

New Co(II), Cu(II) and Ni(II) Complexes with 1,2-Bis(*o*-aminophenoxy)ethane

¹N. TOKMAK, ¹M. ŞEKERCI AND ²H. TEMEL*

¹Faculty of Arts and Sciences,
Chemistry Department, Fırat University, Elazığ, Turkey

²Faculty of Education, Chemistry Department,
Dicle University, Diyarbakır, Turkey

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Summary: 1,2-Bis(*o*-aminophenoxy)ethane was prepared in a one stage process. In this reaction, Pd/C was used as catalyst. 1,2-Bis(*o*-aminophenoxy)ethane was synthesized from 1,2-bis(*o*-nitrophenoxy)ethane. Diamine complexes [CoLCl₂2H₂O], [CuLCl₂]0.5H₂O and [NiL₂(C₂H₅O)₂] have been synthesized and characterized by elemental analyses, Λ_M, IR, UV-VIS, ¹H NMR and magnetic measurements.

Introduction

Amines and their derivatives (monodentate, bidentate, etc.) have been known to produce stable complexes with transition metals [1]. Nowadays, the metal complexes of aromatic diamines have different applications, especially in the field of chemotherapy. Although potentiometric, spectrophotometric and even conventional (batch) calorimetric studies have been frequently used in the research of metal-nitrogenated- ligand complexes. The preparation of coordinating agents derived from aromatic diamines is of special interest since the use of nitrogen atoms for coordination to a single cation is directly related to their situation in *ortho*, *meta* or *para* positions. The ligands derived from *m*- or *p*- phenylenediamines can only coordinate one nitrogen atom to any one metal cation. The formation of species with an excess of ligand (2: 1 ligand:metal ratio), with an excess of metal (1: 2 ratio), and monomers (1: 1 ratio) is now possible. Moreover, the special conformation of the ligands with nitrogen atoms in *meta* or *para* positions on the aromatic ring facilitates the formation of dimer complexes since the ligands act as a bridge. The dinuclear complexes of those ligands with paramagnetic ions may present magnetic coupling. With the nitrogen atoms in *para* position, polymer complexes are also possible since the ligand acts as a bridge. In spite of this importance, little work has been done on this type of diamine metal complexes [2-5].

In the present work, the Co (II), Cu (II) and Ni (II) complexes of the aromatic diamine were prepared and characterized.

Results and Discussion

Micro analytical, molar conductance and magnetic susceptibility data of the ligand and its complexes are given in Table-1. The stoichiometries of the ligand and its complexes were confirmed by their elemental analyses. The molar conductance measured in DMF of 10⁻³ M solutions of these complexes fall in the range 5.3-8.2 ohm⁻¹cm²mol⁻¹ that indicates their non-electrolytic behavior [6-10].

The metal/ligand mole ratio was found to be 1:1 or 1/2. The ligand (L), on reaction with Co (II), Cu (II) and Ni (II) salts yields complexes corresponding to the general formula [CoLCl₂2H₂O], [CuLCl₂]0.5H₂O and [NiL₂(C₂H₅O)₂]. In addition Cu (II) complex was present 0.5 mol additional molecules of water of crystallization, but the Co (II) complex has two additional coordinated water molecules. The observed magnetic moment of Co (II) complex 1.94 B. M. This value suggested octahedral stereo chemistry of complex. The observed magnetic moment of Cu (II) complex 1.48 B. M. This value suggested square-planar stereo chemistry of complex. The observed magnetic moment of Ni (II) complexes 2.94 B. M. This value suggested octahedral stereo chemistry of complex. The complexes give fine powders and we could not manage to prepare single crystals to obtain X-rays. Characteristic ¹H NMR bands for ligand (DMSO- d₆, TMS, δ ppm): 7.2-6.5 (bs, 8H, aromatic H); 4.0-4.3 (bs, 4H, -OCH₂); 4.1-3.4 (bs, 4H, -NH₂). Since the complexes are paramagnetic, their ¹H NMR spectra could not be obtained.

*To whom all correspondence should be addressed.

Table-1: The Colours, Formulas, Formula Weight, Yields, Melting Points, and Elemental Analyses Results of the Ligand (L) and the Complexes

Compounds	F.W g/mole	M.p. (°C)	Yield (%)	Elemental analyses calculated (found), %			μ_{eff} (B.M)	Λ°
				C	H	N		
Ligand (white) C ₁₄ H ₁₆ N ₂ O ₂	244.0	130- 131	78.0	68.85 (68.80)	6.56 (6.409)	11.48 (11.10)	-	-
[CoLCl ₂ 2H ₂ O] (dark Blue)	409.9	150	56.0	40.98 (40.17)	4.87 (4.51)	6.83 (6.71)	1.94	6.2
[CuLCl ₂]0.5H ₂ O (black)	387.5	270	54.0	43.35 (44.00)	4.39 (4.23)	7.23 (7.40)	1.48	5.3
[NiL ₂ (C ₂ H ₅ O) ₂] (green)	708.7	275	45.5	64.43 (63.90)	5.92 (5.85)	7.90 (8.00)	2.94	8.2

^aohm⁻¹ mol⁻¹ cm²(measured in 10⁻³ M solution in DMF).

Table-2: Some IR Frequencies (in cm⁻¹) of ligand and Its Complexes

Ligand	[CoLCl ₂ 2H ₂ O]	[CuLCl ₂]0.5H ₂ O	[NiL ₂ (C ₂ H ₅ O) ₂]	Assignment
-	3567m	3613 w	-	v(H ₂ O)
3445, 3363m	3238 w	3212, w	3445, 3362, 3338, 3317, 3266, 3241w	v(NH ₂)
3059, 1759- 1886 w	3042, 1932, 1886 w	3078, 3022 w	3061w	v(arom., C-H)
2951, 2884 m	2966, 2874 w	2925, 2854 w	2956, 2879, 1930, 1758 w	v(aliph., C-H)
751 m	745 m	748 m	739 m	v(aromatic o-disubstitute)
1611 m	1600 m	1591 m	1611 m	δ (NH)
1504 m	1509 m	1504 m	1504 m	v(Arom., C=C)
1275, 1250 m	1295 m	1280, 1245 m	1275, 1265, 1250 m	v(arom., C-N)
1087, 1061, 1035 m	1077, 1056, 1031 m	1046 m	1087, 1061, 1041, 1020 (-CH ₂ O) m	v(arom., O-C)

IR Spectra

The IR characteristic bands and their assignments are listed in Table-2. A broad and weak band occurring around 3613- 3567 cm⁻¹ may be attributed to the OH vibration of water molecules in the complexes [7-11]. The spectra display bands near 3445, 3363, 1611, 1504, 1275-1250, 1087-1035 cm⁻¹. These bands are assigned to v(NH₂), δ (NH), v(C=C) of the benzene ring, v(arom.-C-N) and v(arom.-O-C), respectively. The shift observed in v(NH₂) to lower frequencies in the spectra of the complexes relative to those of the ligand confirms the coordination though the amino group [1, 2, 11]. For Ni (II) complex, there is a new band about 1020 cm⁻¹ in IR bands. This band is assigned to C₂H₅-O-M and it is supported by elemental analysis too [12]. In addition, Melting Point of Ni (II) complex is high. So it may be convert a stronge ligand like C₂H₅O⁻ in Ni (II) complex.

Electronic Spectra

The electronic spectral data of the synthesized compounds were recorded in dimethyl formamide (DMF) solutions. The absorption spectrum of the diamine is characterized mainly by two absorption bands in the region 240-410 nm. In the spectrum of the ligand, the aromatic bands at 240 nm are attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band at

470 nm is assigned to the imino $\pi \rightarrow \pi^*$ transition. Compared to the free ligand, the imine $\pi \rightarrow \pi^*$ transitions of the complexes were shifted to some extent, probably because of coordination of the nitrogen atom of the ligand imine group to the metal ion [12, 13].

The electronic spectrum of the Cu (II) complex shows absorption bands at 530 nm, 725 nm attributed to the ²E_g → ²B_{1g}, and ²B_{2g} → ²B_{1g} transition, which is compatible with this complex having a square-planar structure¹⁴.

The electronic spectrum of the Co (II) complex shows absorption bands at 525 nm, 598 nm, 623 nm and 725 nm attributed to the ²E_g → ²A_{2g} (F), ²E_g → ²A_{1g} (G), ²E_g → ²T_{2g} (G) and ²E_g → ³T_{1g} (G) transition, which is compatible with this complex having a octahedral structure [15-16].

The electronic spectrum of the Ni(II) complex shows absorption bands at 460 nm, 525 nm and 775 nm attributed to the ³A_{2g}(F) → ³T_{1g}(P), ³A_{2g} → ³T_{1g}(P) and ³A_{2g}(F) → ³T_{2g}(F) transition, which is compatible with this complex having a octahedral [15-16] (Table-3).

Table-3: Electronic Spectral Data for ligand and its complexes (λ_{max} / nm)

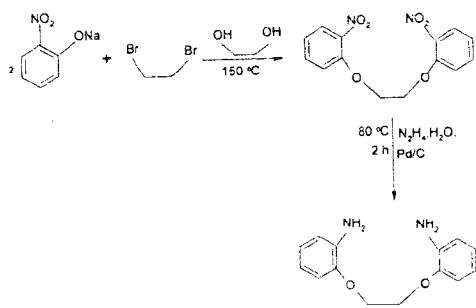
Ligand	λ_{max} / nm
[CoLCl ₂ 2H ₂ O]	380- 430, 525, 598, 623, 725
[CuLCl ₂]0.5H ₂ O	375- 440, 530, 725
[NiL ₂ (C ₂ H ₅ O) ₂]	298- 410, 460, 525, 775

Experimental

All the chemicals, such as the metal salts [CoCl₂.6H₂O, CuCl₂.2H₂O, NiCl₂.6H₂O], Hydrazine hydrate, Pd/C and solvents, were Merck product and were used without purification. Conductivities of 10⁻³ M solution of the complexes were measured in DMF at 25 °C using a Conductivity Hand-Held Meter LF 330. The electronic spectra of the complexes in UV-VIS region were recorded in DMF solutions using a Shimadzu Model 160 UV Visible Spectrophotometer. The IR spectra of the complexes were recorded with a Midac 1700 instrument in KBr pellets. ¹H NMR spectra were recorded on a BRUKER DPX-400 High Performance Digital FT-NMR spectrometer in DMSO-d₆. Magnetic moments were determined on a Sherwood Scientific magnetic moment balance (Model N0: MK1) at room temperature (25 °C) using Hg[Co(SCN)₄] as a calibrant: diamagnetic corrections were calculated from Pascal's constants⁵. The elemental analyses were conducted on Carlo Erba instrument.

Synthesis of Ligand [1,2-bis-(*o*-aminophenoxy)ethane] (L)

The reaction steps for synthesis of L are given in Fig. 1. The first step is synthesis of 1,2-bis-(*o*-nitrophenoxy)ethane (1) from reaction of sodium *o*-nitro phenolate and 1,2-dibromoethane. In the second step, 1,2-bis-(*o*-nitrophenoxy)ethane and Pd/C as catalyst in hydrazine hydrate were reacted to obtain 1,2-bis-(*o*-aminophenoxy)ethane (2). M.P: 130- 132 °C, yield: 90 %.

Fig. 1: Synthesis of Ligand : 1,2-bis-(*o*-aminophenoxy)ethane (L).

Synthesis of Co(II), Cu(II) and Ni(II) Complexes

A solution of metal salt (CoCl₂.6H₂O, CuCl₂.2H₂O, NiCl₂.6H₂O) in absolute ethanol (1 mmol for Co (II) and Cu (II) or 2 mmol for Ni (II)) was mixed with the ligand in absolute ethanol (1 mmol, 0,24 g; 2 mmol, 0,48 g) in a 1: 1 or 1: 2 molar ratio. The contents were refluxed in 100 mL of absolute ethanol on a water-bath for two to three hours. The refluxed solution was then poured into ice cold water when a colored solid separated out. The product was isolated by filtration, washed with ether, recrystallized from dimethyl sulfoxide and dimethyl formamide and dried over anhydrous CaCl₂ in vacuum at room-temperature. The yield was 46-56 % in all the complexes with respect to the ligand. They decompose at 150-275 °C and are almost insoluble in common organic solvents such as ethanol, methanol, benzene, acetone, nitrobenzene, dichloromethane and chloroform. However, they are slightly to fairly soluble in polar organic solvents (dimethyl sulfoxide and dimethyl formamide).

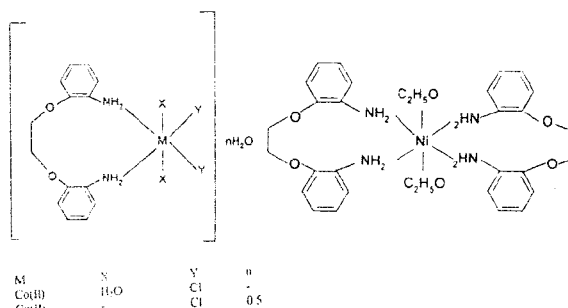


Fig. 2: Suggested Structure of the octahedral Co (II) and Ni (II), Square-planar Cu (II) Complexes of the Ligand.

Acknowledgements

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