of salicylaldehyde (SAL), o-hydroxyacetophenone (HAP), o-hydroxypropionophenone (HPP) and o-hydroxy-5-methylbenzophenone (HMIBP) have been determined at 25°C in water and in 75% (v/v) dioxane. The differences in the values of ionization constants and thermodynamic parameters of the above ligands have been interpreted in terms of the inductive, mesomeric, resonance and hyperconjugation effects. The higher free energy and the lower enthalpy change accompanying the ionization of SAL and HAP in 75% (v/v) dioxane as compared to those in water have been attributed to greater work done for ionization in a medium of lower dielectric constant.

Although a large number of studies have been reported on the proton-ligand stability constants of structurally analogous ligands salicylaldehyde (SAL), o-hydroxyacetophenone (HAP) and o-hydroxypropionophenone (HPP), the results are not conclusive. Kamat and Datar have suggested that the methyl substituted ligands are more acidic than the parent ligands while Patel and Patel have observed that the methyl substituent decreases the acidity. In view of this the thermodynamic parameters for the ionization of SAL, HAP, HPP and o-hydroxy-5-methylbenzophenone (HMIBP) have been measured in aq. dioxane (75%, v/v).

SAL (Koch-Light), HAP (Koch-Light) and HPP (Fluka) were distilled before use. HMIBP (Aldrich Chemicals) was used as such. The standardization of glass electrode, the calculation of mean activity coefficient, volume correction factor, ionic product of water in 75% (v/v) dioxane and dissociation constants along with other experimental details have been described earlier.

The pK values of SAL, HAP, HPP and HMIBP in water and in 75% (v/v) dioxane are presented in Table 1. The present values are in good agreement with those reported in literature. It may be noted that the pK values of SAL and HAP in 75% (v/v) dioxane are significantly higher than the corresponding values in water as expected on the basis of the dielectric constant of the media. The pK values of the ligands are in the following order: HMIBP > HPP > HAP > SAL. Because of the CH₃, CH₂ and C₆H₅ substituents, higher electron density at the carbonyl oxygen will be observed in the cases of HMIBP, HPP and HAP compared to that in unsubstituted SAL. This will lead to stronger hydrogen bond formation with >C=O and hence higher ionization energies of phenolic OH bonds in agreement with the above order of pK values.

The values of the changes in free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($-\Delta S^\circ$) associated with the ionization of the ligands are reported in Table 1. The literature values of $\Delta H^\circ$ and $\Delta S^\circ$ of SAL and HAP in water at 25°C are in good agreement with the present values. The $\Delta G^\circ$ values of SAL and HAP in water are lower as compared to those in 75% (v/v) dioxane while the $\Delta H^\circ$ values are significantly higher in water as compared to the corresponding values in 75% (v/v) dioxane as expected on the basis of the dielectric constant of the media. It may be noted that in a given medium the $\Delta S^\circ$ values for the ionization of all the four ligands are same within the limits of experimental error. Since $\Delta G^\circ$ values for the ionization of the ligands vary and $-\Delta S^\circ$ values are constant, the $\Delta H^\circ$ values for the ionization of the ligands will therefore follow the same order as the $\Delta G^\circ$ values. This is in agreement with our experimental results.

Since -CH₃ and -C₆H₅ groups have positive inductive effects (+I) they increase the electron density at the oxygen atom of the >C=O group facilitating a stronger hydrogen bonding as compared to that present in unsubstituted ligand, SAL. Increased hydrogen bonding will hamper the ionization of phenolic -OH group and lead to a higher pK value. Inductive effect is known to decrease rapidly with distance hence, in HMIBP, the contribution from the +I effect of the -CH₃ group is expected to be very small. But by virtue of the CH₃ group being...