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The Synthesis and Co(II), Cu(II) and Ni(II) Complexes of 4-(2, 4-DiaminobutyI)-2-PhenyI-1, 3-Dioxolane

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## THE SYNTHESIS AND Co(II), Cu(II) AND Ni(II) COMPLEXES OF 4-(2,4-DIAMINOBUTYL)-2-PHENYL-1,3-DIOXOLANE

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#### ABSTRACT

4-(2,4-Diaminobutyl)-2-phenyl-1,3-dioxolane (L) has been synthesized starting from 4-chloromethyl-2-phenyl-1,3-dioxolane, which has been prepared from the reaction of epichlorohydrin and benzaldehyde. The complexes of this ligand with Co(II), Ni(II) and Cu(II) salts were prepared. The structures of the ligand and its complexes are proposed based on elemental analyses, IR, UV-VIS, <sup>1</sup>H and <sup>13</sup>C NMR spectra, magnetic susceptibility measurements, thermogravimetric analyses (TGA) and differential thermal analyses (DTA).

#### **INTRODUCTION**

It is important to use amines, containing at least two nitrogens, since they have chelate effects and produce quite stable complexes with transition metals. The purpose of this study is to prepare new amine ligand and complexes and to investigate their structures.

Compounds containing pendant 1,3-dioxolane groups have received much attention because of their useful properties as solvents, additive compounds and corrosion retardants while polymers containing 1,3-dioxolane groups exhibit semiconducting behaviour<sup>1,2</sup>.

Amines and their derivatives (monodentate, bidentate...) have been known to produce stable complexes with transition metals<sup>3,4,5,6</sup>. A lot of amine complex

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compounds have been synthesized and their properties (carcinogenic, optical and biological activity) established<sup>6,7</sup>.

Vaughn *et al.*<sup>8-10</sup> have reported the synthesis and complexation characteristics of  $[CrF(H_2O)(diamines)_2]X_2$  or  $[CrF(X)(diamines)_2]X$  (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or SCN<sup>-</sup>). The preparation and structure of complexes of benzenediamines have been reported<sup>11-15</sup>. Mostly, these complexes have been prepared by direct admixture of solutions containing appropriate amounts of the metal salt and the ligand. Four types of complexes have been established in which the ligand is bidentate, MLX, MLX<sub>2</sub>, ML<sub>2</sub>X<sub>2</sub> and ML<sub>3</sub>X<sub>2</sub> (M = Zn(II), Cu(II), Ni(II), and Co(II); X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>).

In the present paper, as a part of our study to determine the coordination properties of various diamines which are attached to oxolane groups towards transition metal ions, we have synthesized three new complexes of 4-(2,4-diaminobutyl)-2-phenyl-1,3-dioxolane (L) (Fig. 1.) and its Co(II), Ni(II) and Cu(II) complexes. As far as we know, this is the first report on this ligand.

#### **RESULTS AND DISCUSSION**

4-(2,4-Diaminobutyl)-2-phenyl-1,3-dioxolane (L) was prepared in a two stage process as shown in Fig. 2. The first step is the synthesis of 4-chloromethyl-2-phenyl-1,3-dioxolane (1) from benzaldehyde and epichlorohydrin. In this reaction BF<sub>3</sub>·OEt<sub>2</sub> was used as catalyst. In the second step, 4-chloromethyl-2phenyl-1,3-dioxolane and 1,2-diaminoethane were reacted to obtain 4-(2,4diaminobutyl)-2-phenyl-1,3-dioxolane (2). The structure of L was determined by a combination of elemental analyses, IR, UV-VIS, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The characterization data of (1) and (2) are given in the experimental section.

In the IR spectrum of (1) the most characteristic bands are at 1114 cm<sup>-1</sup>, v(C-O-C), and 745 cm<sup>-1</sup>, v(C-Cl). Characteristic <sup>1</sup>H and <sup>13</sup>C NMR peaks are given in the experimental section. <sup>1</sup>H NMR peaks occur at 3.50 ppm (-CH<sub>2</sub>-Cl), 4.10 ppm (-O-CH<sub>2</sub>), 4.20 ppm (-O-CH-), and 7.27 ppm (aromatic-CH). On the other hand, in the <sup>1</sup>H NMR spectra of (1), peaks appear at 5.70 and 5.87 ppm for Ph-CH< (1H) as two singlet peaks and in the <sup>13</sup>C NMR spectrum of (1), each carbon atom, namely C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub> (Fig. 1) has double resonances, (126.20 and 126.50), (129.27 and 129.58), (138.20 and 138.51), (104.65 and 105.87), (69.56 and 70.18) and (45.24 and 45.55) ppm, respectively, which



Fig. 1. The Structure of the Ligand L



Fig. 2. Synthesis Scheme of the Ligand L

indicates that the compound (1) exists as a mixture of <u>cis-trans</u> isomers<sup>34,35</sup>. The isomer ratios were found to be 56 % <u>cis</u>-isomer and 44 % <u>trans</u>-isomer from the <sup>1</sup>H NMR and <sup>13</sup>C NMR data. This is consistent with <u>cis-trans</u> isomers of the oxolane ring of the molecule (1). According to the elemental analyses IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR results, the structure of ligand was determined to be as shown in Fig. 1.

In the IR spectrum of (2), the characteristic bands are at 3367-3265 cm<sup>-1</sup> which is assigned to v(NH) and  $v(NH_2)$  (the broadening of the latter band may caused by intramolecular hydrogen bonding) and at 1114 cm<sup>-1</sup> assigned to

v(C-O-C). There is no C-Cl band in the IR spectrum of (2). In the <sup>1</sup>H NMR spectra of (2), peaks appear at 2.62-3.07 ppm (N-CH<sub>2</sub>) and at 1.57 ppm (-NH-, and -NH2) as broad peak. These peaks for -NH- and -NH2 disappeared on addition of D<sub>2</sub>O. Observation of the -O-CH<sub>2</sub> peaks at 3.50-3.87 and 3.90-4.19 ppm and of the -O-CH- peaks at 4.20-4.50 ppm, in each case are multiplets. On the other hand, in the <sup>1</sup>H NMR spectra of (2), peaks appear at 5.77 and 5.89 ppm for Ph-CH< (1H) as two singlet peaks and in the  $^{13}C$  NMR spectrum of (2), each carbon atom, namely C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub> (Fig. 2) has double resonances (128.68 and 128.41), (131.15 and 130.72), (139.70 and 139.30), (106.10 and 105.14), (70.28 and 70.00) and (78.13 and 78.08) ppm, respectively, which indicates that the compound (2) exists as a mixture of cis-trans isomers<sup>34,35</sup>. The isomer ratios were found to be 56 % cis-isomer and 44 % trans-isomer from the <sup>1</sup>H NMR and <sup>13</sup>C NMR data. This is consistent with <u>cis-trans</u> isomers of the oxolane ring of the molecule (2). According to the elemental analyses IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR results, the structure of the ligand was determined to be as shown in Fig. 1.

The ligand L, on interaction with Co(II), Ni(II) and Cu(II) salts yields complexes corresponding to the general formula  $ML_2Cl_2$ , and in the case of Co(II),  $[ML_2Cl_2]\cdot 2H_2O$ . The analytical data for all these complexes are presented in Tables I-V.

The metal to ligand ratio of the Co(II), Ni(II) and Cu(II) complexes was found to be 1:2 in addition to two chloride ligand. But the Co(II) complex has two additional water of crystallization<sup>16</sup> molecules. The infrared band observed near about 3361-3285 cm<sup>-1</sup> which is assigned to the -NH-, and -NH<sub>2</sub> frequencies is shifted to lower frequencies after complexation with respect to the free ligand. The strong absorption at 3642-3265 cm<sup>-1</sup> for the ligand can be assigned to the intramolecularly hydrogen bonded<sup>17</sup> v(NH<sub>2</sub>) frequencies (3285-3182 cm<sup>-1</sup>) is due to N,N-metal coordination<sup>18,19</sup>. At the same time, the band observed at 1651 cm<sup>-1</sup> in the free ligand which is assigned to v(NH<sub>2</sub>) is shifted to lower frequencies after complexation<sup>20</sup>. These shifts indicate that the primary and secondary amino groups take part in complexation

The Co(II), Ni(II) and Cu(II) complexes are paramagnetic, and their magnetic susceptibility values are 5.01, 2.85, 1.76 B.M., respectively. For all of these complexes, additional analytical data are given in the Tables I-V. According to

Compoundo	EW		1	Elemental analyses			
Compounds	F.W		IVI.p.	70		ited (Four	ia)
	g/mole	Color	C	<u> </u>	<u> </u>	N	0
Ligand		Color-		64.86	8.11	12.61	14.31
$C_{12}H_{18}N_2O_2$	222.00	less	-	(64.79)	(8.25)	(12.65)	(14.54)
$[Co(L)_2Cl_2]\cdot 2H_2O$				43.28	6.56	9.18	15.74
C22H36N4O6Cl2C0	609.93	Brown	88	(43.11)	(6.61)	(9.20)	(15.44)
$Ni(L)_2Cl_2$				46.02	6.27	9.76	11.16
C <sub>26</sub> H <sub>40</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub> Ni	573.71	Green	105	(46.03)	(6.43)	(9.45)	(11.29)
$\overline{Cu(L)_2Cl_2}$				45.63	6.22	9.68	11.06
C22H36N4O4Cl2Cu	578.54	Viola	150_	(45.45)	(6.10)	(9.30)	(11.23)

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

Table II. Characteristic IR Bands (cm<sup>-1</sup>) of the Complexes as KBr Pellets

Compounds	O-H	N-H	Arom. C-H	Aliph. C-H	C-O-C	C-N
Ligand	-	3367- 3265 s	3055-3080 m; 1700-2000 w; 706-782 s	2953-2876 s	1114 s	1042 m
$[Co(L)_2Cl_2] \cdot 2H_2O$	3642- 3265 s	3234 s; 1625 m	3106 m; 782-706 s	2953-2876 s	1089 s	1038 m
Ni(L) <sub>2</sub> Cl <sub>2</sub>	-	3285- 3182 s; 1625 m	3080 m; 1957-1855 w; 782-706 s	2953-2876 s	1089 s	1038 m
Cu(L) <sub>2</sub> Cl <sub>2</sub>	-	3208- 3106 s; 1625 m	3131-3055 s; 782-706 m	2953-2876 s	1089 s	10 <b>38 m</b>

Table III. DTA Data of the Complexes

Compounds	Exothermic Peaks, °C	Endothermic Peaks, °C
$[Co(L)_2Cl_2] \cdot 2H_2O$	140.9, 178.6, 647.2	13.6, 189.7, 295.0, 329.7
Ni(L)2Cl2	262.6, 562.5	253.9, 612.2
Cu(L) <sub>2</sub> Cl <sub>2</sub>	219.2, 517.0, 652.2, 717.2, 849.3	205.5, 634.9

Compounds	First Step °C	Second Step °C	Third Step °C	Residue, % Calculated (Found)
$[Co(L)_2Cl_2] \cdot 2H_2O$	39.2-115.2	115.2-603.2	603.2-770.0	12.28 (13.47)
Ni(L) <sub>2</sub> Cl <sub>2</sub>	285.5-528.9	528.9-713.0	-	13.02 (12.64)
Cu(L) <sub>2</sub> Cl <sub>2</sub>	208.8-243.3	243.3-602.5	602.5-949.9	13.74 (14.56)

Table IV. TGA Data of the Complexes

Table V. TGA Data of the Complexes. [Calculated (Found), Weight loss %]

Compounds	First Step	Second Step	Third Step	Weight Loss, %
$[Co(L)_2Cl_2] \cdot 2H_2O$	5.90 (6.10)	62.47 (64.02)	19.35 (16.41)	87.72 (86.53)
Ni(L) <sub>2</sub> Cl <sub>2</sub>	66.42 (66.96)	20.56 (20.40)	-	86.98 (87.36)
$Cu(L)_2Cl_2$	12.27 (12.68)	57.59 (53.39)	20.40 (19.37)	86.26 (85.44)

the above results, a distorted octahedral high-spin geometry for the Co(II), Ni(II) and Cu(II) complexes is proposed<sup>21,22</sup>. The suggested structures of the complexes are shown in Fig. 3. Since all the metal complexes are paramagnetic, their <sup>1</sup>H NMR spectra could not be obtained.

The electronic spectra of the complexes show intense  $n \rightarrow \sigma^*$  bands around 285-395 nm as absorptions due to the ligand, and weak d-d transitions are observed for the Co(II), Ni(II), and Cu(II) complexes at 615, 468, 415; 612, 473; and 617 nm, respectively.

The complexes are non-electrolytes as shown by their molar conductivity ( $\Lambda_M$ ) measurements in absolute ethanol which are in the range<sup>27</sup> 4-6  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

#### Thermal Studies

The thermogravimetric (TGA) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10° C/min. in nitrogen atmosphere over a temperature range of 25-950° C.

In the decomposition process of the Ni(II) complex, the mass losses



Fig. 3. Suggested Structure of the Octahedral Complexes of the Ligand, L

correspond to the 4-methyl-2-phenyl-1,3-dioxolane/chloro groups and the 1,2diaminoethane groups leaving in the first and second stage decompositions, respectively.

In the decompositon process of the Cu(II) complex, the mass losses correspond to the chloro groups, 4-methyl-2-phenyl-1,3-dioxolane and the 1,2diaminoethane groups leaving in the first, second and third stage decompositions, respectively.

In the decompositon process of the Co(II) complex, the mass losses correspond to the two water molecules, the 4-methyl-2-phenyl-1,3dioxolane/chloro groups and the 1,2-diaminoethane groups leaving in the first, second and third stage decompositions, respectively. These are characterized by endothermic peaks within the temperature range 39.2-115.2° C corresponding to the loss of hydration water. The complex of Co(II) exhibits a weight loss (6.10 %) corresponding to the percent of coordinated water within the complex molecule. This is confirmed by the very weak endothermic DTA peak<sup>30</sup> at 113.6° C. The IR spectra of the complexes are characterized by the appearance of a broad band in region 3642-3265 cm<sup>-1</sup> due to the v(O-H) of water of crystallization<sup>16</sup>. This water content was also identified by the elemental analyses. As it can be seen in Table IV, the most stable complex is [Ni(L)<sub>2</sub>Cl<sub>2</sub>]. The decomposition processes of all complexes are irreversible. All of the complexes undergo complete decomposition to the corresponding metal oxides, CuO, NiO or CoO<sup>31,32,33</sup> (Tables III, IV and V).

#### **EXPERIMENTAL**

#### **Reagents and Measurements**

Reagent grade chemicals were used. Benzaldehyde and epichlorohydrin were purchased from Merck (pure) and used without further purification. 4-Chloromethyl-2-phenyl-1,3-dioxolane<sup>28</sup> and 4-(2,4-diaminobutyl)-2-phenyl-1,3-dioxolane<sup>34</sup> were synthesized according to Fig. 2.

The elemental analyses were determined in the TUBITAK Laboratory (Scientific and Technical Research Council of Turkey), IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets, <sup>13</sup>C and <sup>1</sup>H NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz high performance digital FT-NMR spectrometer or a JEOL FX 90Q FT-NMR. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (20° C) using Hg[Co(SCN)<sub>2</sub>] as a calibrant; diamagnetic corrections were calculated from Pascal's constants<sup>28</sup>. The refractive index of the substances was determined on a Bellingam + Stanley Ltd. 60/70 Abbe refractometer (calibration oil RI = 1.47577 at 20° C). Thermogravimetric (TGA) and dilferential thermal analyses (DTA) curves were recorded on a Shimadzu TG-50 thermobalance. Electronic spectra were measured on a CMD 750 WPA conductometre ( $10^{-3}$  M in absolute ethanol).

#### Synthesis of 4-Chloromethyl-2-phenyl-1,3-dioxolane(1)

In a three necked flask with a thermometer, a drying CaCl<sub>2</sub> tube and a dropping funnel, 106.0 g (1.0 mole) of purified benzaldehyde and 15-20 drops of boron trifluoride ethyl ether complex were mixed. This mixture was cooled to 10 to 15° C and keeping the mixture at this temperature, 28.0 g (0.30 mole) of epichlorohydrin was added dropwise in a 1 h period with continuous stirring. The reaction mixture was then further stirred for 3 h at 20° C. The product distilled directly from the crude reaction mixture at 130-133° C at 4 mm Hg. Yield: 40 g (66 %);  $d_4^{20} = 1.2169$  and  $n_D^{20} = 1.5258$ . Characteristic IR bands: 3055-3080 cm<sup>-1</sup> v(arom. C-H), 1700-2000, and 706-782 cm<sup>-1</sup> v(arom. mono subst.), 2978-2876 cm<sup>-1</sup> v(aliph. C-H), 1114 cm<sup>-1</sup> v(C-O-C), 745 cm<sup>-1</sup> v(C-Cl). Characteristic

<sup>1</sup>H NMR peaks (CCl<sub>4</sub>, TMS,  $\delta$  ppm): 7.27 (5H, m, aromatic), 5.70 and 5.87 (1H, s, Ph-CH<), 4.20 (1H, m, -O-CH-), 4.10 (2H, m, -O-CH<sub>2</sub>-), 3.50 (2H, t, J = 6.24 Hz, -CH<sub>2</sub>-Cl). Characteristic <sup>13</sup>C NMR peaks (CCl<sub>4</sub>, TMS,  $\delta$  ppm): C<sub>1</sub> (128.66), C<sub>2</sub> (126.20 and 126.50), C<sub>3</sub> (129.27 and 129.58), C<sub>4</sub> (138.20 and 138.51), C<sub>5</sub> (104.65 and 105.87), C<sub>6</sub> (69.56 and 70.18), C<sub>7</sub> (76.64 and 76.95), C<sub>8</sub> (45.24 and 45.55). The product was found to be soluble in common solvents such as chloroform, benzene, diethyl ether or ethanol.

#### Synthesis of 4-(2,4-Diaminobutyl)-2-phenyl-1,3-dioxolane (2)

In a reaction flask with a thermometer, a drying CaCl<sub>2</sub> tube and a dropping funnel, 6.0 g (100 mmole) of 1,2-diaminoethane, 2.49 (25 mmole) of triethylamine and 60 mL absolute xylene were mixed and heated to 90° C. To this solution, a solution of 4.96 g (25 mmole) of 4-chloromethyl-2-phenyl-1,3-dioxolane in 50 mL xylene was added dropwise. Subsequently, the mixture was further refluxed for 48 h and then cooled to room temperature. The precipitated triethylammonium salt was filtered and the filtrate was evaporated to remove excess 1,2-diaminopropane and the product distilled from the filtrate at 138° C at 4 mm Hg. Yield: 4.20 g  $(76 \%); d_4^{20} = 1.0826; n_0^{20} = 1.5315$ . Characteristic IR bands (NaCl cell, cm<sup>-1</sup>): 3367-3265; 1651 cm<sup>-1</sup> v(-NH, and -NH<sub>2</sub>), 3055-3080 cm<sup>-1</sup> v(arom. C-H), 1700-2000 and 706-782 cm<sup>-1</sup> v(arom. mono subst.), 2953-2876 cm<sup>-1</sup> v(aliph. C-H), 1114 cm<sup>-1</sup> v(C-O-C). Characteristic <sup>1</sup>H NMR peaks (CDCl<sub>3</sub>, TMS, δ ppm): 7.30-7.78 (5H, m, arom. C-H), 5.77 and 5.89 (1H, s, Ph-CH<), 4.20-4.50 (1H, m, -O-CH-), 3.50-3.87 and 3.90-4.19 (2H, m, -O-CH2-), 2.62-3.07 (6H, m, -N-CH2-8,9,10), 1.57 (3H, s, exchanging, -NH and -NH2). Characteristic <sup>13</sup>C NMR peaks (CDCl<sub>3</sub>, TMS, δ ppm): C<sub>1</sub> (130.16), C<sub>2</sub> (128.68 and 128.41), C<sub>3</sub> (131.15 and 130.72), C4 (139.70 and 139.30), C5 (106.10 and 105.14), C6 (70.28 and 70.00), C<sub>7</sub> (78.13 and 78.08), C<sub>8</sub> (54.08), C<sub>9</sub> (53.97), C<sub>10</sub> (42.00). The product is soluble in common solvents such as chloroform, benzene, water, xylene or ethanol.

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

A quantity of 0.222 g (1.0 mmole) of the ligand was dissolved in 10 mL absolute ethanol and a solution of 0.5 mmole of metal salts  $[CoCl_2(0.0649 \text{ g})]$ ,

Compound	Wave Length in nm (ε) <sup>a</sup>				
Ligand	-	-	-	$295 (25000)$ $n \rightarrow \sigma^*$	
$[Co(L)_2Cl_2]$ -	615 (3900)	468 (4700)	415 (7300)	290 (23300)	
·2H <sub>2</sub> O	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2}(F)$	$^{4}T_{1g}(F) \rightarrow 4A_{2}(F)$	$^{4}T_{1g}(F) \rightarrow $	n→σ <sup>*</sup>	
	12g(F)	A2g(r)	$- 4\Gamma_{1g}(P)$		
$Ni(L)_2Cl_2$	612 (1200)	473 (2100)		295 (22900)	
	$^{3}A_{2g} \rightarrow ^{3}T_{1g}(F)$	$^{3}A_{2g} \rightarrow ^{3}T_{1g}(P)$		n→σ <sup>*</sup>	
$Cu(L)_2Cl_2$	617 (6300)	-	-	285 (23100)	
	$^{2}E_{g} \rightarrow ^{2}T_{2g}$			n→σ <sup>*</sup>	

Table VI. Characteristic UV-VIS Bands of the Ligand and the Complexes in C2H5OH

 $a_{\varepsilon} = \text{molar extinction coefficient } (L \text{ mol}^{-1} \text{ cm}^{-1})$ 

NiCl<sub>2</sub>·5H<sub>2</sub>O (0.1098 g) and CuCl<sub>2</sub> (0.0672 g)] in 5 mL absolute ethanol was added dropwise in a period of 15 min. with stirring continuously at room temperature. Meanwhile, it began to precipitate and the precipitation was completed in a few minutes. Then it was filtered and precipitate was washed with absolute ethanol. After dissolving of precipitate in chloroform, <u>n</u>-hexane (1/5) was added to crystallize the complex. The obtained crystals was left to dry in air at room temperature. Yields of the complexes are 0.43 g (70 %) for Co(II), 0.41 g (72 %) for Ni(II) and 0.44 g (76 %) for Cu(II).

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