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SYNTHESIS AND THERMAL BEHAVIOR OF Ni(II), Cu(II), Co(II) AND Fe(III) METAL COMPLEXES WITH ONO TYPE SCHIFF BASE LIGAND

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ABSTRACT

This paper presents a simple coordinating behavior of Schiff base ligand with Ni(II), Cu(II), Co(II) and Fe(III) ions. A Schiff base ligand; 1-(N-ortho-hydroxyacetophenimine)-ethan-2-ol was reported in our previous literature, synthesized by the condensation of 2-hydroxyacetophenone and ethanolamine. Various metal ions such as Cu(II), Co(II), Ni(II) and Fe(III) were reacted with this receptor in 1:2 molar ratio to form their corresponding complexes. These complexes were characterized by elemental analysis, powder X-ray diffraction, spectroscopic methods (FT-IR, UV-Vis, Mass spectrometry, conductance measurements) and thermogravimetric analysis, which confirmed the formation of $[Cu(L)_2(H_2O)_2]Cl_2$, $[Co(L)_2(H_2O)_2](NO_3)_2$, $[Ni(L)(NO_3)](NO_3)$ and $[Fe(L)_2]Cl_3$ complexes (where L is Schiff base ligand).

Keywords: 1-(N-ortho-hydroxyacetophenimine)-ethan-2-ol,Thermogravimetric analysis,Molar conductance,Ni(II), Cu(II), Co(II), Fe(III)metal complexes.

1. INTRODUCTION

Schiff base complexes have been amongst the most prevalent coordination compounds in the past due to the availability of versatile synthons, easy preparatory routes, and a wide range of complexation capability [1]. Schiff bases offer opportunities for inducing substrate chirality [2], tuning the metal centered electronic factor, and enhancing the solubility and stability of either homogeneous [3] or heterogeneous catalysts [4]. They are also becoming increasingly significant as biochemical, analytical and antimicrobial reagents because they play an important role in catalysis and enzymatic reactions [5-8]. Schiff base moieties are used for designing and synthesizing highly selective and sensitive chemo sensors for the detection of metal ions in aqueous and nonaqueous medium [9, 10].

A simple Schiff base ligand, 1-(N-orthohydroxyacetophenimine)-ethan-2-ol reported in our previous literature [11], derived from 2-ethanolamine and 2-hydroxycetophenone showed very fascinating coordination behavior with copper ions. In an attempt, Koner *et al.* isolated square planar complex of this receptor with copper(II) centers, which were linked via nitrate O atoms at the two axial positions resulting in a helical chain structure [12]. The formation of helix was attributed to the asymmetric arrangement of nitrate bridged chain. It was also proved as selective and highly efficient catalyst with 100% conversion of styrene and its derivatives in the presence of hydrogen peroxide, which is otherwise quite difficult due formation the of benzaldehyde or phenylacetaldehyde. In another approach, Mitra et. al. isolated self-assembly of two dinuclear units of the copper-Schiff base ligand complex joined through doubly phenoxo bridging using same receptor [13]. Besides, Bohme et al. isolated five and six coordinate silicon complexes with this receptor. The complex with Ph₂SiCl₂ was trigonalbipyramidal in which ligand coordinates in a capping fashion with the two terminal O atoms in equatorial and the central N atom in the apical position. The complex with SiCl₄ is distorted octahedral with meridionalgeometry, where four O atoms are arranged in one plane [14]. Despite of identical synthetic conditions and similar metal centres, diverse coordinating behaviour was observed for this ligand. To explore the coordinating versatility of this ligand

towards various metal ions, we synthesized its complexes using metal salts like copper(II) chloride, cobalt(II) nitrate, nickel(II) nitrate and iron(III) chloride. The compounds were isolated as microcrystalline solids (which were not suitable for single crystal X-ray diffraction) and their crystalline nature was confirmed by powder X-ray diffraction. The formation of complexes was confirmed by elemental analysis, infrared spectroscopy, electronic spectra and their molar conductance. The stability of compounds was investigated by thermogravimetric analysis.

2. EXPERIMENTAL

2.1. Chemicals and equipments

All the reagents like 2-hydroxyacetophenone (Merck, India), 2-aminoethanol (Acros), copper(II) chloride dihydrate (Merck), cobalt (II) nitrate (Merck), nickel(II) nitrate (Merck) and iron(III) chloride (Merck) were purchased commercially and used as such without further purification. The organic solvents were purchased from Merck, India (methanol, diethyl ether, and THF) and purified by the reported methods [15].

Infrared spectra were routinely obtained on Thermo Scientific NICOLET IS50 FT-IR and Perkin Elmer RX-I FT IR Spectrophotometer. Mass spectral measurements (ESI source with capillary voltage 2500 V) were carried out on a VG Analytical (70-S) spectrometer. Microanalytical (CHN) data were obtained on a FLASH-2000 organic elemental analyzer. Electronic spectral measurements were carried out using ESICO 23750 double beam spectrophotometer in the range 200-700 nm. Thermogravimetric analysis was carried out in dynamic nitrogen atmosphere, with heating rate of 20°C min⁻¹ using TA Q600 analyzer. Crystalline nature of complexes was studied from X-Ray Diffraction patterns (XRD) obtained by Powder X-ray Diffraction technique using PANalyticalXPert PRO spectrophotometer equipped with Cu-K α radiation ($\lambda^{1/4}=1.541$ Å) in 2 θ range from 20° to 80°. The average crystallite size was calculated using the Debye Scherrer equation. Molar Conductance of different complexes in methanol was measured using Systronics conductivity meter 304.

2.2. Synthesis of Schiff base metal complex

The Schiff base ligand, 1-(N-orthohydroxyacetophenimine)-ethan-2-ol reported earlier [11] was further used to form metal complexes. All the metal complexes were prepared by a similar method. Solution of Schiff base ligand (5.5 mmol) in THF (20 mL) was mixed with solution of metal salt (2.7 mmol) in THF (10 ml) keeping metal-ligand ratio 1:2 with continuous stirring. The colour of solution changed immediately on adding metal salt. The contents were stirred for 2 h at room temperature. Afterwards the solid was separated by filtration and washed with diethyl ether to remove the unreacted impurities.



Scheme 1: Synthetic route for Schiff base metal complexes (1-4)

2.2.1. Synthesis of $[Cu(L)_2(H_2O)_2]Cl_2(1)$

Deep green solid; Yield: 89%; M.P.: 121°C; Anal. Calcd. For $C_{20}H_{26}Cl_2CuN_2O_6$: C, 45.77; H, 4.99; N, 5.34; Found: C, 43.96; H, 5.18; N, 5.41. *FT-IR (cm⁻¹)*: 3247 m (OH), 1627 s, 1599 s (-C=N-), 1315 m (C-N), 1230 m (C-O), 558 w (Cu-O). *MS*: *m/z* (relative *abundance, %)*: 180 (100), 145 (4.64), 119 (4.1), 91 (4.9). *UV-Vis:* (\mathcal{E}_{max} ·10⁴ molL⁻¹cm⁻¹): 267 (0.866), 350 (0.303). *Molar conductivity*: 162 (Ohm⁻¹ mol⁻¹cm⁻²).

2.2.2. Synthesis of $[Co(L)_2(H_2O)_2](NO_3)_2$ (2)

Deep brown solid; Yield: 68%; M.P.: 109°C; Anal. Calcd. For $C_{20}H_{26}CoN_4O_{12}$: C, 41.89; H, 4.57; N, 9.7; Found: C, 41.48; H, 5.00; N, 7.84. *FT-IR (cm⁻¹)*: 3326 m (OH), 1617 m, 1596 m (-C=N-), 1323 m (C-N), 1159 m (C-O), 580 m (Ni-O). *MS*: *m/z* (relative abundance, %): 476 (4.87), 397 (8.20), 385 (27.82),

52

342 (7.82), 180 (100), 91 (5.91). UV-Vis: $(\varepsilon_{max} \cdot 10^4 \text{ mol}L^{-1}\text{cm}^{-1})$: 270 (0.612), 388 (0.334). Molar conductivity: 171 (Ohm⁻¹mol⁻¹cm⁻²).

2.2.3. Synthesis of $[Ni(L)(NO_3)](NO_3)$ (3)

Light green solid; Yield: 75%; M.P.: 111°C; Anal. Calcd. For C $_{10}H_{11}NiN_3O_8$: C, 33.37; H, 3.08; N, 11.68; Found: C, 34.71; H, 4.77; N, 8.68. *FT-IR (cm⁻¹)*: 3332 m (OH), 1628 m, 1598 m (–C=N–), 1303 m (C– N), 1213 m (C–O), 535 m (Ni–O). *MS*: *m/z* (relative *abundance, %)*: 415 (46.15), 397 (46.15), 180 (100), 145 (3.88), 91 (5.14). *UV-Vis:* ($\varepsilon_{max} \cdot 10^4 molL^{-1}cm^{-1}$): 270 (0.649), 383 (0.293). *Molar conductivity*: 122 (Ohm⁻¹mol⁻¹cm⁻²).

2.2.4. Synthesis of $[Fe(L)_2]Cl_3(4)$

Brown solid; Yield: 52%; M.p.: 107°C; Anal. Calcd. For $C_{20}H_{22}Cl_3FeN_2O_4$: C, 47.93; H, 5.83; N, 6.08; Found: C, 46.50 H, 4.29; N, 5.42. *FT-IR (cm⁻¹)*: 3257 s (OH), 1626 s, 1594 s (–C=N–), 1314 m (C–N), 1218 m (C–O), 594 m (Fe–O). *MS*: *m/z* (relative abundance, %): 481 (5.74), 397 (0.79), 382 (0.63), 180 (100), 145 (2.97), 91 (2.70). UV-Vis: (ε_{max} ·10⁴ molL⁻¹cm⁻¹): 267 (0.851), 329 (0.345), 489 (0.040). *Molar conductivity*: 280 (Ohm⁻¹ mol⁻¹cm⁻²).

3. RESULTS AND DISCUSSION

Synthesis of Schiff base receptor was achieved by the 2condensation of ethanolamine and hydroxyacetophenone as reported in our previous literature [11]. The synthesized receptor was a tridentate ligand and can coordinate with various metal ions through its ONO donor system. The synthetic route for various metal complexes is depicted in Scheme 1 with expected structures. In the present work, Schiff base receptor coordinated with Cu(II), Co(II) and Fe(III) in 2:1 (L: M) ratio to form di-Schiff base complexes and in 1:1 (L:M) ratio and with Ni(II) to form mono-Schiff base complex. The structures of these complexes were elucidated on the basis of CHN analysis, mass spectrometry, IR spectroscopy and conductance measurements. The characterization data revealed that Cu(II) and Co(II) are surrounded by octahedral coordination sphere in which two coordination sites are occupied by water molecules and remaining four coordination sites are attached to two Schiff base moieties. On the other hand, water molecules are not found in the coordination sphere of Ni(II) and Fe(III).

3.1. IR Spectroscopy

The most characteristic aspects of the IR spectra of prepared complexes is the stretching frequencies of azomethine(>C=N-) groups. Schiff base receptor showed a strong peak at 1606 cm⁻¹, which was attributed to the vibrational band for the azomethine (>C=N-) group, shifted to lower frequency in the range of 1600-1592 cm⁻¹ in all the compounds. Strong peaks appeared in the range 1400-1300 cm⁻¹ and 3400-3100 cm⁻¹ may be assigned to the nitrate and -OH stretching frequencies, respectively in the corresponding complexes (also confirmed by CHNS analysis). The peaks appearing in 2847-2950 cm⁻¹ and 480-491 cm⁻¹ may be attributed to the vibration of methylene ($-CH_2-$) groups and M–O vibration, respectively of all complexes.

3.2. Thermogravimetric analysis

Thermogravimetric analysis of receptor showed a sharp mass loss at around 165°C indicating the complete decomposition of receptor. In the similar manner, all metal complexes showed a regular mass loss after 165 °C due to the decomposition of ligand part in the form of volatiles. Thermogravimetric analysis of metal complexes confirmed the coordination of water molecules as they showed the corresponding mass loss in the 80-120°C range (Fig. 1).



Fig. 1: Thermogravimetric curves for (a) Schiff base Ligand(L) (b) $[Cu(L)_2(H_2O)_2]Cl_2$ (c) $Co(L)_2(H_2O)_2](NO_3)_2$ (d) $[Ni(L)(NO_3)](NO_3)$ (e) $[Fe(L)_2]Cl_3$

3.3. Molar Conductance Measurements

The molar conductance values of the complexes (Λ_m) were calculated using relation $\Lambda_m = K/C$, where C is the molar concentration of the metal complex solutions. The

chelates were dissolved in methanol and the molar conductivities of 10⁻³ M solutions were measured at 25 \pm 2°C. Molar conductance values of Cu(II) and Co(II) complexes revealed the ionic nature of complexes. These compounds were found to be 2:1 electrolytes as they showed molar conductance of 162 and 171 Ω^{-1} mol⁻¹ cm², respectively. The conductance value of Ni(II) complex, i.e. 122 Ω^{-1} mol⁻¹ cm², showed it 1:1 electrolyte. Molar conductance studies of Fe(III) complex (280) Ω^{-1} mol⁻¹ cm²) indicated non bonding of chloride ions in its coordination sphere and showed it as 3:1 electrolyte. It also indicated the non-bonding of the chloride ions to Fe(III) in the coordination sphere.

3.4. Mass spectrometry

2200

2000 1800

Mass spectra of all complexes also confirmed the coordination sphere around metal ions. Some of the structural moieties observed as fragments in the mass spectrum are given in Scheme **S1**. All the complexes showed cleavage of receptor into fragments with m/e

162, 145, 119 and 91. Peaks corresponding to the cleavage of $-CH_3$ group attached to azomethineC were also observed in all the complexes. Molecular ion peak for Ni complex at m/e 358 (M+K) revealed its 1:1 (M:L) nature.

3.5. Powder XRD

2000

1800

1600

Powder XRD pattern of the Schiff base metal complexes were recorded in $2\theta = 0^{\circ} \cdot 80^{\circ}$ range (Fig. 2). All the metal complexes show the intense sharp peaks and relatively weak peaks, indicating their crystalline nature. The crystallite size of the complexes was calculated from Scherre's formula: $d_{XRD} = 0.9k/\beta \cos \theta$, where k is the wavelength, β is the full-width half maximum of the characteristic peak and θ is the diffraction angle for the hkl plane. From the observed d_{XRD} patterns, the average size of Co(II), Ni(II), Cu(II) and Fe(II) metal complexes was found to be 40, 27, 27 and 48 nm, respectively, suggesting their nanocrystalline phase.



4. CONCLUSION

Metal complexes of Cu(II), Co(II), Ni(II), Fe(III) have been isolated using a Schiff base ligand; 2-(1-(2hydroxyethylimino)ethyl)phenol in 1:2 ratio except for nickel metal ion. Molar conductivity of different metal complexes confirmed their complexation behavior and the XRD patterns revealed the nanocrystalline nature of metal complexes.

5. ACKNOWLEDGEMENT

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