

# The Synthesis and Characterization of 1,2-*O*-Cyclohexylidene-4-aza-8-aminooctane and Some of its Transition Metal Complexes

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**ABSTRACT:** 1,2-*O*-Cyclohexylidene-4-aza-8-aminooctane (L) has been synthesized starting from 1-chloro-2,3-*O*-cyclohexylidene, which has been prepared by the reaction of epichlorohydrin with cyclohexanone. The complexes of this ligand with Co(II), Ni(II), Cu(II), and UO<sub>2</sub>(VI) 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, and differential thermal analyses. © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:254–260, 2000

## INTRODUCTION

The purpose of this study is to prepare a new amine ligand and its 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.

Compounds containing pendant 1,3-dioxolane groups have received much attention because of their use as solvents, additive compounds, and corrosion retardants, while polymers containing 1,3-dioxolane groups exhibit semiconducting behavior [1,2].

Amines and their derivatives (monodentate, bidentate, etc.) have been known to produce stable complexes with transition metals [3–6]. Many amine complex compounds have been synthesized and

their properties (carcinogenic, optical, and biological activity) have been established [6,7].

Vaughn et al. [8–10] have reported the synthesis and characterization of [CrF(H<sub>2</sub>O)(diamines)<sub>2</sub>]X<sub>2</sub> or [CrF(X)(diamines)<sub>2</sub>]X. The preparation and structures of the complexes of benzenediamines recently have been reported [11–15]. Mostly, these complexes have been prepared by direct mixing of solutions containing appropriate amounts of the metal salt and the ligand. Three types of complexes have been established in which the ligand is bidentate, 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 article, as a part of our study to determine the coordination and semiconductor properties of various diamines that are attached to oxolane groups towards transition metal ions, we have synthesized four new complexes of 1,2-*O*-cyclohexylidene-4-aza-8-aminooctane (L) (Figure 1.) with Co(II), Ni(II), Cu(II), and UO<sub>2</sub>(VI). As far as we know, this is the first report on the synthesis and metal complexes of this ligand.

## RESULTS AND DISCUSSION

1,2-*O*-Cyclohexylidene-4-aza-8-aminooctane (L) was prepared in a two-stage process as shown in Figure 2. The first step is the synthesis of 1-chloro-2,3-*O*-cyclohexylidene (1) from the reaction of cyclohexanone and epichlorohydrin. In this reaction BF<sub>3</sub>·OEt<sub>2</sub> was used as catalyst. In the second step, 1-chloro-2,3-*O*-cyclohexylidene and 1,4-diaminobutane were reacted to obtain 1,2-*O*-cyclohexylidene-4-

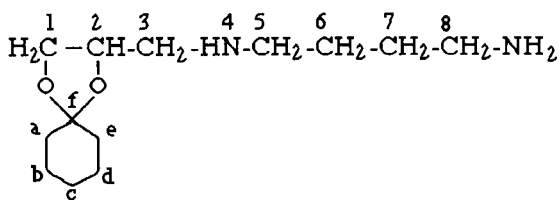


FIGURE 1 1,2-*O*-cyclohexylidene-4-aza-8-aminooctane (L)

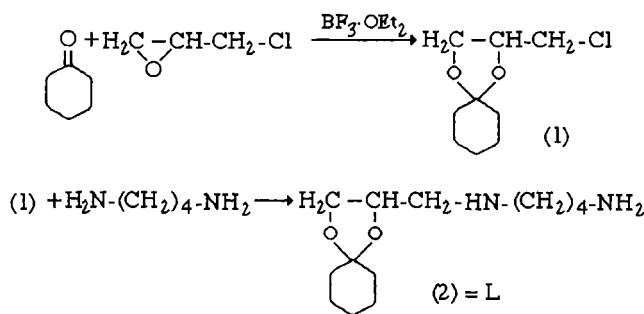


FIGURE 2 Syntheses Scheme for the Preparation of the Ligand

aza-8-aminooctane (2). The structure of L was determined by a combination of elemental analyses, IR, UV-vis,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy. The structural characterization data of (1) and (2) are given in the Experimental section.

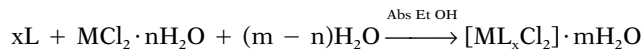
In the IR spectrum of (1) the most characteristic peaks are at  $1114\text{ cm}^{-1}$  (C–O–C) and  $745\text{ cm}^{-1}$  (C–Cl) [34], and the  $^1\text{H}$  NMR peaks are at 1.65, 3.44–3.57, 4.25, and 3.85–4.03 ppm. These are attributable to  $-\text{CH}_2-$  in the cyclo structure,  $-\text{O}-\text{CH}_2-$ ,  $-\text{O}-\text{CH}-$ , and  $-\text{CH}_2-\text{Cl}$ , respectively [16].

In the IR spectrum of (2), the characteristic peaks are at  $3336\text{--}3453\text{ cm}^{-1}$ , which are assigned to  $\nu(\text{N}-\text{H})$  and  $\nu(-\text{NH}_2)$  and  $1114\text{ cm}^{-1}$  that is assigned to the oxalane group. In the  $^1\text{H}$  NMR spectrum, there are two characteristic peaks, 1.30 and 3.56–3.80 ppm, which are attributable to the  $-\text{NH}-$ , and  $-\text{NH}_2$  groups (which were also identified by  $\text{D}_2\text{O}$  exchange) and  $-\text{O}-\text{CH}_2-$  groups, respectively. There is another  $-\text{O}-\text{CH}_2-$  peak at 3.46–3.39 ppm, which is assigned to one other isomer of ligand 2. Compound (2) has *cis-trans* isomerism; 3.46–3.39 ppm for the *cis*-isomer and 3.56–3.80 ppm for the *trans*-isomer. The isomers were found to be 51.81% *cis*-isomer and 48.19% *trans*-isomer [16,17] (the ratio of *cis-trans* isomers is about 1:1) from the  $^1\text{H}$  NMR data. In the spectrum, the  $-\text{CH}-\text{O}$  peak is at 4.10, and  $-\text{CH}_2-$  (in cyclo structure) peak at 1.55 ppm.  $-\text{CH}_2-\text{CH}_2-$  (aliph.) peaks are observed at 1.75–2.30 ppm. According to the elemental analyses IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR results,

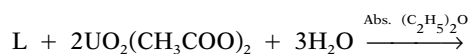
the structure of the ligand was determined to be as shown in Figure 1.

The ligand L, on reaction with Co(II), Ni(II), and Cu(II) salts yields complexes corresponding to the general formula  $[\text{CoL}_2\text{Cl}_2]\cdot\text{H}_2\text{O}$ ,  $[\text{NiL}_2\text{Cl}_2]$ , and  $[\text{CuLCl}_2]\cdot 0.5\text{H}_2\text{O}$ . For the uranyl complex, the composition  $[(\text{UO}_2)_2\text{L}(\text{OH})_2(\text{CH}_3\text{COO})_2]\cdot\text{H}_2\text{O}$  was found. The analytical data for all of the complexes are presented in Tables 1–5.

The complexes were prepared by the general reaction shown below.



M =	Ni(II),	Co(II),	Cu(II)	L =	$\text{C}_{13}\text{H}_{26}\text{N}_2\text{O}_2$
x =	–	2	–		
n =	5	–	–		
m =	–	1	–0.5		



The metal-to-ligand ratio of the Ni(II) and Cu(II) complexes was found to be 1:1; in addition there were present two chloride ligands. But the Cu(II) complex apparently has an additional half molecule of water of crystallization [18]. The metal-to-ligand ratio of the Co(II) complex was found to be 1:2, in addition to two chloride ligands, and the Co(II) complex has one additional molecule of water of crystallization [18]. The infrared band observed near  $3370\text{--}3240\text{ cm}^{-1}$ , which is assigned to the  $-\text{NH}-$ , and  $-\text{NH}_2$  frequency, is shifted to lower frequency after complexation with respect to the free ligand. The strong absorption at  $3370\text{--}3240\text{ cm}^{-1}$  in the ligand can be assigned to  $\nu(\text{NH}_2)$  of the intramolecularly hydrogen bonded [19] 1,4-diaminobutane moiety. The shift of the N–H vibration to lower frequencies ( $3255\text{--}3200\text{ cm}^{-1}$ ) is due to N,N-metal coordination [20,21]. At the same time, the band observed at  $1657\text{ cm}^{-1}$  in the free ligand assigned to the  $\nu(\text{NH}_2)$  is shifted to lower frequencies after forming the complexes [22]. This indicates that the amino group takes part in complexation. In the spectra of the complexes, a few new bands occur at lower regions which are attributed to the  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{Cl})$  vibrations, respectively [23–25].

The Co(II), Ni(II), and Cu(II) complexes are paramagnetic, and their magnetic susceptibility values are 4.99, 3.01, and 1.89 B.M., respectively. Analytical data for the complexes are given in the Tables 1–5. According to the aforementioned results, a tetrahedral geometry for the Ni(II) and Cu(II) complexes and a distorted octahedral high-spin geometry for the Co(II) is proposed [11–15,26]. The

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

Compounds	F.W (g/mole)	Yield (%)	m.p. (°C)	Elemental Analyses Calculated (Found) (%)			
				C	H	N	O
Ligand	242.00	46.00	—	64.46	10.75	11.57	13.22
C <sub>13</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> (Colorless)				(64.45)	(10.70)	(11.61)	(13.24)
[Co(L) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	631.93	73.00	117.0	49.37	8.55	8.86	12.66
C <sub>26</sub> H <sub>54</sub> N <sub>4</sub> O <sub>5</sub> Cl <sub>2</sub> Co (Brown)				(49.11)	(8.51)	(8.80)	(12.65)
NiCl <sub>2</sub>	371.69	66.00	102.0	41.97	7.00	7.53	8.61
C <sub>13</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> Ni (Dark Pale)				(42.25)	(7.25)	(7.62)	(8.60)
[Cu(LCl <sub>2</sub> )·0.5H <sub>2</sub> O]	385.50	70.00	90.3	40.46	7.00	7.26	10.37
C <sub>13</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4.5</sub> Cu (Dark Green)				(41.18)	(7.27)	(7.20)	(10.33)
[(UO <sub>2</sub> ) <sub>2</sub> (L)(OH) <sub>2</sub> - (CH <sub>3</sub> COO) <sub>2</sub> ]·H <sub>2</sub> O	932.04	45.00	262.0 (dec)	21.89 (22.20)	3.22 (3.00)	3.00 (3.17)	22.32 (22.30)
C <sub>17</sub> H <sub>30</sub> N <sub>2</sub> O <sub>13</sub> U <sub>2</sub> (Orange)							

**TABLE 2** Characteristic IR Bands (cm<sup>-1</sup>) of the Complexes in KBr Pellets

Compounds	O-H	N-H	C-H	C-O-C	M-N	Others
[Co(L) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	3650-3200 s	3234 m; 1651 s	3978-2876 s	1114 s	398 w	M-Cl 300 w
NiCl <sub>2</sub>	—	3255 m; 1625 m	2953-2876 s	1114 m	402 w	M-Cl 298 w
[Cu(LCl <sub>2</sub> )·0.5H <sub>2</sub> O]	3591-3250 s	3212 m 1651 m	2953-2876 s	1114 m	398 w	M-Cl 302 w
[(UO <sub>2</sub> ) <sub>2</sub> (L)-(OH) <sub>2</sub> - (CH <sub>3</sub> -COO) <sub>2</sub> ]·H <sub>2</sub> O	3458-3220 s; 1730 w	3200 s; 1600 m	2953-2876 s	1114 m	406 w	O=U=O (910) s, C=O (1548) s

**TABLE 3** DTA Data of the Complexes

Compounds	Exothermic Peaks, °C	Endothermic Peaks, °C
[Co(L) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	119.4, 451.2, 721.5, 805.0	420.0, 519.0, 679.0
NiCl <sub>2</sub>	319.6, 524.4	127.2, 144.0, 260.0, 435.0
[Cu(LCl <sub>2</sub> )·0.5H <sub>2</sub> O]	243.0, 371.0, 457.6, 593.0	99.9, 318.6, 430.2, 503.2
[(UO <sub>2</sub> ) <sub>2</sub> (L)(OH) <sub>2</sub> -(CH <sub>3</sub> COO) <sub>2</sub> ]·H <sub>2</sub> O	222.0, 352.3, 450.3, 515.2	103.0

**TABLE 4** TGA Data of the Complexes

Compounds	I. Step (°C) Weight Loss Calculated (Found), %	II. Step (°C) Weight Loss Calculated (Found), %	III. Step (°C) Weight Loss Calculated (Found), %	Weight Loss Calculated (Found) (%)	Residue Calculated (Found) (%)
[Co(L) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	27.7–133.0 2.84 (2.76)	133.0–402.1 49.06 (48.01)	402.1–949.9 38.77 (38.70)	90.67 (89.47)	CoO 9.33 (10.53)
NiCl <sub>2</sub>	118.0–305.0 41.70 (42.40)	305.0–708.6 42.50 (42.00)		84.20 (84.40)	NiO 15.80 (15.60)
[Cu(LCl <sub>2</sub> )·0.5H <sub>2</sub> O]	23.0–98.0 2.33 (2.30)	98.0–349.9 40.20 (39.44)	349.9–756.9 40.98 (39.12)	83.51 (80.86)	CuO 16.49 (19.14)
[(UO <sub>2</sub> ) <sub>2</sub> (L)-(OH) <sub>2</sub> (CH <sub>3</sub> -COO) <sub>2</sub> ]·H <sub>2</sub> O	25.8–97.0 1.93 (1.97)	97.0–231.0 16.63 (16.88)	231.0–610.5 25.64 (28.47)	44.20 (47.32)	U <sub>3</sub> O <sub>8</sub> 55.80 (52.68)

**TABLE 5** Characteristic UV-vis Bands of the Ligand and the Complexes in C<sub>2</sub>H<sub>5</sub>OH

Compound	Wavelength in nm( $\epsilon$ ) <sup>a</sup>			
Ligand				295 (26000) n → $\sigma^*$
[Co(L) <sub>2</sub> Cl <sub>2</sub> ] · H <sub>2</sub> O	630 (4100)	477 (4900)	435 (7600)	282 (23000) n → $\sigma^*$
NiLCl <sub>2</sub>	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F)	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	n → $\sigma^*$
	765 (7300)	620 (9500)	395 (8700)	287 (22300)
[CuLCl <sub>2</sub> ]0.5H <sub>2</sub> O	<sup>3</sup> T <sub>1</sub> ( <sup>3</sup> F) → <sup>3</sup> T <sub>2</sub> ( <sup>3</sup> F)	<sup>3</sup> T <sub>1</sub> ( <sup>3</sup> F) → <sup>3</sup> T <sub>1</sub> ( <sup>3</sup> P)	<sup>3</sup> T <sub>1</sub> ( <sup>3</sup> F) → <sup>3</sup> A <sub>2</sub> ( <sup>3</sup> F)	n → $\sigma^*$
	615 (10200)			293 (21100)
[(UO <sub>2</sub> ) <sub>2</sub> L(OH) <sub>2</sub> -(CH <sub>3</sub> COO) <sub>2</sub> ] · H <sub>2</sub> O	<sup>2</sup> T <sub>2</sub> → <sup>2</sup> E			n → $\sigma^*$
	Charge transfer	Charge transfer		302 (25000)
	L → UO <sub>2</sub>	UO <sub>2</sub> → L		n → $\sigma^*$
	415–440 (3200)	340–350 (9100)		

<sup>a</sup> $\epsilon$  = molar extinction coefficient (L mol<sup>-1</sup> cm<sup>-1</sup>).

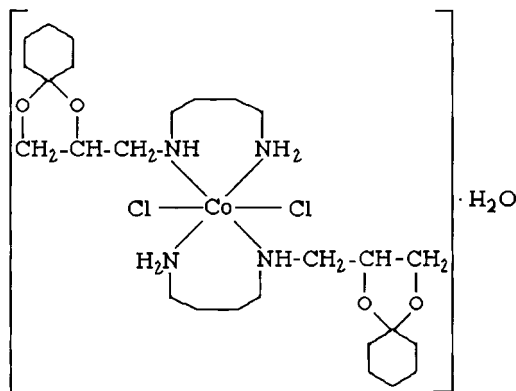
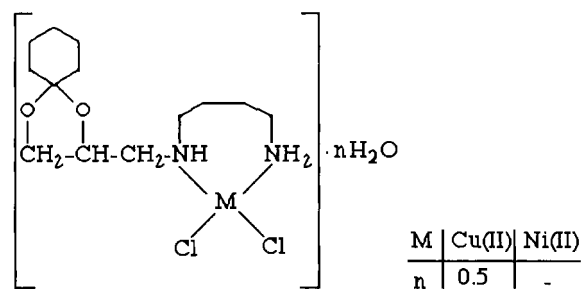
suggested structures of the complexes are shown in Figure 3 and Figure 4. Since all the metal complexes are paramagnetic, their <sup>1</sup>H NMR spectra could not be obtained.

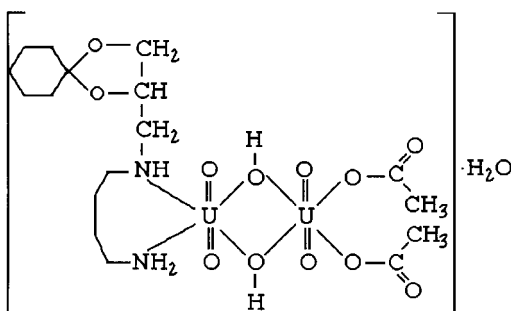
The electronic spectra of the complexes contain intense n →  $\sigma^*$  bands around 283–310 nm, absorptions due to the ligand, and weak d-d transitions for the Co(II), Ni(II), and Cu(II) complexes at 630, 477, 435; 765, 620, 395; and 615 nm, respectively.

The uranyl complex exhibits a different structure. In the IR spectra [27,28], the UO<sub>2</sub>(VI) complex shows a band at 905 cm<sup>-1</sup>, which is assigned to  $\nu$ (O=U=O), and there is an N–H (3200; 1600 cm<sup>-1</sup>) band. The band observed at 910 cm<sup>-1</sup> is characteristic for  $\nu$ (O=U=O) stretches, and the N–H stretching vibration of the amino group still appears as a broad band because of hydrogen bonding. Two oxygens in the uranyl ion are axial and two  $\mu$ -hydroxo bridges are equatorial [20]. The acetate carbonyl of the uranyl complex was shifted to the lower energy side (1548 cm<sup>-1</sup>) because the C=O bond electrons are strongly attracted by the uranyl group [22]

whereas  $\nu$ (CO) of acetic acid is seen at 1720 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of the uranyl complex shows three resonances for the deuterium-exchangeable -NH-, and -NH<sub>2</sub> protons (6.83 ppm) and  $\mu$ -hydroxo bridge protons (7.61 and 7.68 ppm [27,30]). The  $\mu$ -hydroxo bridge protons of the uranyl complex are shifted to the low-field side (7.61 and 7.68 ppm) because the O–H bond electrons are strongly attracted by the uranyl group. In the <sup>1</sup>H NMR spectra of the UO<sub>2</sub>(VI) complex, the bands at 7.61 and 7.68 ppm are assigned to a  $\mu$ -hydroxo bridge in a nonplanar structure. At the same time, this complex is diamagnetic. The UO<sub>2</sub>(VI) complex has a broad charge transfer band between 340–350 ( $\epsilon$  = 9100) and 415–440 nm ( $\epsilon$  = 3200). There are not any processes 5f → 5f or 5f → 6d because UO<sub>2</sub>(VI) has a 5f<sup>0</sup> 6d<sup>0</sup> 7s<sup>0</sup> electronic configuration [20]. A suggested structure of the complex is shown in Figure 5.

The complexes are nonelectrolytes as shown by their molar conductivity ( $\Lambda_M$ ) measurements in absolute ethanol, which are in the range [32] 6 of 12  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

**FIGURE 3** Suggested Structure of the Distorted Octahedral Co(II) Complexes of the Ligand L**FIGURE 4** Suggested Structure of the Tetrahedral Cu(II) and Ni(II) Complexes of the Ligand L



**FIGURE 5** Suggested Structure of the Uranyl Complex of the Ligand L

### EXPERIMENTAL

Reagent grade chemicals were used. Cyclohexanone and epichlorohydrin were purchased from Merck (Pure) and used without further purification. 1,2-*O*-Cyclohexylidene-4-aza-8-aminoctane was synthesized as described in the literature [16].

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,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz high performance digital FT-NMR spectrometer or a JEOL FX 90Q FT-NMR spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (20°C) using  $\text{Hg}[\text{Co}(\text{SCN})_2]$  as a calibrant; diamagnetic corrections were calculated from Pascal's constants [33]. The refractive indices of the substances were determined on a Bellingam + Stanley Ltd. 60/70 Abbe (calibration oil RI = 1.47577 at 20°C) refractometer. Thermogravimetric (TGA) and differential thermal analyses (DTA) curves were recorded on a Shimadzu TG-50 thermobalance. Electronic spectra were recorded on a Secomam S 1000 spectrometer. Molar conductances were measured on a CMD 750 WPA conductometer (1.10 $^{-3}$  M in absolute ethanol).

#### *Synthesis of 1-Chloro-2,3-O-Cyclohexylidene propane (1)*

Boron trifluoride etherate (15–20 drops) was added dropwise to 98 g (1000 mmol) of cyclohexanone. Then 23 g (250 mmol) 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. The product was distilled at 108–110°C at 13 mmHg. Yield 15.2 g (80%); relative density of the product was found to be 1.1484, using a pycnometer  $n_D^{20} = 1.4772$ . Char-

acteristic IR bands (NaCl cell,  $\text{cm}^{-1}$ ): 2953–2876 (aliph, C-H), 1114 (-C-O-), 745 (C-Cl), Characteristic  $^1\text{H}$  NMR bands ( $\text{CCl}_4$ , TMS,  $\delta$  ppm): 1.65 (10H, m, cyclo- $-\text{CH}_2-$ ), 3.44–3.57 (2H, m,  $-\text{O}-\text{CH}_2-$ ), 3.85–4.03 (2H, m,  $-\text{CH}_2-\text{Cl}$ ), 4.25 (1H, m,  $-\text{CH}-\text{O}$ ). Characteristic  $^{13}\text{C}$  NMR bands ( $\text{CDCl}_3$ , TMS,  $\delta$  ppm):  $\text{C}_a$  (35.60),  $\text{C}_b$  (24.48),  $\text{C}_c$  (25.90),  $\text{C}_d$  (25.00),  $\text{C}_e$  (37.20),  $\text{C}_f$  (110.00),  $\text{C}_1$  (67.80),  $\text{C}_2$  (75.00),  $\text{C}_3$  (45.30). The product is soluble in common solvents such as chloroform, benzene, water xylene, or ethanol.

#### *Synthesis of 1,2-O-Cyclohexylidene-4-aza-8-aminoctane (2)*

13.3 g (151 mmole) of 1,4-diamino butane, 7.49 g (75 mmole) of triethylamine and 50 mL of absolute xylene were mixed in a reaction vessel and stirred at room temperature. To this solution, a solution of 14.5 g (75 mmole) of (1) in 50 mL absolute xylene was added dropwise. The mixture was refluxed for 35 hours with continuous stirring. After cooling to room temperature, the mixture was filtered. The filtrate was distilled at 158–163°C at 5 mmHg. Yield 8.5 g (46 %); relative density of the product was found to be 1.0430 using a pycnometer,  $n_D^{20} = 1.4827$ . Characteristic IR bands (NaCl cell,  $\text{cm}^{-1}$ ): 3370–3240; 1657 (-NH-, and  $-\text{NH}_2$ ), 2953–2876 (aliph. C-H), 1114 (-C-O-C-), Characteristic  $^1\text{H}$  NMR bands ( $\text{CDCl}_3$ , TMS,  $\delta$  ppm): 1.30 (3H, as broadband, exchangeable with  $\text{D}_2\text{O}$ , -NH- and  $-\text{NH}_2$ ), 1.55 (cyclo- $-\text{CH}_2$ , 10H, as broadband), 1.75–2.30 ( $-\text{CH}_2-\text{CH}_2-$ , 4H, as broadband), 2.50–2.75 (N- $-\text{CH}_2-$ , 6H, m), 3.56–3.80 and 3.39–3.46 (O- $-\text{CH}_2-$ , 2H, as broadband), 4.10 ( $-\text{CH}-\text{O}$ , 1H, as broadband). Characteristic  $^{13}\text{C}$  NMR bands ( $\text{CDCl}_3$ , TMS,  $\delta$  ppm):  $\text{C}_a$  (35.37),  $\text{C}_b$  (23.81),  $\text{C}_c$  (24.80),  $\text{C}_d$  (24.10),  $\text{C}_e$  (37.10),  $\text{C}_f$  (110.13),  $\text{C}_1$  (67.08),  $\text{C}_2$  (75.10),  $\text{C}_3$  (53.20),  $\text{C}_5$  (50.00),  $\text{C}_6$  (31.03),  $\text{C}_7$  (25.39),  $\text{C}_8$  (42.30). The product is soluble in common solvents such as chloroform, benzene, water xylene, or ethanol.

#### *Synthesis of the Co(II), Cu(II), Ni(II), and UO<sub>2</sub>(VI) Complexes*

The ligand (0.242 g, 1.0 mmole) was dissolved in 10 mL of absolute ethanol in a 50 mL round-bottom flask. A solution of 1.0 mmole of metal salt [ $\text{NiCl}_2 \cdot 5\text{H}_2\text{O}$  (0.2196 g) and  $\text{CuCl}_2$  (0.1344 g)] in 5 mL of absolute ethanol was added dropwise in a 15 minute period with continuous stirring at room temperature. The ligand 2 (0.242 g, 1.0 mmole) was dissolved in 10 mL absolute ethanol in a 50 mL round bottom flask. A solution of 0.5 mmole of the metal salt  $\text{CoCl}_2$  (0.0648 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 24 hours at room 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 the complexes were found to be 0.23 g (73%) for Co(II), 0.25 g (66%) for Ni(II), and 0.26 g (70%) for Cu(II).

For the UO<sub>2</sub> complex, a quantity of 0.121 g (0.5 mmole) of the ligand **2** was dissolved in 15 mL of absolute ether in a 50 mL round-bottom flask. A solution of 1.0 mmole of UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> (0.3880 g) in 10 mL of absolute ether was added dropwise in a 15 minute period with continuous stirring at room temperature. The reaction mixture was then further stirred for 24 hours at room temperature. The yellow precipitate was filtered off and washed with absolute ether. The product was dissolved in chloroform and precipitated by addition of *n*-hexane (1/5). The resulting crystals were filtered off and dried at room temperature. The yield of the complex was 0.21 g (45%). Characteristic <sup>1</sup>H NMR resonances (CDCl<sub>3</sub>, TMS, δ ppm): 7.61 and 7.68 (2H, s, exchangeable with D<sub>2</sub>O, μ-hydroxo bridge), 6.83 (3H, s, exchangeable with D<sub>2</sub>O, -NH- and -NH<sub>2</sub>), 4.17 (1H, m, -CH-O-), 4.07 (2H, m, -O-CH<sub>2</sub>-O-), 2.68 (6H, m, -NCH<sub>2</sub>), 3.27 (2H, br, exchangeable with D<sub>2</sub>O, H<sub>2</sub>O), 1.67 (10H, br, cyclo -CH<sub>2</sub>-), 1.63 (4H, br, aliph. -CH<sub>2</sub>-CH<sub>2</sub>-), 1.17 (6H, s, CH<sub>3</sub>COO<sup>-</sup>). This complex is soluble in chloroform, dimethylsulphoxide, dichloromethane, ethanol, and water.

### Thermal Studies

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°C/min in a nitrogen atmosphere over the temperature range of 23.0–949.9°C.

The Ni(II) complex is stable up to 118.0°C and its decomposition starts at 118.0°C and is completed at 708.6°C. The Ni(II) complex decomposes to a NiO (residue: 15.60%) in two steps in the temperature ranges 118.0–305.0°C and 305.0–708.6°C. In the decomposition process of the Ni(II) complex, the mass losses correspond to the 2,3-*O*-cyclohexylidene group and the other organic moieties for the first and second stage decompositions, respectively. The two stages of decomposition of the Ni(II) complex are irreversible.

The Cu(II) complex is stable up to 23.0°C and its decomposition starts at 23.0°C and is completed at 756.9°C. The Cu(II) complex decomposes to a CuO (residue: 19.14%) in three steps in the temperature ranges 23.0–98.0°C, 98.0–349.9°C and 349.9–756.9°C. In the decomposition process of the Cu(II) complex,

the mass losses correspond to the water of the hemihydrate, the 2,3-*O*-cyclohexylidene group and the other organic moieties for the first, second, and third stage decompositions, respectively. The three stages of decomposition of the Cu(II) complex are irreversible.

The Co(II) complex is stable up to 27.7°C, the point at which dehydration begins, and its decomposition starts at 27.7°C and is completed at 949.9°C. The Co(II) complex decomposes to a CoO (residue: 10.53%) in three steps in the temperature ranges 27.7–133.0°C, 133.0–402.1°C, and 402.1–949.9°C. In the decomposition process of the Co(II) complex, the mass losses correspond to one water molecule, the 2,3-*O*-cyclohexylidene group and the other organic moieties for the first, second and third stage decompositions, respectively. The three stages of decomposition of the Co(II) complex are irreversible.

The UO<sub>2</sub>(VI) complex is stable up to 25.8°C, the point at which dehydration begins, and its decomposition starts at 25.8°C and is completed at 610.5°C. The UO<sub>2</sub>(VI) complex decomposes to a U<sub>3</sub>O<sub>8</sub> (residue: 52.68 %) in three steps in the temperature ranges 25.8–97.0°C, 97.0–231.0°C and 231.0–610.5°C. In the decomposition process of the UO<sub>2</sub> complex, the mass losses correspond to one water molecule, the 2,3-*O*-cyclohexylidene group, and the other organic moieties for the first, second, and third stage decompositions, respectively. The three stages of decomposition of the UO<sub>2</sub>(VI) complex are irreversible. The DTA data show that all of the complexes have exothermic and endothermic peaks (Table 3).

The nickel complex is thermally stable up to 118.0°C, whereas the [(UO<sub>2</sub>)<sub>2</sub>(L)(OH)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>]·H<sub>2</sub>O, [Co(L)<sub>2</sub>Cl<sub>2</sub>]·H<sub>2</sub>O and [CuLCl<sub>2</sub>]·0.5H<sub>2</sub>O complexes are thermally stable up to 25.8°C, 27.7°C, and 23.0°C, respectively. In the TGA curve of the [Co(L)<sub>2</sub>Cl<sub>2</sub>]·H<sub>2</sub>O complex, 2.76% weight loss was observed at 133.0°C. In the TGA curve of the [(UO<sub>2</sub>)<sub>2</sub>(L)(OH)<sub>2</sub>-(CH<sub>3</sub>COO)<sub>2</sub>]·H<sub>2</sub>O complex, 1.97% weight loss was observed at 97.0°C. In the TGA curve of the [CuLCl<sub>2</sub>]·0.5H<sub>2</sub>O complex, 2.30% weight loss was observed at 98.0°C. This shows that the complexes contain 1, 1, and 0.5 mole of water of crystallization per complex molecule, respectively. The IR spectra of the complexes are characterized by the appearance of a broad band in the region 3200–3591 cm<sup>-1</sup> due to the ν(O–H) frequency of water of crystallization [34]. This water content was also identified by the elemental analyses. As can be seen in Table 4, the most stable complex is that of NiLCl<sub>2</sub>. 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

in Table 1. All these complexes undergo complete decomposition to the corresponding metal oxides, CuO, NiO, CoO or U<sub>3</sub>O<sub>8</sub> [35–37].

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