



Synthesis and Spectroscopic Characterization of New Axially Coordinated Cobalt(III) Schiff Base Complexes

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Cobalt(III) complexes with tetradentate Schiff bases, H_2L , derived from salicylaldehyde and diamines such as 2,3-diaminopyridine, 2,3-diamino toluene and 3,4-diaminotoluene have been synthesized and characterized by IR and ¹H NMR spectroscopy and elemental analysis. The experimental results support the binding of ligands with two N and two O donor sites to cobalt ion.

Key Words: Tetradentate, Schiff bases, Cobalt(III) complexes, Synthesis, Spectral studies.

INTRODUCTION

The function of a metal ion in natural biological systems depends on the structural arrangement of the coordination sphere and the electronic environment of the ligand^{1,2}.

Schiff base ligands constitute an interesting class of chelating agents capable of coordinating metal ions given complexes which serve as models for biological systems^{1,3}. The cobalt complexes have been used as catalysts for the oxygenation reactions, dioxygen carriers and oxygen activators and enantioselective and asymmetric catalysis⁴⁻⁶.

In the area of bioinorganic chemistry, cobalt(III) Schiff base complexes with relatively labile axial ligands are more stable and exhibit higher antiviral and antimicrobial activities in biological systems⁷. The synthesis and reactivity of these complexes have also been playing an important part in the development of coordination chemistry⁴. Having the above-mentioned background in our mind, we report the synthesis and spectroscopic characterization of $[Co^{3+}(L)-(morpholine)_2]ClO_4$ complexes where $L = 2,2'-(1E,1'E)-(4-methyl-1,2-phenylene)-bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol$, $2,2'-(1E,1'E)-(3-methyl-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol$ and $2,2'-(1E,1'E)-(pyridine-2,3-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol$.

EXPERIMENTAL

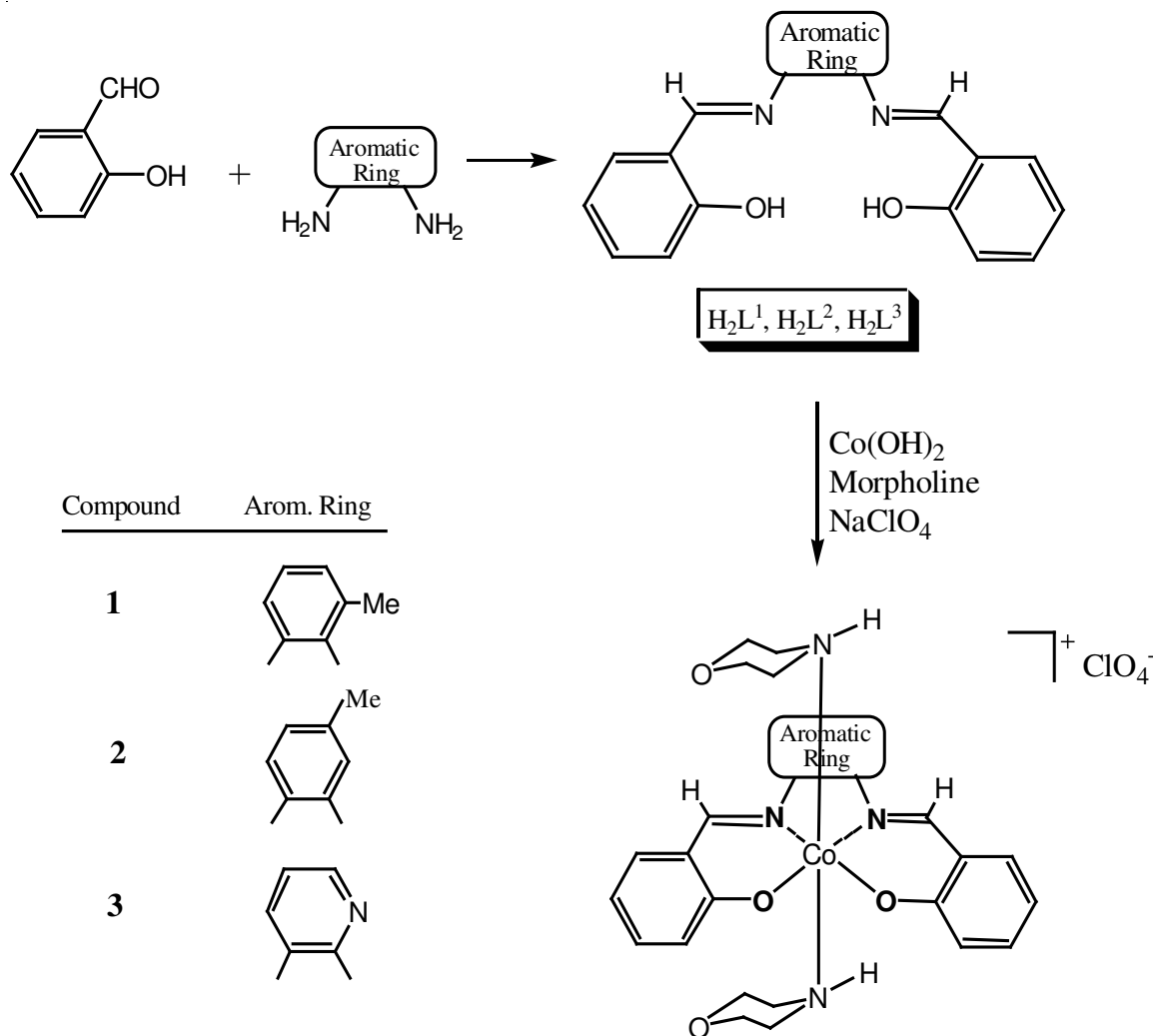
All chemicals and solvents used in this study were purchased from Merck chemical. Melting points were determined

on a Kofler hot stage apparatus and are uncorrected. The IR spectra were obtained on a Shimadzu 470 spectrophotometer. ¹H NMR spectra was recorded using a Varian 400 spectrometer and chemical shifts are reported in parts per million (ppm) relative to TMS as internal standard. Elemental analyses were carried out on CHN rapid elemental analyzer (GmbH-Germany) for C, H and N and the results are within $\pm 0.4\%$ of the theoretical values.

Tetradentate Schiff bases, $H_2L^1-H_2L^3$, were synthesized from salicylaldehyde and diamines such as 2,3-diaminopyridine, 2,3-diaminotoluene and 3,4-diaminotoluene. Cobalt(III) complexes with tetradentate Schiff bases were prepared from the reaction of ligands with cobalt nitrate, morpholine and sodium perchlorate (**Scheme-I**).

General procedure for the preparation of Schiff base ligands: To a stirring solution of salicylaldehyde (2 mmol) in ethanol (40 mL) was added a solution of diamine (1 mmol) in ethanol (10 mL) drop wise and the reaction mixture was refluxed for 2 h. The precipitated Schiff-base was filtered and recrystallized from hot ethanol giving $2,2'-(1E,1'E)-(4-methyl-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol$, $2,2'-(1E,1'E)-(3-methyl-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol$ and $2,2'-(1E,1'E)-(pyridine-2,3-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol$ which abbreviated here as H_2L^1 , H_2L^2 and H_2L^3 ; respectively. Some physical data of the ligands are as follows:

$2,2'-(1E,1'E)-(4-Methyl-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol$ ($C_{21}H_{18}N_2O_2$)



Scheme-I

(**H₂L¹**): Orange solid, yield 72 %, m.p: 119 °C. ¹H NMR (400 MHz, CDCl₃): phenolic O-H [δ 13.03 (s, 1H), δ 12.72 (s, 1H)], aldimine proton [δ 8.67 (s, 1H), δ 8.45 (s, 1H)], aromatic protons [δ 7.30-6.90 (m, 11H)], methyl proton [2.34 (s, 3H)]. FT-IR (KBr, ν_{\max} , cm⁻¹): 3300-3450 (m, OH), 1619 (s, imine C=N), 1271 (phenolic C-O).

2,2'-(1E,1'E)-(3-Methyl-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol (H₂L²): Yellow solid, yield 78 %, m.p. 120 °C. ¹H NMR (400 MHz, CDCl₃): phenolic O-H [δ 13.14 (s, 1H), 13.08 (s, 1H)], aldimine proton [δ 8.64 (s, 1H), 8.63 (s, 1H)], aromatic protons [δ 7.39-6.91 (m, 11H)], methyl proton [δ 2.43 (s, 3H)]. FT-IR (KBr, ν_{\max} , cm⁻¹): 3320-3470 (m, OH), 1617 (s, imine C=N), 1279 (phenolic C-O).

2,2'-(1E,1'E)-(Pyridine-2,3-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol (H₂L³): Yellow solid, yield 68 %, m.p: 178 °C. ¹H NMR (400 MHz, CDCl₃): phenolic O-H [δ 12.65 (s, 1H), 12.51 (s, 1H)], H₆ pyridine [δ 8.68 (d, 1H, *J* = 6 Hz)], H₄ pyridine [δ 8.55 (d, 1H, *J* = 6 Hz)], aldimine proton [δ 8.64 (s, 1H), 8.63 (s, 1H)], aromatic protons [δ 6.93-7.44 (m, 9H)]. FT-IR (KBr, ν_{\max} , cm⁻¹): 3340-3450 (m, OH), 1613 (s, imine C=N), 1287 (phenolic C-O).

General procedure for the preparation of the complexes

Preparation of [Co³⁺(L)(morpholine)₂ClO₄]: Step-1: A solution of NaOH (4 mmol) in ethanol (10 mL) was added dropwise to a stirring solution of Co(NO₃)₂·6H₂O (2 mmol) in the same solvent (10 mL) to give Co(OH)₂ as a green-blue precipitate which was filtered and washed with cold ethanol. **Step-2:** In three-necked round-bottomed flask fitted with a reflux condenser and an argon gas inlet, a solution of 2 mmol appropriate Schiff base in methanol was added dropwise to a solution of Co(OH)₂ (step-1) in methanol, then the mixture was refluxed for 6 h. After cooling, to this solution was added 2 mmol of morpholine followed by 2 mmol of NaClO₄. In order to oxidize the Co(II) to Co(III), air was bubbled for 3 h. The crude products were washed with ethanol and dried over P₄O₁₀. Some physical data of the complexes are as follows:

[Co³⁺(L¹)(morpholine)₂ClO₄]: Brown solid, yield 67 %, m.p. 230 °C. Elemental analysis (%), found C: 52.67, H: 5.09, N: 8.41, calculated for C₂₉H₃₄N₄O₈ClCo, C: 52.70, H: 5.18, N: 8.48. ¹H NMR (400 MHz, CDCl₃): aldimine proton [δ 9.07 (s, 1H), 8.712 (s, 1H)], aromatic protons [δ 8.44 (d, 1H), 7.71-7.29 (m, 8H), 6.76-6.72 (m, 2H)], morpholine protons [δ 4.08 (br t, 2H, *J* = 8Hz, NH), 3.40-3.36 (m, 8H, OCH₂)], methyl proton [δ 2.90 (s, 3H)], morpholine protons [δ 2.08-1.83 (m,

8H, NCH], FT-IR (KBr, ν_{\max} , cm^{-1}): 1606 (s, imine C=N), 1379 (phenolic CO), 1091 (s, br, ClO_4^-).

[Co³⁺(L²)(morpholine)₂ClO₄]: Brown solid, yield 63 %, m.p. 217 °C. Elemental analysis (%), found C: 52.65, H: 5.07, N: 8.41, calculated for C₂₉H₃₄N₄O₈ClCo, C: 52.70, H: 5.18, N: 8.48. ¹H NMR (400 MHz, CDCl₃): aldimine proton [δ 8.75 (s, 1H), 8.70 (s, 1H)], aromatic protons [δ 8.1-8.03 (m, 2H), 7.62 (m, 2H), 7.44-7.28 (m, 5H), 6.79 (m, 2H)], morpholine protons [δ 3.43-3.33 (m, 6H), 2.70-2.62 (m, 4H)], methyl proton [δ 2.52 (s, 3H)], morpholine protons [δ 2.24-1.98 (m, 8H)], FT-IR (KBr, ν_{\max} , cm^{-1}): 1608 (s, imine C=N), 1374 (phenolic CO), 1093 (s, br, ClO_4^-).

[Co³⁺(L³)(morpholine)₂ClO₄]: Brown solid, yield 58 %, m.p. 220 °C. Elemental analysis (%), found C: 50.01, H: 4.77, N: 10.76, calculated for C₂₇H₃₁N₅O₈ClCo, C: 50.05, H: 4.82, N: 10.81. ¹H NMR (400 MHz, DMSO): aldimine proton [δ 9.18 (s, 1H), 8.86 (s, 1H)], aromatic protons [δ 7.48-7.39 (m, 8H), (7.11-6.97 (m, 3H)], morpholine protons [δ 3.53-2.09 (m, 18H)], FT-IR (KBr, ν_{\max} , cm^{-1}): 1606 (s, imine C=N), 1279 (phenolic CO), 1085 (s, br, ClO_4^-).

RESULTS AND DISCUSSION

In the IR spectrum of H₂L shows a broad band characteristic of the OH group at 3470-3300 cm^{-1} . The disappearance of this band in the IR spectra of complexes indicates that the OH group has been deprotonated and bonded to metal ions. The $\nu(\text{C}=\text{N})$ band of free ligands are observed at 1619-1613 cm^{-1} . In the complexes, these bands are shifted to the lower frequencies, indicating the formation of a new chelate ring between the imine nitrogens and cobalt(III)^{8,9}. The $\nu(\text{C}-\text{O})$ stretching frequency are shifted in the complexes towards higher energy as a result of coordination of the oxygen to the metal ions¹⁰.

The presence of one perchlorate counter ion is expected for every Co(III) ion complex. The appearance of a broad

strong band in the IR spectra of the complexes with a max at the range of 1085-1093 cm^{-1} is attributable to the perchlorate vibrations⁹.

NMR spectra: Disappearance of the OH proton signals on the ¹H NMR spectra of the complexes, compared to the spectra of the ligands, is indicated the fact that the equatorial ligand is coordinated. The aromatic protons are resolved in the ¹H NMR of the cobalt complexes and are generally shifted to lower fields showing a common pattern in all complexes.

Conclusion

Three novel complexes of cobalt(III) containing general formula [Co³⁺(L)(morpholine)₂ClO₄] are synthesized and characterized.

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