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Preparation of Complexes of 1-Amino-6,7-*O*-Cyclohexylidene-4-Azaheptane with Transition Metal Acetates

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Abstract — 1-Amino-6,7-*O*-cyclohexylidene-4-azaheptane (L) has been synthesized starting from 1-chloro-2,3-*O*-cyclohexylidenepropane prepared by the reaction of epichlorohydrin with cyclohexanone, catalyzed by BF_3OEt_2. Complexes of this ligand with Co(II), Ni(II) and Cu(II) acetates were prepared. The structures of the ligand and its complexes are proposed based on the elemental analyses, IR, UV-VIS, and ^{1}H and ^{13}C NMR spectra, magnetic susceptibilities, and conductomety data.

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Complexes formed by reactions of diamines with transition metals have a wide range of applications [1–7]. For instance, they are used in the determination of mercury in natural waters, production of colored thermoplastic resins and cross-linked epoxy resins, determination of selenium by instrumental methods, prevention of corrosion, pressure-sensitive color imaging technologies, powdered hair dyes, cation-exchange copolymerizations, and some antiallergenes of medical use [8].

1,3-Dioxolane complexes are also used as monomers for homo- or copolymer synthesis. Oguchi *et al.* have studied the semiconducting properties and biologic activity of 1,3-dioxolane–vinyl polymers [9]. Finally, 1,3-dioxolane complexes can be used as solvents, additives, and corrosion-preventing materials [10].

Proceeding with our research into the coordination activity of various diamines containing an oxolane group toward transition metal ions, in the present work we synthesized three new complexes of 1-amino-6,7-*O*-cyclohexylidene-4-azaheptane (L) with Co(II), Ni(II) and Cu(II) acetates.

1-Amino-6,7-*O*-cyclohexylidene-4-azaheptane (L) was prepared by a two-step procedure (Scheme 1). The first step was the synthesis of 1-chloro-2,3-*O*-cyclohexylidenepropane (**I**) from of cyclohexanone and epichlorohydrin. In this reaction, $BF_3 \cdot OEt_2$ was used as catalyst. In the second step, 1-chloro-2,3-*O*-cyclohexylidenepropane was reacted with 1,3-diaminopropane to obtain the target product. The structures of L was determined by a combination of elemental analyses, IR, UV-VIS, and ^{1}H NMR spectroscopy, magnetic susceptibility measurements, and conductometry (see Experimental).

Scheme 1.

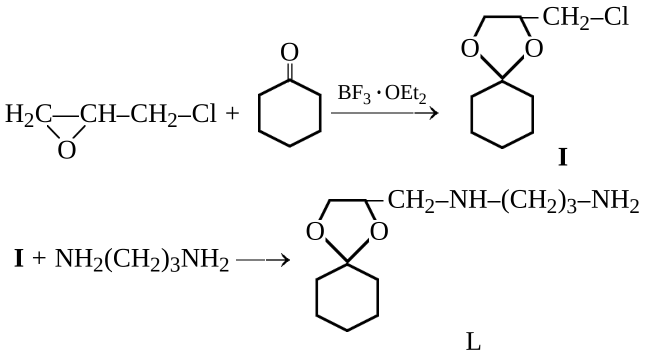


Table 1. Yields, colors, elemental analyses, and molecular weights of ligands and complexes

Compound	Yield, %	Color	mp, °C	Found, %			Formula	Calculated, %			*M*
				C	H	N		C	H	N	
I	75	Colorless	–	–	–	–	$C_9H_{15}ClO_2$	–	–	–	190.50
Ligand	65	″	–	–	–	–	$C_{12}H_{24}N_2O_2$	–	–	–	228.00
$[Co(L)_2(OAc)_2]\cdot H_2O$	75	Dark red	210	50.50	8.74	8.15	$C_{28}H_{56}CoN_4O_5$	51.54	8.59	8.61	586.93
$[Ni(L)_2(OAc)_2]$	55	Claret red	240	53.69	7.68	8.64	$C_{28}H_{54}N_4NiO_4$	53.11	8.54	8.86	568.71
$[Cu(L)_2(OAc)_2]$	75	Parliament blue	220	51.22	7.68	8.12	$C_{28}H_{54}CuN_4O_4$	52.70	8.47	8.78	573.54

Table 2. Characteristic IR bands (cm^{-1}) of complexes in KBr

Compound	OH (H_2O)	N–H	C–H_{aliph}	C–O–C	C–N	C=O (OAc)
$[Co(L)_2(OAc)_2]\cdot H_2O$	3444	3300–3270, 1610	2982–2880	1114	1035	1583 as, 1389 s
$[Ni(L)_2(OAc)_2]$	–	3310, 3265, 3200, 1610	2985–2882	1114	1035	1597 as, 1417 s
$[Cu(L)_2(OAc)_2]$	–	3265, 3214, 3180, 1610	2983–2910	1114	1038	1603 as, 1451 s

The IR spectrum of **I** contains characteristic bands at 2959–2877 [ν(CH_{aliph})], 1114 [ν(COC)], and 760 cm^{-1} [ν(CCl)] [11]. The characteristic ^1H NMR signals appear at 1.70 (ring CH_2), 3.54 (OCH_2), 3.92 (CH_2Cl), and 4.30 pm (OCH).

The IR spectrum of L contains characteristic bands at 3330–3275 cm^{-1} [ν(NH) and ν(NH_2)] and 1114 cm^{-1} [ν(COC)] and lacks C–Cl bands. The ^1H NMR spectra of L displays a multiplet at 2.66 ppm (NCH_2) and a singlet at 1.18 ppm (NH, NH_2). The NH and NH_2 signals disappear on addition of D_2O [12]. On the other hand, the ^1H NMR spectra of L contains multiplets at 4.19 ppm (OCH). Based on the elemental analyses and IR and ^1H and ^{13}C NMR spectra, we assigned to the ligand the structure shown in Scheme 1.

The ligand L reacts with Cu(II), Ni(II) and Co(II) acetates to form complexes of the general formula $[M(L)_2(OAc)_2]\cdot H_2O$ (M = Cu(II), Ni(II), Co(II); *n* = 1). Analytical data for all the complexes are presented in Tables 1–3.

The complexes were prepared by Scheme 2.

Scheme 2.

$$M(OAc)_2\cdot mH_2O + 2L \xrightarrow{\text{abs. EtOH/abs. }CHCl_3} [M(L)_2(OAc)_2]\cdot nH_2O + zH_2O,$$

M = Cu(II), Ni(II), Co(II); L = $C_{12}H_{24}N_2O_2$.

m	6	5	6
n	–	–	1
z	6	5	5

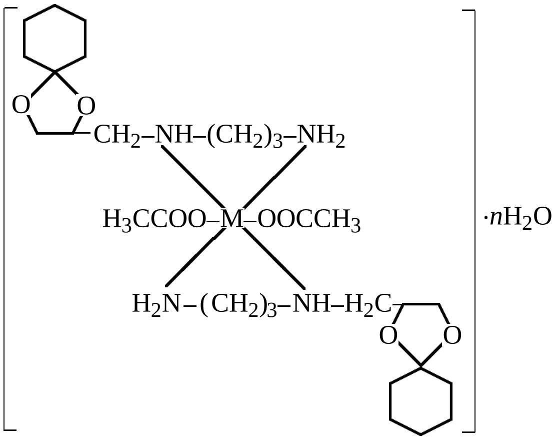
The metal-to-ligand ratios in the Co(II) and Ni(II) complexes were found to be 1 : 2; in addition, the complexes contain two acetate ligands. The Co(II) complexes has one additional moilecule of water of crystallization. The IR absorption band near 3330–3275 cm^{-1} can be assigned to ν(NH_2) of the intramolecularly H-bonded 1,3-diaminopropane moiety. The shift of the N–H band to lower frequencies (3330–3180 cm^{-1}) is due to N,N-metal coordination. At the same time, the band at 1650 cm^{-1} in the free ligand assigned to ν(NH_2) is shifted to lower frequencies (1610 cm^{-1}) in the complexes. This fact suggests that both the primary and secondary amino groups are involved in complex formation [13]. The new absorption bands at 1583–1603 and 1389–1451 cm^{-1} in the spectra of the complexes provide evidence to show that the CH_3COO^- group is coordinated to the metal ion. The IR spectra of $[Cu(L)_2(OAc)_2]$, $[Ni(L)_2(OAc)_2]$, and $[Co(L)_2(OAc)_2]\cdot H_2O$ show two new bands at 1583–1603 and 1389–1451 cm^{-1} assignable to acetate ν_{as}(C–O) and ν_s(C–O), respectively. The acetate group in $[Cu(L)_2(OAc)_2]$, $[Ni(L)_2(OAc)_2]$, and $[Co(L)_2(OAc)_2]\cdot H_2O$ acts as monodentate ligand, as evidenced by the great difference between the ν_{as}(C–O) and ν_s(C–O) frequencies (1603–1451 = 152; 1597–1417 = 180, and 1583–1389 = 194 cm^{-1}, respectively) [14, 15].

Table 3. Characteristic UV-VIS bands of complexes in C_2H_5OH

Compound	λ, nm (ε, l mol^{-1} cm^{-1})		
$[Co(L)_2(OAc)_2] \cdot H_2O$	420.0–463.0 (1200)	485–550 (2400)	–
	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
$[Ni(L)_2(OAc)_2]$	430.0–460.0 (1900)	545 (1700)	578–610 (1800)
	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$
$[Cu(L)_2(OAc)_2]$	538.0–588.0 (1450)	–	–
	$^2E_g \rightarrow {}^2T_{2g}$		

The Co(II), Ni(II) and Cu(II) complexes are paramagnetic, and their magnetic suscuptibilities 5.28, 2.89, and 1.80 BM, respectively. Based on the data in Tables 1–3, the complexes were assigned a distorted octahedral high-spin geometry [16–18]. The suggested structures of the complexes are shown in Scheme 3. Since all the metal complexes are paramagnetic, their ^1H NMR spectra could not be obtained.

Scheme 3.



M = Co(II), n = 1; M = Ni(II), Cu(II), n = 0.

The electronic spectra of the complexes contain strong $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ bands around 220–295 nm [19,20], as well as absorption bands of the ligand and the acetate groups, as well as those formed by weak *d–d* transitions in the Co(II), Ni(II), and Cu(II) complexes at 420.0–463 and 485–550; 430–460, 545 and 578–610; 538–588 nm, respectively.

The complexes are nonelectrolytes, as shown by their molar conductivities (Λ_M) in absolute ethanol: 7.80, 8.40, and 6.50 Ω^{-1} cm^2 mol^{-1} for the the Co(II), Ni(II), and Cu(II) complexes, respectively [21].

EXPERIMENTAL

The IR spectra were recorded on an Ati-Lnicom Mattson 1000 FT-IR spectrometer in KBr pellets. The ^{13}C and ^1H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) or a JEOL FX 90QFT spectrometer. The magnetic susceptibilities were determined on a Christon balance at room temperature (20°C); the diamagnetic corrections were calculated from Gouy's constants [24]. The molar conductivities were determined on a CMD 750WPA conductometer. The elemental analyses were performed at the TUBITAK Laboratory (Scientific and Technical Research Council of Turkey).

Reagent grade chemicals were used. Epichlorohydrin and cyclohexanone were purchased from Merck (Pure) and (Sigma), respectively, and used as received. 1-Chloro-2,3-*O*-cyclohexylidinepropane (**I**) and 1-amino-6,7-*O*-cyclohexylidene-4-azaheptane (L) were synthesized as described in [22, 23].

Synthesis of 1-chloro-2,3-*O*-cyclohexylidinepropane (I). In a three-necked flask with a thermometer, a $CaCl_2$ drying tube, and a dropping funnel, 14.7 g (0.15 mole) cyclohexanone and 15–20 drops of boron trifuoride–ether complex were mixed. This mixture was cooled to 10–17°C. While maintaining the mixture at this temperature, 34.5 g (0.38 mole) of epichlorohydrin was added dropwise with continuous stirring over the course of 20 min. The reaction mixture was further stirred for 2 h at 40°C under nitrogen. The product was distilled 105–110°C (37 mm Hg). Yield 22.69 g (75%). IR spectrum, ν, cm^{-1}: 2959–2877 (CH_{aliph}), 1114 (COC), 760 (CCl). Characteristic ^1H NMR signals (400 MHz, $CDCl_3$, δ, ppm):

1.70 d (8H, CH_2); 3.54 m (2H, CH_2O); 3.92 m (2H, CH_2Cl); 4.30 m (1H, CHO). The product is soluble in ordinary solvents, such as chloroform, benzene, diethyl ether, or ethanol.

Synthesis of 1-amino-6,7-*O*-cyclohexylidene-4-azaheptane (II). In a reaction flask with a thermometer, a $CaCl_2$ drying tube, and a dropping funnel, 18.42 ml (0.22 mol) of 1,3-diaminopropane, 8.0 ml (0.057 mol) of triethylamine, and 60 ml of absolute xylene were mixed. To this solution, a solution of 13.3 g (0.07 mol) of 1-chloro-2,3-*O*-cyclohexylidenepropane in 25 ml of xylene was added dropwise with continuous stirring. After this, the mixture was refluxed at 122–130°C for 30 h and cooled to room temperature under nitrogen. The precipitated triethylammonium salts were filtered off, and the filtrate was evaporated to remove excess 1,3-diaminopropane. The product was distilled at 135–150°C (4 mm Hg). Yield 10.82 g (65%). Characteristic IR bands, ν, cm^{-1} (NaCl cell): 3330–3275; 1650 (NH and NH_2), 2980–2880 (CH_{aliph}), 1114 (COC), 1038 (CN). ^1H NMR spectrum ($CDCl_3$), δ, ppm): 4.19 pm (1H, CHO), 3.57–4.14 t (2H, CH_2O), 2.66 m (6H, $CH_2NHCH_2 \cdot CH_2CH_2NH_2$), 1.57 m (10H, cyclo-$CH_2$) 1.35 s (2H, $CH_2CH_2CH_2$), 1.18 s (3H, NH and NH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.87, 23.73, 25,16, 33.82, and 35.17 (5C, cyclo-CH_2), 109.56 (1C, cyclo-CH_2), 67.39 (CH_2O), 75.82 (CHO), 52.81 ($CH_2NH \cdot CH_2CH_2CH_2NH_2$), 48.12 ($NHCH_2CH_2CH_2NH_2$), 36.64 ($NHCH_2CH_2CH_2NH_2$), 40.50 ($NHCH_2CH_2CH_2 \cdot NH_2$). The product is soluble in ordinary solvents, such as chloroform, benzene, water, xylene, or ethanol.

Synthesis of the Co(II), Cu(II) and Ni(II) complexes. The ligand, 0.457 g was dissolved in 10 ml of absolute ethanol in a 50-ml round-bottom flask. A solution of 1 mmol of metal acetate [$Co(CH_3COO)_2 \cdot 6H_2O$ (0.498 g), $Ni(CH_3COO)_2 \cdot 5H_2O$ (0.130 g). or $Cu(CH_3COO)_2 \cdot 6H_2O$ (0.254 g)] in 5 ml of absolute ethanol and chloroform was added dropwise with continuous strirrring over the course of 15 min at room temperature. The reaction mixture was then stirred for 1 h at room temperature. The resulting precipitates were filtered off and washed with absolute ether. The products were dissolved in chloroform and precipitated with *n*-hexane (1 : 5). The crystals were filtered and dried at room temperature. Yield 0.18 g (75%) for Co(II), 0.033 g (55%) for Ni(II), and 0.18 g (75%) for Cu(II).

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