Metal Complexes of 2-Acetylacetonimino-5-(p-anisyl)-1,3,4-oxadiazole

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Metal complexes of the type [M(SB)₂(H₂O)₂] [where M = Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II), Hg(II), Mn(II) and SB = deprotonated 2-acetylacetonimino-5-(p-anisyl)-1,3,4-oxadiazole] have been prepared in the ethanolic medium and characterised on the basis of analytical, UV and IR spectral and magnetic susceptibility data. The complexes have been assigned octahedral stereochemistry on the basis of magnetic and spectroscopic studies. The crystal field parameters for Co(II) and Ni(II) complexes have been calculated; these agree fairly well with the reported values for known octahedral complexes of Co(II) and Ni(II).

There has been a growing interest in the synthesis of compounds containing -N-S-N- grouping because of their biological importance. Oxadiazole and its derivatives have been shown to possess analgesic and anticonvulsant activities because of their biological importance. Oxadiazole and its derivatives have been reported to display anti-inflammatory and hypotensive activities. More recently, 2,5-disubstituted oxadiazole and its derivatives have been reported to display antinociceptive and anticonvulsant activities. 1,3,4-Oxadiazole moiety and similar heterocyclic residues have been investigated for their biological importance. Oxadiazole and its derivatives have been prepared in the ethanolic medium and characterised on the basis of analytical, UV and IR spectral and magnetic susceptibility data. The complexes have been assigned octahedral stereochemistry on the basis of magnetic and spectroscopic studies. The crystal field parameters for Co(II) and Ni(II) complexes have been calculated; these agree fairly well with the reported values for known octahedral complexes of Co(II) and Ni(II).

Preparation of the complexes

Appropriate metal acetate or nitrate and the ligand were taken in 1:2 molar ratio in ethanol and refluxed on a water-bath for ~3 hr. Then a few drops of 0.01 N sodium hydroxide solution were added and pH adjusted to 8, when a precipitate was formed. The precipitate was aged by digestion on a water-bath for 30 min. Then it was filtered, washed with a small quantity of ethanol followed by ether and was dried in vacuo for ~12 hr. The complexes were analysed by standard methods. The analytical data indicate M(SB)₂.2H₂O composition for the complexes. The complexes are insoluble in water and common organic solvents, but are slightly soluble in dioxan and DMSO. The complexes do not have sharp melting points and a few decompose above 250°C.

Electronic spectra of the freshly prepared complexes were recorded in dioxan as well as in nujol. Infra red spectra were recorded in KBr in the range 4000-400 cm⁻¹ on a Perkin-Elmer 398 spectrophotometer. Magnetic susceptibilities were determined by the Gouy method at room temperature.

The ligand, 2-acetylacetonimino-5-(p-anisyl)-1,3,4-oxadiazole (HSB), is reported to exist in solution in a tautomeric equilibrium of the keto and enol forms. The IR spectrum of the ligand in solid state shows a sharp and strong band at 3320 cm⁻¹ which could be due to vOH of the enolic form or vNH in the keto form obtained by the migration of a CH₂ proton to the azomethine nitrogen. However, the UV spectrum of the ligand shows an intense band around 35,700 cm⁻¹ (280 nm) which is characteristic of acetylacetone with extended conjugation. This further confirms the existence of the keto form of the ligand.

The band at ~3320 cm⁻¹ in the spectrum of the ligand disappears in the spectra of the complexes suggesting the coordination of the nitrogen atom of the azomethine group to the metal ion. Sharp and broad bands at ~3560 cm⁻¹ and 3400-3300 cm⁻¹ respectively are observed in the spectra of the complexes which are assigned to the v₁ and v₃ vibrations of the coordinated water molecules. The complexes were heated in an oven to ~200°C for a period of 1 hr and cooled. The IR spectra of these samples were recorded and it was found that vOH and δHOH modes remained unaltered confirming the presence of coordinated water molecules.

A strong and sharp band at 3140 cm⁻¹ in the spectrum of the ligand is characteristic of vOH vibration of intramolecularly hydrogen bonded OH group indicating the existence of enolic tautomeric
The characteristic bands for ring skeletal vibration of the oxadiazole heterocyclic system appearing at ~1030, 840, 750, 690 and 620 cm\(^{-1}\) (ref. 6, 8-10) remain unchanged in the complexes suggesting non-participation of the ring nitrogen in coordination. However, the band at ~910 cm\(^{-1}\) characteristic of \(\nu(N-N)\) vibration of the oxadiazole ring\(^6\) is shifted to 950 cm\(^{-1}\) in the complexes. This is perhaps due to \(\pi\) electron interaction of the heterocyclic ring with the hydrogen bonded coordinated water molecules as described earlier.

Three additional bands are observed in the spectra of the complexes around 525, 480 and 320 cm\(^{-1}\). The first may be tentatively assigned to \(\nu(M-N)\) mode while the two latter bands may be assigned to \(\nu(M=O)\) mode.

The magnetic moment of the copper(II) complex (brownish green) is 1.8 B.M. and its electronic spectrum shows a broad band with \(\lambda_{\text{max}}\) at ~15,400 cm\(^{-1}\). This band may be due to \(^2E_g\rightarrow^2T_{2g}\) transition in an approximately octahedral ligand field. The width and asymmetry of the band suggest tetragonal distortion which may be due to coordination to hetero atom and Jahn-Teller effect. Besides the ligand field band, a charge-transfer band is also observed at ~22,500 cm\(^{-1}\).

The cobalt(II) complex (buff) shows a band at ~16,000 cm\(^{-1}\) and exhibits a magnetic moment value of 4.8 B.M. at room temperature. These observations are the characteristic features of octahedral complexes of cobalt(II) ion. Hence, the electronic spectral band may be assigned to \(^4T_{2g}(F)\rightarrow^4T_{2g}(P)\) transition in an approximately octahedral field.

The electronic spectrum of nickel(II) complex (golden yellow) shows ligand field bands at ~10,420, 16,670 and 27,000 cm\(^{-1}\). The band at 27,000 cm\(^{-1}\) is weak and can be assigned to \(^3A_g(F)\rightarrow^3T_{2g}(P)\) transition. The other two bands are assigned to \(^3A_g(F)\rightarrow^3T_{2g}(P)\) and \(^3A_g(F)\rightarrow^3T_{2g}(P)\) transitions respectively in an octahedral field. The complex exhibits a magnetic moment value of 2.83 B.M. which supports octahedral geometry\(^11\).\(^13\).

The nephelauxetic ratios (\(\beta\)) for Co(II) and Ni(II) complexes have been calculated to be 0.80 and 0.798 respectively, which are less than one, suggesting partial covalency in the metal-ligand bond. The crystal field splitting energy (\(D_q\)), the Racah parameters (\(B\) and \(C\)) and the Slater-Condon parameters (\(F_2\) and \(F_4\)) have been also calculated for these complexes:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(D_q)</th>
<th>(B)</th>
<th>(C)</th>
<th>(F_2)</th>
<th>(F_4) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(SB)}_2(\text{H}_2\text{O})_3])</td>
<td>698</td>
<td>775</td>
<td>3592</td>
<td>1288</td>
<td>102.7</td>
</tr>
<tr>
<td>([\text{Ni(SB)}_2(\text{H}_2\text{O})_3])</td>
<td>1080</td>
<td>831</td>
<td>3913</td>
<td>1390</td>
<td>111.8</td>
</tr>
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</table>

The values obtained agree with the values reported for known octahedral complexes of Co(II) and Ni(II)\(^8\).\(^9\).

The magnetic moment for manganese(II) complex (leaf brown) is 6.1 B.M. Its electronic spectrum displays bands at 17,240, 22,220, 24,390, 26,320 and 28,570 cm\(^{-1}\) which may be assigned to the transitions \(^6A_g(S)\rightarrow^4T_{2g}(G)\), \(^4T_{2g}(G)\rightarrow^4T_{2g}(F)\), \(^4T_{2g}(F)\rightarrow^4T_{2g}(P)\) respectively.

Zn(II), Cd(II), and Hg(II) being \(d^{10}\) ions are diamagnetic and do not show \(d-d\) transitions. The information on their structures has therefore been derived from IR spectral measurements only. In view of the close resemblance of the characteristic IR spectral bands of these complexes with those of Cu(II), Co(II) and Ni(II) complexes and the analytical data, an
octahedral ligand arrangement is suggested in conformity with earlier reports.\(^1,18\)

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References


