

Preparation of Complexes with Acetates of Transition Metal of Amino Compounds Including 1,3-Dioxalane Group

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Abstract

In this study, 6,7-O-Cyclopentylidene-1-amino-4-azaheptane (L) has been synthesized starting from 1-chloro-2,3-O-cyclopentylidene-propane (1), which has been prepared by the reaction of epichlorohydrin and cyclopentanone. In this reaction $\text{BF}_3 \cdot \text{OEt}_2$ was used as catalyst. The complexes of this ligand with Co(II), Ni(II) and Cu(II) acetate salts were prepared. The structures of the ligand and its complexes are proposed based on elemental analyses, IR, UV-vis, $^1\text{H-NMR}$ spectra, magnetic susceptibility measurement, conductivimetry, thermogravimetric and differential thermal analyses. The suggested structure for the all of complexes is octahedral geometry. All complexes are paramagnetic and mononuclear.

Keywords: Diamino, Cyclopentylidene, Co(II), Ni(II) and Cu(II) Acetate.

INTRODUCTION

The purpose of this study is to prepare a amine ligand and its new metal complexes and to investigate their structures. It is important to use amines, containing at least two nitrogens, since they produce quite stable complexes with transition metals. [1-3].

Compounds containing pendant 1,3-dioxalane groups and their metal complexes have received much attention because of their rich inorganic chemical properties, reactivity patterns and potential applications in many important chemical process in the areas of medicine and industry [4-8]. Amines and their derivatives (monodentate, bidentate, etc.) have been known to produce stable complexes with transition metals [7-9]. Many amine complex compounds have been synthesized and their properties (carcinogenic, biological activity, semiconductors, optical, thermals, crystallography,) have been investigated [7-10].

In the present paper, the Co(II), Ni(II) and Cu(II) complexes of the 6,7-O-Cyclopentylidene-1-amino-4-azaheptane (L) (Figure 1) were prepared and characterized.

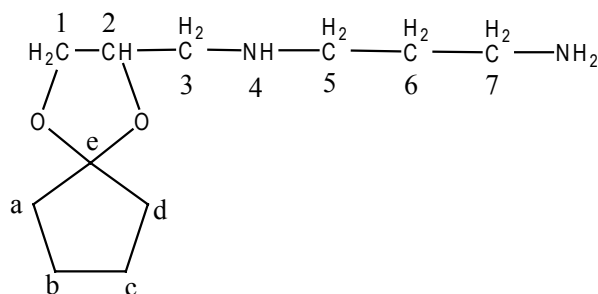


Figure 1 6,7-O-Cyclopentylidene-1-amino-4-azaheptane (L)

MATERIALS AND METHODS

Reagent grade chemicals were used. Epichlorohydrin and cyclopentanone were purchased from Merck (Pure) and (Sigma), respectively, used without further purification. 1-Chloro-2,3-O-cyclopentylidene-propane (1) [11] and 6,7-O-cyclopentylidene-1-amino-4-azaheptane (L) [12] were synthesized as described in the literature.

The elemental analyses were determined in the TUBITAK Laboratory (Scientific and Technical Research Council of Turkey). IR spectra were recorded on a Ati-Lnicom Mattson 1000 FT-IR spectrometer as KBr pellets, $^1\text{H-NMR}$ spectra was recorded on a JEOL FX 90Q FT-NMR spectrometer. Magnetic susceptibilities were determined on a Christon magnetic susceptibility balance at room temperature (20°C) using $\text{Hg}[\text{Co}(\text{SCN})_2]$ as a calibrant; diamagnetic corrections were calculated from Gouy's constants [12,13]. Molar conductances were measured on a CMD 750WPA conductometer (1.10^{-3} M in absolute ethanol) [14]. Thermogravimetric (TGA) and differential thermal analyses (DTA) curves were recorded on a Shimadzu DSC-60A and Shimadzu DTG-60AH thermobalances. Electronic spectra were recorded on a Pharmacia LKB-Ultraspec III spectrometer.

Preparation of 1-Chloro-2,3-O-cyclopentylidene-propane (1)

Boron trifluoride ethyl ether (30-40 drops) was added dropwise to 16.8 g (0.20 mol) of cyclopentanone. Then 46.0 g (0.50 mole) of epichlorohydrin was added dropwise to the reaction mixture at 10-17°C with continuous stirring. The reaction mixture was then further stirred for 2 hours at 20°C under nitrogen atmosphere. The product was distilled at 78°C at 2 mm-Hg. Yield: 30 g (84.98 %). Characteristic IR peaks (in NaCl cell, cm^{-1}): 2559-2877 (aliph. C-H), 1111 (C-O-C), 758 (C-Cl). Characteristic $^1\text{H-NMR}$ signals (CDCl_3 ; δ , ppm; 90 MHz): 4.25 (1H, m, -O-CH-), 3.89 (2H, m, -O-CH₂-), 3.51 (2H, m, -CH₂-Cl), 1.72 (8H, d, -C-CH₂). The product is soluble in

common solvents such as chloroform, benzene, diethyl ether or ethanol [12].

Preparation of 6,7-O-Cyclopentylidene-1-amino-4-azaheptane (L)

16,74 mL (0.20 mol) of 1,3-diaminopropane, 8.0 mL (0.06 mol) of triethylamine and 60 mL absolute xylene were mixed in a reaction vessel and stirred at room temperature. To this solution, a solution of 8.83 g (0.05 mol) of 1-chloro-2,3-O-cyclopentylideneopropane in 20 mL absolute xylene was added dropwise. The mixture was refluxed for 28 hours with continuous stirring. After cooling to room temperature, the mixture was filtered. The filtrate was distilled at 111 °C at 1 mm-Hg. Yield: 5.0 g (46.73 %). Characteristic IR peaks (in NaCl cell, cm^{-1}): 3361-3292; 1592 (-NH, and -NH₂), 2873-2934; (aliph. C-H), 1111 (C-O-C), 1042 (C-N). Characteristic ¹H-NMR signals (CDCl₃; δ , ppm; 90 MHz): 4.03 (1H, p, -O-CH-), 3.67 (2H, t, -O-CH₂-), 2.68 (6H, m, -CH₂-N), 1.69 and 1.29 (13H, m, -C-CH₂). The product is soluble in common solvents such as chloroform, benzene, water, xylene or ethanol [12].

Preparation of the Co(II), Ni(II) and Cu(II) complexes of ligand (L)

The ligand (L) (0.214 g, 1.0 mmol) was dissolved in 10 mL absolute ethanol in a 50 mL round-bottom flask. A solution of 2.0 mmol of metal salts [Co(OAc)₂·4H₂O] (0.498 g), Ni(OAc)₂·4H₂O (0.496 g) in 5 mL of absolute ethanol was added dropwise in a 15 minute period with continuous stirring at room temperature. The ligand (L) (0.214 g, 1.0 mmol) was dissolved in 10 mL absolute ethanol in a 50 mL round-bottom flask. A solution of 1.0 mmol of the metal salt Cu(OAc)₂·H₂O (0.199 g) in 5 mL of absolute ethanol was added dropwise in a 30 minute period with continuous stirring at room temperature. The reaction mixtures were then further stirred for 8 h at 150 °C temperature. The resulting precipitates were filtered off and washed with absolute ether. The products were dissolved in chloroform and precipitated by addition of *n*-hexane (1/5). The resulting crystals were filtered off and were dried at room temperature. Yields of complexes were found to be 0.36 g (56.26 %) for Co(II), 0.26 g (39.55 %) for Ni(II) and 0.25 g (63.20 %) for Cu(II) [6].

RESULTS AND DISCUSSION

The ligand (L), on reaction with Co(II), Ni(II) and Cu(II) acetate salts yields complexes corresponding to the general formulas, Co₂L(OAc)₄·4H₂O, [Ni₂L(OAc)₄·4H₂O]·H₂O and CuL(OAc)₂. The analytical data for all of the complexes are presented in Tables 1-5.

In this study, 6,7-O-Cyclopentylidene-1-amino-4-azaheptane (L) was prepared in two-stage process as shown in Figure 2. The first step is the synthesis of 1-chloro-2,3-O-cyclopentylideneopropane (1) from of reaction cyclopentanone and epichlorohydrin. In this reaction BF₃·OEt₂ was used as catalyst. In the second step, 1-chloro-2,3-O-cyclopentylideneopropane and 1,3-diaminopropane were reacted to obtain 6,7-O-cyclopentylidene-1-amino-4-azaheptane (L). The structure of ligand was determined by a combination of elemental analyses, IR, UV-vis, ¹H-NMR spectroscopy. The structural characterization data of (1) and (L) are given in the Experimental Section.

In the IR spectrum of (1) the most characteristic peaks are at 1111 cm^{-1} ν (C-O-C) and 758 cm^{-1} ν (C-Cl) [15], and the ¹H-NMR peaks are at 1.72 ppm for (CH₂), 3.51 ppm for (-O-CH₂) and 3.89 ppm for (-CH₂-Cl), 4.25 ppm for (-O-CH-) [6,12].

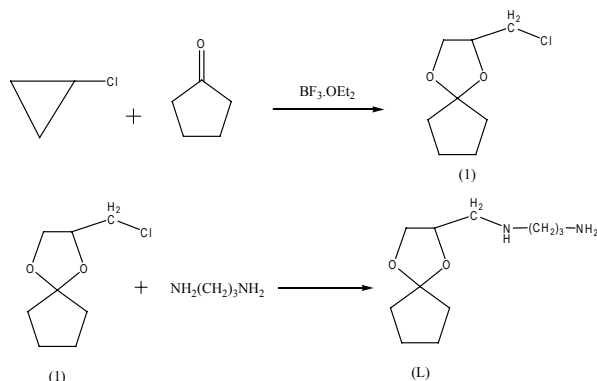


Figure 2 Synthesis scheme for the preparation of the ligand (L)

Table 1 The Colors, Formulas, Formula Weights, Yields, Melting Points, and Elemental Analyses Results of the Ligand and the Complexes

| Compounds | Formula (F.W.) g/mole | Color | Yield (%) | μ_{eff} /atom (B.M.) | Λ_{M} | Elemental analyses | | |
|---|--|------------|-----------|---------------------------------|----------------------|-----------------------|-----------------------|-----------------------|
| | | | | | | Calculated (found), % | | |
| Ligand | C ₁₁ H ₂₂ N ₂ O ₂ (214.0) | Colorless | 46.73 | — | — | C 61.68 (61.38) | H 10.28 (10.42) | N 13.08 (13.23) |
| [Co ₂ L(OAc) ₄ ·4H ₂ O] | Co ₂ C ₁₉ H ₄₂ N ₂ O ₁₄ (639.86) | Dark Brown | 56.26 | 2.10 | 4.89 | 35.63 (35.91) | 6.56 (6.38) | 4.38 (4.62) |
| [Ni ₂ L(OAc) ₄ ·4H ₂ O]·H ₂ O | Ni ₂ C ₁₉ H ₄₄ N ₂ O ₁₅ (657.42) | Green | 39.55 | 2.75 | 14.87 | 34.68 (34.94) | 6.69 (6.34) | 4.25 (4.14) |
| [CuL(OAc) ₂] | CuC ₁₅ H ₂₈ N ₂ O ₆ (395.54) | Dark green | 63.20 | 1.82 | 13.31 | 45.51 (45.29) | 7.08 (6.81) | 7.08 (7.42) |

$$\Lambda_{\text{M}} = (\Omega^{-1}\text{cm}^2\text{mol}^{-1})$$

In the IR spectrum of ligand, the characteristic peaks are at 3361-3292 cm^{-1} , which are assigned to $\nu(\text{N-H})$ and $\nu(\text{-NH}_2)$ and 1111 cm^{-1} that is assigned to the $\nu(\text{C-O-C})$ group. There is no C-Cl band in the IR spectrum of ligand. In the $^1\text{H-NMR}$ spectrum, there are two characteristic peaks, 1.75 and 2.40-3.20 ppm, which are attributable to the -NH- and -NH₂ groups (which were also identified by D₂O exchange) [16] and -O-CH₂- groups, respectively. There is another -O-CH₂- peaks at 4.03 ppm as pentet peaks. According to the elemental analyses, IR, $^1\text{H-NMR}$ results, the structure of the ligand was determined to be as shown in Figure 1. Since all the metal complexes are paramagnetic, their $^1\text{H-NMR}$ spectra not be obtained (Table 1).

Table 2 Characteristic IR Bands (cm^{-1}) of the Complexes in KBr pellets

| Compounds | O-H | N-H | C-H | C-O-C | C-N | C=O |
|--|-------------|----------------|-------------|--------|--------|------------------------|
| $[\text{Co}_2\text{L}(\text{OAc})_4 \cdot 4\text{H}_2\text{O}]$ | 3592-3462 s | 3259 m; 1614 m | 2958-2876 m | 1102 m | 1043 s | 1570 m; 1416-1448 m |
| $[\text{Ni}_2\text{L}(\text{OAc})_4 \cdot 4\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ | 3600-3450 s | 3318 m; 1614 m | 2933-2873 m | 1108 m | 1040 s | 1567 m; 1413-1435 m |
| $[\text{CuL}(\text{OAc})_2]$ | — | 3225 m; 1605 m | 2957-2870 m | 1104 m | 1042 s | 1575 m; 1433 m |

m: medium s: strong

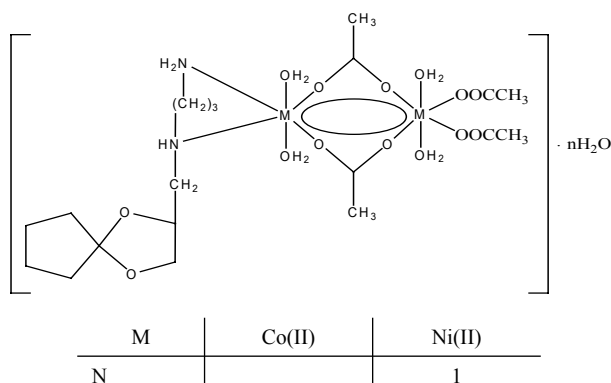


Figure 3 Suggested structure of the octahedral Co(II) and Ni(II) complexes of the ligand (L)

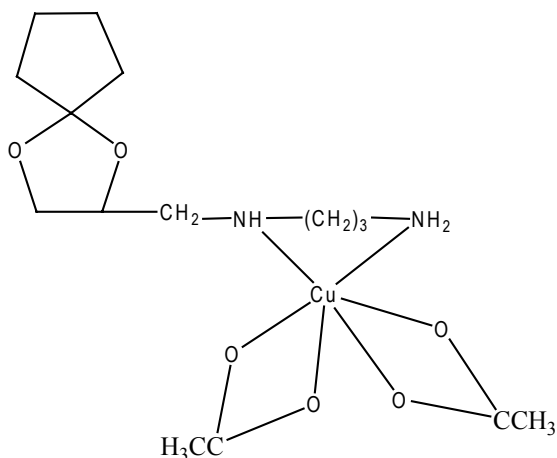


Figure 4 Suggested structure of the distorted octahedral Cu(II) complex of the ligand (L)

The metal-to-ligand ratio of the Co(II) and Ni(II) complexes was found to be 2:1; in addition there were present four acetate and water molecules. But the Ni(II) complex apparently has an additional one molecule of water of crystallization. The metal-to-ligand ratio of Cu(II) complex was found to be 1:1, in addition there were two acetate molecules. The infrared band observed near 3361-3292 cm^{-1} , which is assigned to the -NH-, and -NH₂ frequency is shifted to lower frequency after complexation with respect to the free ligand. The strong absorption at 3318-3225 cm^{-1} in the ligand can be assigned to $\nu(\text{NH}_2)$ of the intramolecularly hydrogen bonded [17] 1,3-diaminopropane moiety. At the same time, the band observed at 1620 cm^{-1} in the free ligand assigned to $\nu(\text{NH}_2)$ is shifted

to lower frequencies after forming the complexes [17-22]. In the spectra of the Co(II), Ni(II) and Cu(II) complexes a few new bands occur at lower regions 453, 461 and 455 cm^{-1} , and 520, 523 and 519 cm^{-1} which are attributed to the $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations, respectively [23]. The IR spectrum of $\text{Co}_2\text{L}(\text{OAc})_4 \cdot 4\text{H}_2\text{O}$, $[\text{Ni}_2\text{L}(\text{OAc})_4 \cdot 4\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ and $\text{CuL}(\text{OAc})_2$ shows two new bands at 1575-1567 and 1433-1493 assignable to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ bands of the acetate group [23-25], respectively. The $\Delta\nu = 154 \text{ cm}^{-1}$ can be taken as evidence for the existence of a bridging acetate groups in the Co(II) and Ni(II) complexes. But, the IR spectra of Cu(II) complex displays bands at 1575 and 1433 cm^{-1} due to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, respectively, of the acetate ligand. The wave number separation value between these two bands $\Delta\nu = 142 \text{ cm}^{-1}$, is characteristic of a bidentate acetate ligand in this complex [23-25]. In addition, two broad bands centered at 2260 and 2278 cm^{-1} were observed in IR spectra of Co(II) and Ni(II) complexes, and are attributed to the O-H stretching of the water molecules [26]. At this time, IR bands at 850 and 835 cm^{-1} , $\nu(\text{M-H}_2\text{O})$ of the water molecules to the Co(II) and Ni(II) metal ions [27] (Table 2).

The UV-vis spectra of the ligand and complexes were recorded in ethanol solution in the wavelength range from 200 to 1100 nm (Table 3). The electronic spectra showed a sharp and intense bands observed at 216-290 nm in the free ligand are reasonably accounted for $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions [19].

The electronic spectrum of the $[\text{Co}_2\text{L}(\text{OAc})_4 \cdot 4\text{H}_2\text{O}]$ complex has absorption bands at 478 and 750-775 nm attributable to the $^2\text{E}_g(\text{G}) \rightarrow ^2\text{A}_2g(\text{F})$ and $^2\text{E}_g(\text{G}) \rightarrow ^2\text{A}_1g(\text{G})$ transitions. This complex has a magnetic moment 2.10 B.M., indicating a low-spin octahedral configuration [28,29].

The magnetic moment of the $[\text{Ni}_2\text{L}(\text{OAc})_4 \cdot 4\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ complex is 2.75 B.M., which is high-spin octahedral geometry. This electronic spectrum of this complex has absorption bands

at 424 and 750-765 nm, assigned to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions [19, 21].

The observed magnetic moment of the $[CuL(OAc)_2]$ complex is 1.82 B.M. The electronic spectrum of this complex shows a shoulder at 640-755 nm, assignable to ${}^2B_{1g} \rightarrow {}^2E_g$ transition of the metal ion, suggesting a distorted octahedral geometry [19,21,27]. The suggested structures of the complexes are shown in Figure 3-4.

The complexes are non-electrolytes as shown by their molar conductivity (Λ_M) measurements in absolute ethanol, which are in the range for Co(II), Ni(II) and Cu(II) complexes at 13.31, 14.87 and $4.89 \Omega^{-1}cm^2mol^{-1}$ [12, 30], respectively (Table 1).

The thermal stability of the complexes was investigated by a combination of TGA and DTA. The TGA and DTA curves were obtained at a heating rate of $10^\circ C/min$. in nitrogen atmosphere over the temperature range of 26.96-819.23°C.

The Co(II) complex is stable up to 123.08°C and its decomposition starts at 123.08°C and is completed at 819.23°C [29]. The Co(II) complex decomposes to a CoO (residue: 18.52%) in two steps in the temperature ranges 123.08-211.54°C and 211.54-819.23°C. In the decomposition process of the Co(II) complex, the mass losses correspond to the 2,3-O-cyclopentylidene group, four coordinated water and the other organic moieties for the first and second stage decompositions, respectively.

The Ni(II) complex is stable up to 26.92°C and its decomposition starts at 26.92°C and is completed at 880.77°C [23,29]. The Ni(II) complex decomposes to a NiO (residue: 18.72%) in three steps in the temperature ranges 26.92-103.85°C, 103.85-226.92°C and 226.92-880.77°C. In the decomposition process of the Ni(II) complex, the mass losses correspond to one water molecule, the 2,3-O-cyclopentylidene group, four coordinated water and the other organic moieties for the first, second and third stage decompositions, respectively.

Table 3. Characteristic UV-vis Bands of the Ligand and the Complexes in C_2H_5OH

| Compound | Wave Length in nm (ϵ) | | |
|---|---|---|--|
| Ligand | — | — | 290 (34483) $n \rightarrow \sigma^*$ |
| $[Co_2L(OAc)_4 \cdot 4H_2O]$ | 478 (20942) ${}^2E_g(G) \rightarrow {}^2A_{2g}(F)$ | 750 (13333)- 775 (12903) ${}^2E_g(G) \rightarrow {}^2A_{1g}(G)$ | 398 (25126) $n \rightarrow \sigma^*$ |
| $[Ni_2L(OAc)_4 \cdot 4H_2O] \cdot H_2O$ | 424 (23585) ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ | 750 (13333)- 765 (13072) ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ | 324 (30864) $n \rightarrow \sigma^*$ |
| $[CuL(OAc)_2]$ | — | 640(15625)- 755 (13254) ${}^2B_{1g} \rightarrow {}^2E_g$ | 346 (28902) $n \rightarrow \sigma^*$ |

ϵ = molar extinction coefficient ($Lmol^{-1}cm^{-1}$)

The Cu(II) complex is stable up to 130.77°C and its decomposition starts at 130.77°C and is completed at 811.54°C [21]. The Cu(II) complex decomposes to a CuO (residue: 15.56%) in two steps in the temperature ranges 130.77-323.08°C and 323.08-811.54°C. In the decomposition process of the Cu(II) complex, the mass losses correspond to the 2,3-O-cyclopentylidene group and the other organic moieties for the first and second stage decompositions, respectively. The two stages of decomposition of Cu(II) complex are irreversible. The DTA show that all of the complexes have exothermic and endothermic peaks (Table 4).

The $Co_2L(OAc)_4 \cdot 4H_2O$ and $CuL(OAc)_2$ complexes are thermally stable up to 123.08°C and 130.77°C, respectively, whereas the $[Ni_2L(OAc)_4 \cdot 4H_2O] \cdot H_2O$ complex is thermally stable up to 26.92°C. In the TGA curve of the $[Ni_2L(OAc)_4 \cdot 4H_2O] \cdot H_2O$ complex, 2.76% weight loss was observed at 103.85°C. This shows that the complex contain 1 mol of water of crystallization of nickel complex. Further, the Co(II) and Ni(II) complexes contain 4 mol of coordinated water. The IR spectra of the complexes are characterized by the appearance of a broad band in the region 3450-3600 cm^{-1} due to the $\nu(O-H)$ frequency of water of crystallization and coordination [23-25]. These waters content were also identified by the elemental analyses. As can be seen in Table 5, the most stable complexes are that of $Co_2L(OAc)_4 \cdot 4H_2O$ and $CuL(OAc)_2$. The weight losses have been found to be approximately the same as the percentages estimated stoichiometrically on the assumption of complete decomposition of complexes for which their formulas are given Table 1. When the complexes are heated to higher temperatures, they decompose to give oxides of the MO type [21, 31].

Single crystals of the complexes could not be isolated from any solutions, thus no definitive structure could be described. However, the analytical, spectroscopic and magnetic data enable us to propose the possible structures.

Table 4 DTA Data of the Complexes

| Compounds | Exothermic Peaks, °C | Endothermic Peaks, °C |
|---|--------------------------------|------------------------|
| $Co_2L(OAc)_4 \cdot 4H_2O$ | 142.31, 192.31, 469.23, 761.54 | 426.92, 603.85 |
| $[Ni_2L(OAc)_4 \cdot 4H_2O] \cdot H_2O$ | 230.77, 411.54, 592.40 | 96.15, 319.23, 430.77 |
| $CuL(OAc)_2$ | 342.31, 573.08 | 130.80, 146.20, 265.45 |

Table 5 TGA Data of the Complexes

| Compounds | I.Step (°C) | II.Step (°C) | III.Step (°C) | Weight Loss Calculated (Found), % | Residue Calculated (Found), % |
|---|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-------------------------------|
| | Weight Loss Calculated (Found), % | Weight Loss Calculated (Found), % | Weight Loss Calculated (Found), % | | |
| $Co_2L(OAc)_4 \cdot 4H_2O$ | 123.08-211.54 | 211.54-819.23 | — | 81.74 (81.48) | CoO 18.26 (18.52) |
| | 211.54-33.60 (33.33) | 48.14 (48.15) | | | |
| $[Ni_2L(OAc)_4 \cdot 4H_2O] \cdot H_2O$ | 26.92-103.85 | 103.85-226.92 | 226.92-880.77 | 82.50 (81.28) | NiO 17.50 (18.72) |
| | 103.85-2.96 (2.76) | 32.70 (32.59) | 46.84 (45.93) | | |
| $CuL(OAc)_2$ | 130.77-323.08 | 323.08-811.54 | — | 84.19 (84.44) | CuO 15.81 (15.56) |
| | 54.36 (54.07) | 29.83 (30.37) | | | |

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