Metal Complexes of 2-(2'-Hydroxy-1'-naphthalidene)-imino-5-(p-anisyl)-1,3,4-oxadiazole

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Metal complexes of the type [M(SB)₂(H₂O)₂] [where M = Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Hg²⁺, Pb²⁺, Cd²⁺, Mn²⁺, and SB = deprotonated 2-(2'-hydroxy-1'-naphthalidene)-imino-5-(p-anisyl)-1,3,4-oxadiazole] have been prepared and characterised on the basis of analytical data and IR and electronic spectra; and magnetic susceptibility measurements. Infrared spectra indicate coordination of the ligand to the metal ion through the phenolic oxygen atom and azomethine nitrogen atom. The Co(II), Ni(II), Cu(II) and Mn(II) complexes are paramagnetic and show normal magnetic moments for an octahedral environment, which is supported by the electronic spectra.

In continuation of our previous investigations¹,² the preparation and characterisation of some more complexes of divalent metal ions with the Schiff base, (2'-hydroxy-1'-naphthalidene)-imino-5-(p-anisyl)-1,3,4-oxadiazole are reported.

Preparation of the ligand and complexes

2-Amino-5-(p-anisyl)-1,3,4-oxadiazole and 2-hydroxy-1-naphthaldehyde were taken in 1:1 molar ratio in glacial acetic acid along with fused sodium acetate and refluxed in an oil-bath at 130°C for 3 hr. The excess of solvent and the water formed in the reaction were removed azeotropically. The mixture was poured into ice cold water with stirring. The yellow solid thus separated was filtered, washed and crystallised from ethanol. It analysed for C₂₀H₁₅O₃N₃; m.p. 205°C; PMR (CDCl₃): δ 3.25 (s, 3H, OCH₃), 7.15 (s, 1H, N = CH), 7.28-7.92 (m, 10H, unsymmetrical aromatic), 9.28 (s, 1H, phenolic OH).

Ethanolic solution of the appropriate metal salt and the ligand in 1:2 proportion was refluxed on a water-bath for 3 hr. The pH of the solution was raised by adding a few drops of 0.1 M sodium hydroxide solution when a coloured solid separated out. This was filtered, washed with ethanol followed by ether and dried in vacuo and analysed by standard methods.⁷

The analytical data indicate the composition [M(SB)₂₂H₂O] for the complexes (Table I). The complexes are insoluble in water and most of the common organic solvents, but sparingly soluble in dioxan and DMF. The complexes are quite stable thermally and melt above 250°C; a few decompose before melting.

IR Spectra of the ligand and the complexes were recorded in KBr in the range 4000-400 cm⁻¹ on a Perkin-Elmer 398 spectrophotometer. Magnetic susceptibilities were measured by Gouy method (Table I). Electronic spectra of the ligand and the metal complexes were recorded in dioxan. The thermogravimetric analyses of the complexes were carried out on an automatic TGA-DTA recording thermogram unit at a heating rate of 10°C/min taking 100 mg of the sample in each case.

The ligand 2-(2'-hydroxy-1'-naphthalidene)-imino-5-(p-anisyl)-1,3,4-oxadiazole(I) exists in solution in an intramolecularly hydrogen bonded form where the phenolic hydroxy group is engaged in hydrogen bonding either with the azomethine nitrogen or the ring nitrogen atom. The electronic spectrum of the ligand shows an intense band around 280 nm (35,700 cm⁻¹) which is characteristic of heterocyclic homoannular conjugated diene system with extended conjugation.⁸

In the IR spectrum of the ligand two strong and sharp bands at 3310 and 3120 cm⁻¹ have been assigned to phenolic v(OH)⁹,¹⁰, the bands are absent in the spectra of the complexes indicating deprotonation of the phenolic OH group and complexation with metal ions through the oxygen atom. A broad band observed in the spectra of the complexes (3400-3320 cm⁻¹) has been attributed to coordinated water.⁹

A strong band observed at ~1650 cm⁻¹ in the spectrum of ligand assigned to v(C = N), appears in the spectra of the complexes around 1620 cm⁻¹ as a strong and broad band suggesting the participation of azomethine nitrogen in bonding.² Two bands of medium intensity in the spectrum of the ligand obtained at 1610 and 1590 cm⁻¹ are characteristic of v(C≡N) cyclic conjugated systems and v(C≡C) in-plane vibrations of phenyl ring respectively; these do not undergo any change on complexation indicating that the nitrogen in oxadiazole ring is not coordinated to the metal ion. This is further confirmed by the appearance of characteristic bands for oxadiazole systems at 1030, 840 and 750 cm⁻¹ both in the spectra of the ligand and the complexes.⁸,¹⁰,¹²

The blue shift in the phenolic v(C-O) from 1330 to 1370 cm⁻¹ clearly shows deprotonation of phenolic hydroxyl group and coordination to the metal ion.
through oxygen atom. Additional bands are observed in the spectra of the complexes around 410-415 and 490-510 cm\(^{-1}\). The former may be assigned to M-.N and the latter to M-.O coordination.

The visible region spectrum of the cobalt(II) complex shows three bands at \(-7140, 15380\) and \(17240\) cm\(^{-1}\). In an octahedral field these bands can be assigned to \(4T_{1g}(F)\)-\(4T_{2g}(F)\), \(4T_{1g}(F)\)-\(4A_{2g}(F)\) and \(4T_{1g}(F)\)-\(4T_{1g}(P)\) transitions respectively. The magnetic moment value (4.99 BM) of the complex is in agreement with octahedral stereochemistry around Co(II) ion.

The Ni(II) complex yields three bands at \(-8760, 14700\) and \(24300\) cm\(^{-1}\). In an octahedral approximation these bands can be assigned to \(3A_{2g}(F)\)-\(3T_{1g}(F)\), \(3A_{2g}(F)\)-\(3T_{1g}(P)\) and \(3A_{2g}(F)\)-\(3T_{1g}(P)\) transitions respectively. The complex possesses normal magnetic moment (2.92 BM) observed for Ni(II) ion in an octahedral environment. The nephelauxetic ratios (\(\beta\)) for Co(II) and Ni(II) complexes have been calculated to be 0.76 and 0.77 respectively indicating partial covalency in the metal ligand bond. The values of the spectral parameters for [Co(SB)\(_2\)(H\(_2\)O)\(_2\)] are: \(D_{q}(843.5\) cm\(^{-1}\)), \(B(733.5\) cm\(^{-1}\)), \(C(3398\) cm\(^{-1}\)), \(F_2(1219)\) and \(F_4(97.09)\). The values for the [Ni(SB)\(_2\)(H\(_2\)O)\(_2\)] are: \(D_{q}(876.4\) cm\(^{-1}\)), \(B(797\) cm\(^{-1}\)), \(C(3753\) cm\(^{-1}\)), \(F_2(1333)\) and \(F_4(107.3)\).

The values fairly agree with those observed for known octahedral complexes of Co(II) and Ni(II) ions.

The copper(II) complex possesses the magnetic moment 2.1 BM. The electronic spectrum shows a broad asymmetric ligand field band in the region 13000-19000 cm\(^{-1}\) with maxima at \(-15000\) cm\(^{-1}\), corresponding to \(2E_g\)-\(2T_{2g}\) transition in a nearly octahedral arrangement. The width and asymmetry of the band suggest tetragonal distortion due to coordination to hetero atom and also Jahn-Teller effect.

The magnetic moment of Mn(II) complex is 5.92 BM. Its electronic spectrum shows a number of bands in the visible region, suggesting an octahedral geometry around the central metal ion in accordance with the previously reported values for Mn(II) ion\(^{16-19}\). Bands observed at 18870, 22220, 25000 and 28500 cm\(^{-1}\) can be assigned to the transitions \(6A_{1g}(S)\)-\(4T_{1g}(G)\), \(6A_{1g}(S)\)-\(4T_{2g}(G)\), \(-4E_g+4A_{1g}(G)\) and \(-4T_{2g}(D)\) respectively.

The Zn(II), Cd(II), and Hg(II) complexes are six-coordinated and have octahedral stereochemistries as indicated by the analytical results and IR spectral data\(^{20}\) (Structure II).

The thermal decomposition pattern of all the complexes was similar and the end products were found to be the respective metal oxides. The initial mass loss in the temperature range 170-300°C in a single step corresponds closely to two water molecules probably coordinated to the central metal ion in a similar chemical environment\(^{21}\). On further heating, the organic components of the complexes decompose...
leading to the formation of the metal oxide around 800°C. The order of thermal stabilities is: Zn > Cd > Mn > Co > Ni > Pb > Cu > Hg.

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References