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Synthesis and characterization of a new Schiff base ligand derived from azomethines and its complexes with cobalt (ii), nickel (ii) and copper (ii)

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Abstract

A new Schiff base ligand. Has been synthesized from the reaction with Co (ll), Ni(II) and Cu(II) salts to form complexes. The ligand and the complexes have been characterized by FTIR. ^{1}H NMR (DMSO-d_6.). UV-vis, elemental analysis, mass Spectra (LC-MS) and magnetic measurements. The metal to the ligand ratio of the Co (II), Ni (II) and Cu (II) complexes have been found to be 1:2. Protonation constants of the ligand and overall formation constants of the complexes have been calculated from potentiometric data using the computer program TITFIT.

Keywords: synthesis, Co(ii), Ni(ii), and Cu(ii) complexes

Introduction

The different kinds of crown ethers have been synthesized in order to produce molecules with superior properties and proper application in various areas [1, 3]. Azomethines is a well-known N-heterocyclic chelating agent with a rigid planar structure. It has been used to develop biomimetic models of metal oenzymes and to prepare supramolecules, self-assembling systems or metal complexes with interesting anticancer properties [4, 5, 6] and anti-microbial activity [7].

Recently, Schiff bases containing a secondary site for coordination have attracted special attention. Crown ether-containing Schiff bases are known to bind cations in the crown ether cavity in addition to the coordination of a transition metal center through the N, O, donor atoms [8, 9, 10]

The synthesis and characterization of aldehyde containing crown ether and 1.10-phenanthroline containing Schiff base ligand and their complexes with Co (II), Cu (II) and Ni (II) are described here. The structures of the ligand and the complexes were determined by their elemental analysis, UV-vis, FTIR. ^{1}H NMR (DMSO-d_6) and mass spectra (LC-MS). Protonation constants of the ligand and formation constants of the complexes have been calculated using the computer program TITFIT [11]

Materials and Methods

The deionized water was used throughout for the potentiometric experiments under an atmosphere of nitrogen. Unless specified otherwise, reagent AR grade reactants and solvents were used as received. High purity potassium nitrate was used as supporting electrolyte. The ionic medium was 1.0 M KNO_3 at the beginning of each potentiometric titration. The FTIR spectra (KBr discs) were recorded in the 4000-400 cm' range on a Mattson 1000 FTIR spectrometer. The spectra and absorbance measurements were recorded on Agilent 8453 UV-vis spectroscopy system. Proton NMR spectra were recorded on Brucker AC-200 MHz (DMSO-do) spectrometer. Magnetic susceptibilities were determined on Sherwood scientific magnetic susceptibility balance. Melting points were obtained with Gallenkamp CAP MPD-350 apparatus in open capillaries. Potentiometric measurements were carried out using a titration system with a Metrohm E-415 dosimate and Metrohm E-510 pH meter. A Metrohm 6.0204.000 combined glass electrode was used for potentiometric titrations, pH and EMF measurements. A thermostated titration vessel of 100 mL capacity was used. The electrode system was calibrated using standard buffer solutions at pH 4.00/7.00.

The following solutions were prepared to obtain the pH-titration curves: Solution A: $HClO_4$ (2.5 mL. 0.1 M), KNO_3 (5 mL, 1.0M). Solution B: Solution A + solution of the ligand in ethanol (2.5 mL, 0.01 M). Solution C-E: Solution B±2.5 mL. 0.01 M metal salt solution i.e. $CuCl_2$, $2H_2O$, $NiCl_2$, $6H_2O$ and $COCl_2$, $6H_2O$ in ethanol. Sufficient amounts of ethanol were added to make up the total volume V_o, which was 25 ±0.1 mL, maintaining temperature at 25.0 ±0.1°C. To the titration vessel, a known volume of ligand solution, an exact volume of metal chloride, then the required quantities of KNO_3 electrolyte were used to minimize variations of the activity coefficients in spite of wide changes in the concentrations of the reagents. The ionic strength was kept constant at 1.0 M KNO_3. These solutions were titrated by progressive addition of standardized carbonate-free 0.1 M NaOH titrant in increments of 0.1 mL and the corresponding change in the pH of the solution was measured.

Synthesis of the Co (II) Complex

Ligand (0.05 g, 0.1 mmol) was dissolved in absolute ethanol (20 mL) and Co $(CH_3\ COO)_2$, $4H_2O$ (0.013 g. 0.052 mmol) in 10 mL of absolute ethanol was added to this solution. After addition of 0.01 M KOH solution in ethanol to raise the pH to 8.0-8.5, the mixture was stirred on a water bath at 90°C for 3 h. A dark brown precipitate was obtained when the solution was cooled to room temperature. It was filtered, washed with diethyl ether. Yield 0.022 g. (44 %); m.pt.

>350°C. IR (KBr): 1625 (C=N), 2953-2876 (CH.$_{liph}$), 1140 (C-O-C$_{aliph}$), 1268 (C-O-C$_{arom}$.). Since the solubility of the complex in organic solvents is very low, 'H NMR spectra could not be taken. Anal. Calcd for $C_{54}H_{58}O_{12}$, N_6Co (1041.9): C, 62.24; H, 5.61: N, 8.07; 0, 18.43 %. Found: C, 63.14; H. 6.84; N. 8.22; 0, 18.63 %.

Synthesis of the Cu (II) complex

Ligand (0.05 g. 0.1 mmol) was dissolved in absolute ethanol (20 mL) and $CuCl_2$.2H 0 (0.01g, 0.05 mmol) in 10 mL of absolute ethanol was added to this solution. After addition of 0.01 M KOH solution in ethanol to raise the pH to 7.0-7.5. The mixture was stirred on a water bath at 90°C for 3 h. A dark-brown precipitate was obtained when the solution was cooled to room temperature. It was filtered, washed with diethyl ether. Yield 0.021 g. (42%); m.pt. >350°C. IR (KBr): 1625 (C=N), 29532876 (CH. $_{aliph}$), 1140 (C-O-$_{Caliph}$), 1268 (C-O-C$_{arom}$.). Since the solubility of the complex in organic solvents is very low, 'H NMR spectra could not be taken. Anal. Calcd for $C_{54}H_{54}.O_{10}.N_6.Cu$ (1010.5): C. 64.18; H. 5.39; N, 8.32; 0, 15.83 %. Found: C, 65.72; H, 5.52; N. 8.65; 0, 18.92 %.

Synthesis of the Ni (II) Complex

Ligand (0.05 g. 0.1 mmol) was dissolved in absolute ethanol (20 mL) and Ni $(CH_3COO)_2$ $4H_2O$ (0.013 g, 0.052 mmol) in 10 mL of absolute ethanol was added to this solution. After addition of 0.01 M KOH solution in ethanol to raise the pH to 8.0-8.5, the mixture was stirred on a water bath at 90°C for 3 h. A dark-brown precipitate was obtained when the solution was cooled to room temperature. It was filtered, washed with diethyl ether. Yield 0.024 g. (48 %); m.pt. >350°C. IR (KBr): 1625 (C=N), 2953-2876 (CH.$_{aliph}$), 1140 (C-O-$_{aliph}$), 1268 (C-O-C$_{arom}$). Since the solubility of the complex in organic solvents is very low, 'H NMR spectra could not be taken. Anal. Calcd for $C_{54}H_{54}.O_{10}.N_6Ni$ (1005.7): C, 64.49; H, 5.41; N. 8.36; 0, 15.9 %. Found: C. 65.82: H. 5.50: N. 8.78; 0, 16.52%

Results and Discussion

The starting compounds. 5-amino-1, 10 phenanthroline and 4-formylbenzo-15-crown-5 were prepared according to known methods [12, 13]. Ligand was synthesized from 5-amino-1.10-phenanthroline and 4-formylbenzo-15-crown-5 with condensation reaction providing good yield. Its metal complexes were prepared by treating the ligand with the corresponding metal salts in 2:1 ratio.

FTIR data provides further useful information on its complexes. The free ligand shows characteristic imine stretching bands at 1625 cm. In the complexes, this band does not shift to the lower or higher wave numbers, suggesting that this imine group is not coordinated to the metal ions. Nitrogens of 1.10-phenanthroline stretching bands at 1651 cm' shift to the lower wave numbers. Suggesting that this nitrogen is coordinated to the metal ions. The aryl and alkyl ether bands of the ligands and complexes are observed at 2850-2920 1268-1276 and 1140-1063 cm^1.

Elemental analyses and its Co (II), Ni (II) and Cu (II) complexes show good agreement with the proposed structures of the ligand and its complexes. The complexes could be prepared in good yield by reacting the divalent metal salts in the ratio of 1:2. The cobalt center adopts a sixcoordinate geometry with the equatorial plane occupied by four coplanar phenanthroline nitrogens and two water molecules in axial positions. The nickel and copper centers adopt a four-coordinate geometry by four coplanar phenanthroline nitrogens [9].

The Co (II) complex possesses magnetic moment (Heir) 4.25 BM, which is in agreement with octahedral geometry. Magnetic moment of the Ni (II) and Cu (II) complexes show them to be diamagnetic. Cu (II) and Ni (II) complexes are suggested to possess a square planar environment in the complexes. The ^{1}H NMR spectrum of ligand in DMSO-d_6, confirmed the proposed structure showing one proton of 8.77 ppm for the H-C=N group upon D_2O exchange. The 3.5 and 4.3 ppm protons can be identified easily because they deform upon D_2O exchange. The assignments of the protons are highly complicated in the region 7.2-7.6 ppm where the signals are due to the protons of aromatic group. The solubility of the metal complexes in organic solvents was insufficient to obtain ^{1}H NMR spectra and further investigations were not possible. The ligand and all complexes are stable at room temperature and are hygroscopic. The ligand is soluble in common polar organic solvents, such as ethanol, methanol, Chloroform but partially soluble in non-polar organic solvents such as, benzene and hexane. The UV-vis spectra of the ligand and metal complexes were recorded in ethanol, chloroform. Methanol solvents. The absorption spectra of the ligand and complexes exhibit metal to ligand charge transfer (MLCT) and ligand centered (LC) bands. The UV-vis spectra of the Schiff base ligand and complexes show low-energy absorption bands at approximately 340-450 nm and high energy bands at approximately 225-276 nm. The electronic absorption spectra of metal complexes are dominated by the ligand-center and $\pi - \pi^*$ $n - \pi^*$ transitions of the Schiff base ligand. The molecular ion peaks m/z 474 [M+1] of the free ligands are present in the LC-MS spectra which supports the proposed structures. The most intense peaks at m/z 207. 283, 299 and 417 correspond to the frangments $[C_{13}H_9N_3]$. $(C_{19}H_{13}N_3]$. $[C_{19}H_{12}N_3O]^+$ and $C_{24}H_{22}N_3O_4]$

The values of proton activity and pK, for these solutions have been calculated from solution A as 1.25 and -14.80. Respectively. Protonation constants of the ligand were calculated by a potentiometric titration method with the TITFIT program. The calculated protonation and formation constants of the ligand are given in Table-1. The values of the protonation constants for the ligand are log K_1 = 9.06. Log K_2 = 7.12, log K_3 = 5.57 and they correspond to the following equations:

$L + H \rightarrow LH^+$

$LH^+ + H^+ \rightarrow LH_2^{2+}$

$LH_2^{2+} + H^+ \rightarrow LH_3^{3+}$

Table 1: Protonation and overall formation constants of the ligand and its complexes at 25ºand ionic strength (1.0 M KNO_3)

Metal ion	**Species**	**log β**	**σ(Standard Deviation)**
Co(II)	CoL^{2+}	0.0016	
	$CoLH^{3+}$	0.0016	
	$CoLH_2^{4+}$	0.0016	
	$CoL_2H_2^{4+}$	29.50	0.0016
Ni(II)	NiL^{2+}	0.004	
	$NiLH^{3+}$	0.004	
	$NiLH_2^{4+}$	22.50	0.004
Cu(II)	CoL^{2+}	0.0013	
	$CoLH^{3+}$	0.0013	
	$CoLH_2^{4+}$	0.0013	
	$CoLH_2^{4+}$	30.50	0.0013

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