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Complexes of some *3d* metal ions of the Schiff's base, *N,N′*-di-4-(4′-pentyloxybenzoate) salicylidene-1″, 3″-diamino-2″-propanol: Synthesis and spectral studies

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ABSTRACT

A nematogenic Schiff's base, *N,N′*-di-4-(4′-pentyloxybenzoate)salicylidene-l″, 3″-diamino-2″-propanol, (abbreviated as H_2L^6), was synthesized and its structure studied by elemental analyses, mass, NMR and IR spectra. The Schiff's base behaves as a dinegative hexa/tetradentate species in its metal complexes of the general formula, $[ML^6]_n$ where M^{II} Mn, Co, Ni, Cu and Zn. Their structural characterizations were made by various spectroscopic techniques.

1. Introduction

Ligands derived from substituted salicylaldimine have played an important part in revealing the preferred co-ordination geometries of metal complexes. Multidentate ligands are extensively used in coordination chemistry, since they can be applied in the construction of new frameworks with interesting properties [1]. Metals containing liquid crystals are called as metallomesogens [2,3], are achieved through changes of molecular conformation, shape and structure; their physico-chemical properties can be turned by the choice of metal ions, substituents, and position of substituents on core moieties [4–6]. Majority of the metallomesogens extensively studied includes those complexes derived from salicylaldimine Schiff's bases [7–9]. As a part of our further investigation [10–12] on transition metal complexes of a series of mesogenic Schiff's base ligands derived from 2,4-dihydroxybenzaldehyde, we report here a square-pyramidal Cu^{II} complex and octahedral Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} complexes on the basis of a logical discussion of spectral data on the bonding nature of ligand (H_2L^6).

2. Experimental section

2.1. Starting materials

All reagents were purchased from commercial sources and used as received: 1-bromopentane, 2,4-dihydroxybenzaldehyde, *N,N′*-dicyclohexylcarbodiimide (DCC), *N,N*-dimethylaminopyridine (DMAP) and 1,3-Diamino-2-propanol are from Sigma-Aldrich, USA; all hydrated metal (M Mn, Co, Ni, Cu and Zn) acetates are from Merck. The solvents received were dried using standard methods [13] when required.

2.2. Physical measurements

The ^1H and ^{13}C NMR spectra were recorded on a JEOL AL-300 MHz FT-NMR multinuclear spectrometer; C, H, and N contents were micro analyzed on an Elemental Vario EL III Carlo Erba 1108 analyzer. Infrared spectra were recorded on a JASCO FT/IR (model-5300) spectrophotometer in the 4000–400 cm^{-1} region. The mass spectra were recorded on JEOL SX-102 FAB mass spectrometer. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday balance. Electronic spectra of the complexes in chloroform solutions were recorded on a Shimadzu spectrophotometer, model, Pharmaspec UV-1700. Electron spin resonance spectra of the Cu^{II} complex were recorded at RT and LNT on a Varian E112 ESR spectrometer using DPPH as the *g*-marker. The mesophases were identified by the defect textures observed by using polarized hot-

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stage binocular microscope (LOMO, USA) equipped with digital camera (Nikon Coolpix 4500).

2.3. Synthesis and analyses

N,N′-di-4-(4′-pentyloxybenzoate)salicylidene-l″, 3″-diamino-2″-propanol, 3 (Scheme 1), was synthesized from the precursor materials, 1 and 2, as reported earlier [10–12]. $[ML^6]_n$ (M Mn, Co, Ni, Cu and Zn) complexes were prepared by refluxing solutions of the Schiff's base, H_2L^6, and the corresponding metal acetate in 1:1 molar ratio in dichloromethane/ethanol medium for ~1 h at 55 °C. The reaction mixture was left over night in the flask closed with guard tube. The solid colored complexes that separated out in each case were filtered under suction, washed repeatedly with cold ethanol and dried over fused $CaCl_2$.

2.3.1. Synthesis of N,N′-di-4-(4′-pentyloxybenzoate)salicylidene-1″, 3″-diamino-2″-propanol, H_2L^6, 3

N,N′-di-4-(4′-pentyloxybenzoate)salicylidene-l″, 3″-diamino-2″-propanol, H_2L^6, 3 was prepared by refluxing together absolute ethanolic solutions of the pentyloxybenzoate ester of 2,4-dihydroxybenzaldehyde (16.41 g, 50 mmol in 100 mL) and 1,3-Diamino-2-propanol (2.25 g, 25 mmol in 50 mL) for ~1.5 h in presence of a few drops of acetic acid and leaving the resultant solution over-night in the reaction flask at room temperature. The micro-crystalline product was filtered off by suction, thoroughly washed with cold ethanol and recrystallized from a mixture of absolute ethanol and chloroform (1:1 v/v) and dried at room temperature. Yield: 67% (23.81 g) as a yellow colored solid; m.p. 165 °C. $C_{41}H_{46}N_2O_9$ (710.81): Calcd. C, 69.28; H, 6.52; N, 3.94; found C, 69.23; H, 6.49; N, 3.92%.

2.3.2. Synthesis of Mn^{II} complex

Yield: 0.53 g (70%) as a blackish green colored solid. mp 210 ^{0}C (decomposes), μ_{eff} = 4.70 B.M.; $MnC_{41}H_{44}N_2O_9$ (763.73): Calcd.: C, 64.48; H, 5.81; N, 3.67; Mn, 7.19; found: C, 68.45; H, 5.83; N, 3.65; Mn, 7.15%.

2.3.3. Co^{II} complex

Yield: 0.52 g (68%) as an olive green solid; mp 260 °C, μ_{eff} = 4.66 B.M; $CoC_{41}H_{44}N_2O_9$ (767.73): Calcd.: C, 64.14; H, 5.78; N, 3.65; Co, 7.68; found: C, 64.12; H, 5.76; N, 3.66; Co, 7.65%.

2.3.4. Ni^{II} complex

Yield: 0.54 g (70%) as a green solid; mp 295 °C, μ_{eff} = 3.48 B.M; $NiC_{41}H_{44}N_2O_9$ (767.49); Calcd.: C, 64.16; H, 5.78; N, 3.65; Ni, 7.65; found: C, 64.17; H, 5.75; N, 3.64; Ni, 7.63%.

2.3.5. Cu^{II} complex

Yield 0.58 g (75%) as a green solid; mp 250 °C, $CuC_{41}H_{44}N_2O_9$ (772.34); Calcd.: C, 63.76; H, 5.74; N, 3.63; Cu, 8.23; found: C, 63.74; H, 5.73; N, 3.64; Cu, 8.21%.

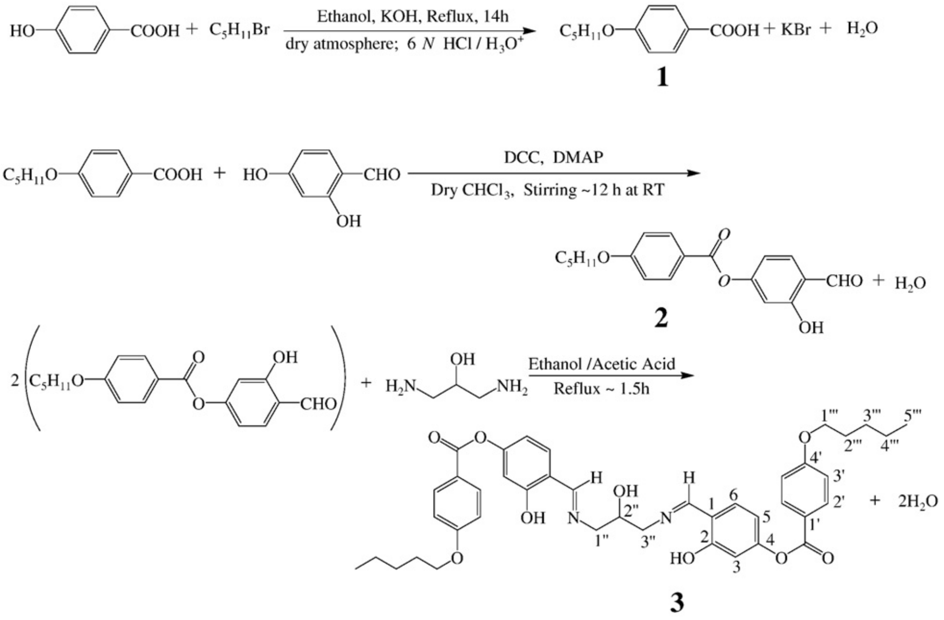
2.3.6. Zn^{II} complex

Yield 0.50 g (65%) as a white colored solid; m.p., 245 °C(decomposes); $ZnC_{41}H_{44}N_2O_9$ (774.19); Calcd.: C, 63.61; H, 5.73; N, 3.62; Zn, 8.45; found: C, 63.56; H, 5.71; N, 3.63; Zn, 8.42%.

3. Results and discussion

The Schiff's base ligand (H_2L^6), 3, and all of the metal complexes are colored and soluble in some non-polar/slightly polar solvents. The electrical conductivity values measured in saturated chloroform solutions of the complexes (3.4–3.6 Ω^{-1} cm^2/mole) imply their non-ionic nature [14]; they show normal μ_{eff} values except Cu^{II} complex.

A comparison of the NMR spectral data of the ligand with that of the Zn^{II} complex shows the absence of the phenolic-OH signal and a significant shift in the $—N{=}C\underline{H}$ peak position which implies [15] coordination through the phenolate anion and the azomethine nitrogen atom of the ligand. Similar shifts observed in the $^{13}C\{^1H\}$ NMR spectra were of considerable magnitude in the case of the carbon atoms directly attached to the bonding atoms ($—\underline{C}OO$ and $—N\underline{C}H$) while those observed for the carbons close to the bonding atoms ($—\underline{C}_4$ and $—\underline{C}_6$) were of lesser magnitude. The broad IR absorption centered at 3460 cm^{-1} in the spectrum of the ligand may be assigned to the ν(O—H) of the phenolic group [16]; the strong intensity bands at 1658, 1742 and 1168 cm^{-1} may be respectively assigned [17] to $\nu(C{=}N)_{azomethine}$, $\nu(C{=}O)_{esteric}$ and $\nu(C—O)_{phenol}$ modes. Bonding of the parent ligand through carbonyl oxygen (presumably of intramolecular type), azomethine nitrogen and phenolate oxygen could be inferred on the basis of (i) bathochromic shifts observed in the $\nu(>C{=}O)$ and $\nu(>C{=}N)$ frequencies and (ii) disappearance of the $\nu(O—H)_{phenolic}$ band in the spectra of the metal complexes; coordination through the nitrogen atoms of the ligand



Scheme 1. Synthetic steps involved in the synthesis of 1 (*p*- pentyloxybenzoic acid), 2 (4- pentyloxy-(4′-formyl-3′-hydroxy)benzoate) and 3 (*N,N′*-di-4-(4′-pentyloxy benzoate) salicylidene-l″,3″-diamino-2″-propanol, H_2L^6).