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Spectroscopic Studies of 1,10-Phenanthroline-5,6-[4,4'-(ethane-1,2-diilbis(oxy))dibenzenamine] and its Transition Metal Complexes

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1,10-Phenanthroline-5,6-[4,4'-(ethane-1,2-diilbis(oxy))dibenzenamine] ligand (L) and It yields different complexes with Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) acetates. The structure of the complexes and ligand determined by using elemental analysis, UV, IR, NMR, TGA, DTA, magnetic measurements.

Key Words: 1,10-Phenanthroline, Spectroscopic studies.

INTRODUCTION

1,10-Phenanthroline (Phen) (Fig. 1) and substituted derivatives, both in the metal-free state and as ligands co-ordinated to transition metals, disturb the functioning of a wide variety of biological systems[1]. Furthermore, when metal-free N,N'-chelating bases are found to be bioactive it is usually assumed that sequestering of trace metals *in situ* was involved and that the resulting metal complexes were the active species[2,3].

EXPERIMENTAL

The chemicals were purchased from Merck used without purification. The electronic spectra of the ligand and the complexes in the UV-Vis region were recorded in DMF solutions using a Shimadzu UV-1700 spectrophotometer. The IR spectra of the ligand and the complexes were recorded with Perkin-Elmer precisely spectrum using KBR pellets in the region of 4000-400 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker GmbH DPX-400 MHz FT in DMSO-d_6, magnetic susceptibilities were determined at room temperature on a Sherwood Scientific MKI model balance. The elemental analyses were conducted on a leco 932 CHNS-O instrument. Thermal analyses were recorded on a Shimadzu TA60-WS.

General procedure

Synthesis of 1,10-phenanthroline-5,6-[4,4'-(ethane-1,2-diilbis(oxy))-dibenzenamine]: 1,10-Phenanthroline-5,6-dione (0.210 g) was solved in ethyl alcohol (20 mL) and 0.244 g 4,4'-(ethane-1,2-diilbis(oxy))dibenzenamine of the solution in ethyl alcohol (10 mL) was added to the mixture for reflux 12 h at 60 °C. The mixture was allowed to cool and the resultant precipitate filtered, washed with water and EtOH and dried, yield (0.25 g, 63 %); m.p. 253 °C[4].

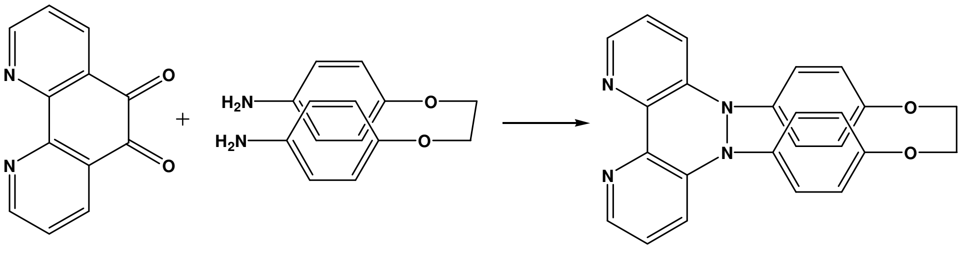

Fig. 1. Synthesis of the ligand

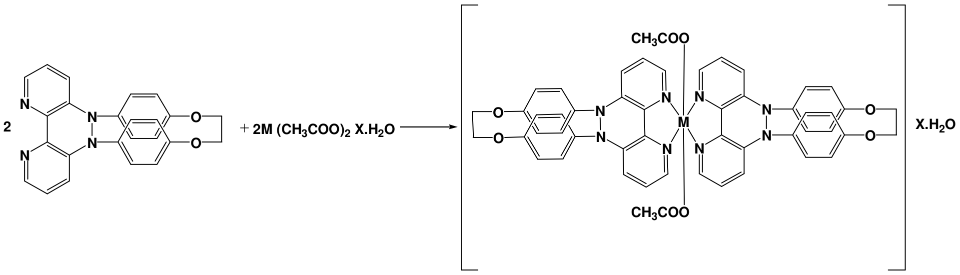

Fig. 2. Synthesis of the complexes

Synthesis of the Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) complexes: The 1,10-Phenanthroline-5,6-[4,4'-(ethane-1,2-diilbis(oxy))dibenzenamine] ligand (L) (0.113 g) was suspended in DMF (15 mL). 0.17 mmol of the corresponding metal acetates was dissolved in 10 mL of hot DMF at 70 °C and added gradually to a stirred hot solution of the ligand (L). The reaction mixture was stirred for 6 h at 60 °C. After that, the solid was filtered and washed EtOH and DMF, dried *in vacuo*, yielded $[M(L)_2(AcO)_2].nH_2O$ ($M = Co^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+} or Cd^{2+}).

RESULTS AND D]ISCUSSION

The colours, metal salts and molar ratios of preparation, magnetic susceptibilities, stoichiometries and elemental analyses of the prepared complexes are listed in Table-1. The analytical data are in good agreement with the proposed stoichiometry of the complexes. All the complexes are soluble in common organic solvents such as methanol, acetone, chloroform and DMF

The ^1H NMR spectra of the ligand (L) has been carried out in DMSO-d_6 at room temperature. The spectra of the ligand showed signals within 9.20-6.50, 4.70-4.00 ppm range assigned to (aromatic -CH, aliphatic -CH), respectively. The ^1H NMR spectrum of the complexes exhibited nearly the same values.

The IR characteristic bands and their assignments are listed in Table-2. The spectra of the ligand (L) display bands near 3217, 2928, 1622 cm^{-1}. These bands are assigned to ν(arom. -CH), ν(Al-CH), ν(C=N), the shift was observed in ν(C=N) to lower frequencies in the spectra of the complexes, relative to those of the ligand confirms the coordination though the C=N group.

TABLE-1
ELEMENTAL ANALYSES OF THE LIGAND AND ITS COMPOUNDS

Compound (m.f.)	F.W. (g/mol)	Yield (%)	Elemental analysis (%): Calcd. (Found)			μ_{eff} (BM)
			C	H	N	
Ligand (L)	341	76	66.86	3.22	20.52	–
($C_{19}H_{11}N_5O_2$)			(67.01)	(3.27)	(21.40)	
$[CoL_2(OAc)_2].8H_2O$	1157	39	56.27	5,27	10.09	4.63
($C_{42}O_{16}N_{10}H_{38}Co$)			(55.40)	(4.69)	(9.89)	
$[NiL_2(OAc)_2].8H_2O$	1157	50	56.28	5.27	10.10	3.18
($C_{42}O_9N_{10}H_{24}Ni$)			(54.91)	(4.96)	(9.56)	
$[CuL_2(OAc)_2].8H_2O$	1163	32	55.03	5.24	10.05	2.01
($C_{42}O_{14}N_{10}H_{34}Cu$)			(53.60)	(5.12)	(9.95)	
$[ZnL_2(OAc)_2]$ .8H_2O	1162	47	55.94	5.24	10.04	–
($C_{42}O_{16}N_{10}H_{38}Zn$)			(54.85)	(5.20)	(9.98)	
$[CdL_2(OAc)_2]$ .8H_2O	1211	37	53.68	5.02	9.63	–
($C_{42}O_8N_{10}H_{17}Cd$)			(51.65)	(5.00)	(9.52)	

TABLE-2
SOME IR FREQUENCIES (cm^{-1}) OF 2-(3-NITROPHENYL)-
1*H*-IMIDAZOLE[4,5-f][1,10]PHENANTHROLINE AND ITS COMPLEXES

Fonksiyonel group	Al. (-CH)	Arom. (-CH)	ν(C=N)	ν_{as}(C=N) (COO^-)	ν_s(C-O) (COO^-)	ν(M-O)	ν(M-N)	ν(O-H)
Ligand (L)	2928	3217	1622	–	–	–	–	–
$[ZnL_2(OAc)_2].8H_2O$	2862	3062	1603	1576	1384	–	–	3401
$[CdL_2(OAc)_2].8H_2O$	2862	3058	1616	1588	1382	490	490	3368
$[CoL_2(OAc)_2].8H_2O$	2923	3049	1600	1561	1380	510	495	3328
$[CuL_2(OAc)_2].8H_2O$	2879	3065	1604	1585	1380	500	490	3378

The IR spectra of the complexes exhibited broad bands at 3454-3379 cm^{-1} that attributed to OH group of the crystal water molecules. In the IR spectrum of the complexes display new bands near 1588-1382 cm^{-1}, these bands assigned to ν_s and ν_{as} of acetate groups. These bands are further supported by the appearance of medium weak bands at 513-495 cm^{-1}, which are assigned to the ν(M-O)[5].

Magnetic moment and UV spectrum: The electronic and spectral data of synthesized ligand and metal complexes were recorded in DMSO solutions. The absorption bands in the ligand were observed at 35000 and 31000 cm^{-1}, attributable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions within the molecule.

The Co(II) compound displays three absorption bands in the regions 7800, 12,500, 17,900 cm^{-1} suggesting octahedral geometry[6-8]. These are assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1), $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2), $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), respectively. The magnetic susceptibility measurement (4.63 BM) for the Co(II) complex also showed of three unpaired electrons per Co(II) ion supported of octahedral environment. The electronic spectra of the copper(II) complex exhibits a broad band 17,241 cm^{-1} assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition considering an octahedral geometry, the magnetic moment value (2.01 BM) of the Cu(II) complex showed an octahedral structure with an unpaired electron.

For the Ni(II) complex showed two bands at 14,800 and 25,600 cm^{-1}, which are attributed to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ (ν_3), respectively[6,9]. Also the value of magnetic moment 3.18 BM is good agreement with this reported for the octahedral structure. The electronic spectra of the Zn(II) and Cd(II) exhibited only a high-intensity band at 21,500 and 19,800 cm^{-1} are assigned to a ligand-metal charge transfer.

Thermal studies: The thermal stability of the complexes were investigated using TGA and DTA. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves were obtained at a heating rate of 15 °C/ min in nitrogen atmosphere over a temperature range of 20-450 °C.

The Ni(II) and Cu(II) complexes are thermally stable up to 65 °C and 70 °C, respectively. In the TGA curve of the Ni(II) complex 12.44 % weight loss was observed at 225 °C. In the TGA curve of the Cu(II) complex 12.38 % weight loss was observed at 285 °C, This shows that Ni(II) and Cu(II) complexes contain 8 mole of water. In the TGA curve of the Co(II), Zn(II) and Cd(II) complexes 12.44, 12.39, 11.89 % weight loss was observed at 220, 200 and 195 °C, respectively. This shows that Co(II), Zn(II) and Cd(II) complexes contain 8 mole of water. The IR spectra of the complexes are characterized by the appearance of a broad band in the region 3456-3379 cm^{-1}, due to the ν(O-H).

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