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THE SYNTHESIS AND Co(II), Ni(II), Cu(II) AND UO_2(VI) COMPLEXES OF 1,2-O-BENZAL-4-AZA-7-AMINOHEPTANE

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ABSTRACT

1,2-O-Benzal-4-aza-7-aminoheptane (L) has been synthesized starting from 1-chloro-2,3-O-benzalpropane, which has been prepared from the reaction of epichlorohydrin and benzaldehyde. The complexes of this ligand with Co(II), Ni(II), Cu(II) and UO_2(VI) salts were prepared. The structures of the ligand and its complexes are proposed based on elemental analyses, IR, UV-VIS, ^1H and ^{13}C NMR spectra, magnetic susceptibility measurements, thermogravimetric analyses (TGA) and differential thermal analyses (DTA).

INTRODUCTION

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 behaviour[1,2].

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

Amines and their derivatives (monodentate, bidentate...) have been known to produce stable complexes with transition metals[3,4,5,6]. A lot of 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 $[CrF(H_2O)(diamines)_2]X_2$ or $[CrF(X)(diamines)_2]X$ (X = Cl, Br, I or SCN). 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_2, ML_2X_2 and ML_3X_2 (M = Zn(II), Cu(II), Ni(II) and Co(II); X = Cl, Br, I, ClO_4, NO_3, HSO_3, HSO_4)

In the present paper, as a part of our study to determine the coordination and semiconductor properties of various diamines which are attached to oxolane groups towards transition metal ions, we have synthesized four new complexes of 1,2-O-benzal-4-aza-7-aminoheptane (L) (Fig. 1.) with Co(II), Ni(II), Cu(II), and UO_2(VI). As far as we know, this is the first report on this ligand.

RESULTS AND DISCUSSION

1,2-O-Benzal-4-aza-7-aminoheptane (L) was prepared in a two-stage process as shown in Fig. 2. The first step is the synthesis of 1-chloro-2,3-O-benzalpropane (1) from of benzaldehyde and epichlorohydrin. In this reaction $BF_3 \cdot OEt_2$ was used as catalyst. In the second step, 1-chloro-2,3-O-benzalpropane and 1,3-diaminopropane were reacted to obtain 1,2-O-benzal-4-aza-7-aminoheptane (L). The structure of L was determined by a combination of elemental analyses, IR, UV-VIS, ^1H and ^{13}C NMR spectroscopy. The structural charaterization data of (1) and (L) are given in the experimental section.

In the IR spectrum of (1) the characteristic peaks are at 1114 cm^{-1} υ(C-O-C) and 745 cm^{-1} υ(C-Cl)[34]. Characteristic ^1H and ^{13}C NMR peaks are given in the experimental section.

In the IR spectrum of L, the characteristic peaks are at 3361-3285 cm^{-1} which are assigned to υ(NH) and $\upsilon(NH_2)$ and at 1114 cm^{-1} which is assigned to the υ(C-O-C) group. There is no C-Cl band in the IR spectrum of L. In the ^1H NMR spectra of L, peaks appear at 2.4-3.2 ppm for ($-N-CH_2$) and at 1.75 ppm for

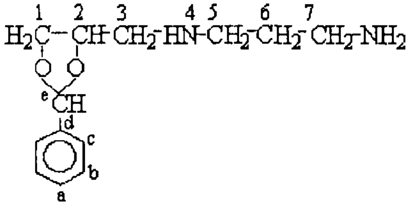


Fig. 1. 1,2-O-Benzal-4-aza-7-aminoheptane (L)

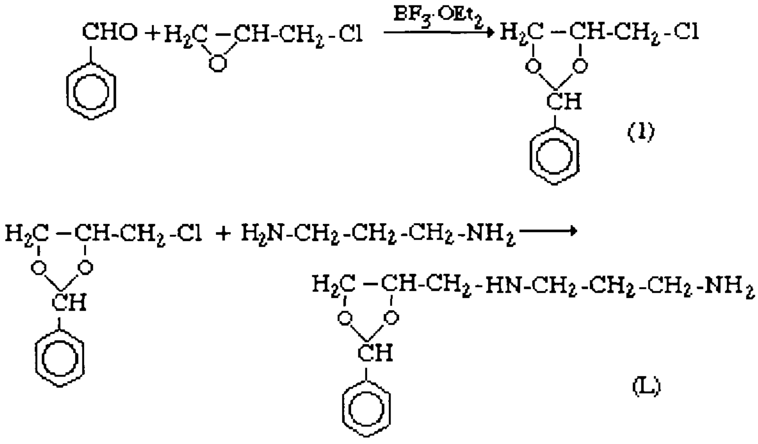


Fig. 2. Syntheses Scheme for the Preparation of the Ligand

-NH-, and -NH$_2$ as broad peak. These peaks for -NH-, and -NH$_2$ disappeared on addition of D_2O[34]. On the other hand, in the ^1H NMR spectra of L, peaks appear at 5.60 and 5.75 ppm for 1H and Ph-CH< as two singlet peaks and in the ^{13}C NMR spectrum of L each carbon atom, namely C_b, C_c, C_d, C_e, C_1 and C_2 (Fig. 1) has double resonances, (131.78 and 132.00), (129.44 and 129.73), (134.70 and 135.30), (107.18 and 108.06), (75.09 and 74.97), and (82.50 and 82.08) ppm, respectively, which indicates that the compound L exists as a mixture of cis-trans isomers[35,36]. The isomer ratios were found to be 56 % cis-isomer and 44 % trans-isomer from the ^1H NMR and ^{13}C NMR data. This is consistent with cis-trans isomers of the oxolane ring of the molecule L. According to the elemental analyses IR, ^1H NMR and ^{13}C NMR results, the structure of the ligand was determined to be as shown Fig. 1.

The ligand L, on interactions with Co(II), Ni(II) and Cu(II) salts yields complexes corresponding to the general formula ML_2Cl_2, in the case of Co(II), $[ML_2Cl_2]\cdot 2H_2O$. For the uranyl complex the composition $[(UO_2)_2L(OH)_2$-$CH_3COO)_2]\cdot H_2O$ was found. The analytical data for all of the complexes are presented in Tables I-V.

The complexes were prepared by the general reactions shown below.

$$2L + MCl_2\cdot nH_2O + (m-n)H_2O \xrightarrow{\text{Abs. EtOH}} [ML_2Cl_2]\cdot mH_2O$$

$$\begin{array}{llll} M = \text{Ni(II)}, & \text{Co(II)}, & \text{Cu(II)} & \qquad L = C_{12}H_{18}N_2O_2 \\ n = \ 5 & 0 & 0 & \\ m = \ 0 & 2 & 0 & \end{array}$$

$$L + 2UO_2(CH_3COO)_2 + 3H_2O \xrightarrow{\text{Abs.}(C_2H_5)_2O}$$
$$[(UO_2)_2(L)(OH)_2(CH_3COO)_2]\cdot H_2O + 2CH_3COOH$$

The metal to ligand ratio of the Co(II), Ni(II) and Cu(II) complexes was found to be 1:2, in addition there were present two chloride ligands. But the Co(II) complex has two additional molecules of water of crystallization[16]. The infrared band observed near 3361-3285 cm^{-1} which is assigned to the -NH-, and $-NH_2$ frequency is shifted to lower frequency after complexation with respect to the free ligand. The strong absorption at 3361-3285 cm^{-1} in the ligand can be assigned to $\upsilon(NH_2)$ of the intramolecularly hydrogen bonded[17] 1,3-diaminopropane moiety. The shift of the N-H vibration to lower frequencies (3234-3106 cm^{-1}) is due to N,N-metal coordination[18,19]. At the same time, the band observed at 1641 cm^{-1} in the free ligand assigned to $\upsilon(NH_2)$ is shifted to lower frequencies after forming the complexes[20]. This indicates 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 4.97, 2.79, 1.80 B.M. respectively. Analytical data for the complexes are given in the Tables I-V. According to the above results, a distorted octahedral high-spin geometry for the Co(II), Ni(II) and Cu(II)

Table I. 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 $C_{12}H_{18}N_2O_2$ (Colorless)	236.00	76.00	-	66.10 (66.09)	8.47 (8.49)	11.86 (11.85)	13.56 (13.54)
$[Co(L)_2Cl_2]\cdot H_2O$ $C_{26}H_{44}N_4O_6Cl_2Co$ (Brown)	634.93	72.83	88	49.14 (49.11)	6.93 (6.91)	8.82 (8.80)	15.12 (15.14)
$Ni(L)_2Cl_2$ $C_{26}H_{40}N_4O_4Ni$ (Bottle-Green)	601.71	39.88	105	51.85 (51.83)	6.65 (6.63)	9.31 (9.35)	10.64 (10.69)
$Cu(L)_2Cl_2$ $C_{26}H_{40}N_4O_4Cu$ (Violet)	606.65	85.75	150	51.44 (51.45)	5.59 (5.60)	9.23 (9.20)	10.55 (10.53)
$[(UO_2)_2(L)(OH)_2$- $(CH_3COO)_2]\cdot H_2O$ $C_{13}H_{30}N_2O_{13}U_2$ (Orange)	946.06	80.37	250 (dec)	19.03 (19.00)	3.17 (3.07)	2.96 (2.89)	21.99 (21.93)

Table II. Characteristic IR Bands (cm^{-1}) of the Complexes in KBr Pellets.

Compounds	O-H	N-H	Arom.C-H	Aliph. C-H	C-O-C	Others
$[Co(L)_2Cl_2]$-$\cdot 2H_2O$	3412-3227 s	3222 s, 3157 s; 1625 m	3080-3055 m; 1700-2000 w; 782-706 s	2953-2876 s	1089 s	-
$Ni(L)_2Cl_2$	-	3234 s, 3157 s; 1625 m	3055 m; 782-706 s	2953-2876 s	1089 s	-
$Cu(L)_2Cl_2$	-	3208 s, 3106 s; 1625 m	3080-3055 m; 782-706 s	2953-2876 m	1089 s	-
$[(UO_2)_2(L)$-$(OH)_2(CH_3$-$COO)_2]\cdot H_2O$	3464-3225 s; 1730 w	3200 s; 1600 m	3100 s; 782 m	2978 s	1114 m	O=U=O (910) s, C=O (1548) s

Table III. DTA Data of the Complexes.

Compounds	Exothermic Peaks, ° C	Endothermic Peaks, ° C
$[Co(L)_2Cl_2]\cdot 2H_2O$	159.6, 405.0, 491.1, 557.7 590.7	324.0, 445.0
$Ni(L)_2Cl_2$	120.0, 209.2, 449.0, 525.0, 593.0	160.2, 502.0
$Cu(L)_2Cl_2$	162.5,328.2, 426.8, 599.9, 630.0	164.3, 520.0
$[(UO_2)_2(L)(OH)_2$-$(CH_3COO)_2]\cdot H_2O$	302.0, 339.3, 422.0, 456.1, 510.0	-

Table IV. TGA Data of the Complexes.

Compounds	First Step, ° C	Second Step, ° C	Weight Loss Found, %
$[Co(L)_2Cl_2]\cdot 2H_2O$	105.3-497.3	497.3-631.5	89.87
$Ni(L)_2Cl_2$	121.0-472.2	472.2-606.8	87.61
$Cu(L)_2Cl_2$	152.0-470.0	470.0-654.5	86.61
$[(UO_2)_2(L)(OH)_2\text{-}(CH_3COO)_2]\cdot H_2O$	100.0-425.7	425.7-495.7	40.21

Table V. Characteristic UV-Vis Bands of the Ligand and the Complexes in C_2H_5OH

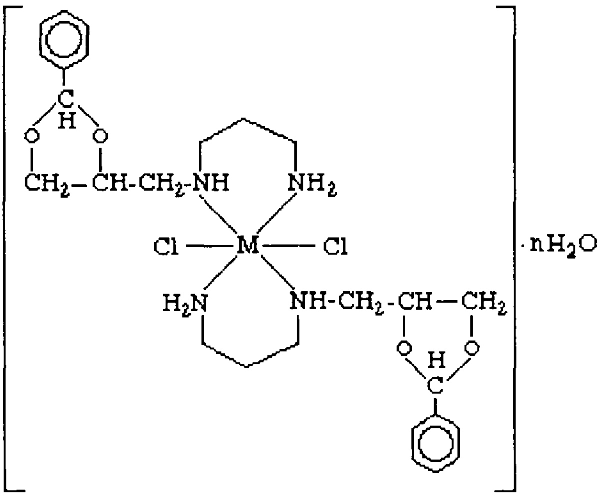
Compound	Wave Length in nm (ε)		
Ligand	-	-	290 (24000) $n\rightarrow\sigma^*$
$[Co(L)_2Cl_2]\cdot 2H_2O$	640 (4000) $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$	480 (5300) $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$	287 (22500) $n\rightarrow\sigma^*$
$Ni(L)_2Cl_2$	605 (1400) $^3A_{2g}\rightarrow{}^3T_{1g}(F)$	475 (2300) $^3A_{2g}\rightarrow{}^3T_{1g}(P)$	290 (22300) $n\rightarrow\sigma^*$
$Cu(L)_2Cl_2$	610 (6000) $^2E_g\rightarrow{}^2T_{2g}$	-	295 (21100) $n\rightarrow\sigma^*$
$[(UO_2)_2L(OH)_2\text{-}(CH_3COO)_2]\cdot H_2O$	Charge transfer $L\rightarrow UO_2$ 425-450 (3500)	Charge transfer $UO_2\rightarrow L$ 330-345 (7300)	300 (25000) $n\rightarrow\sigma^*$

ε = molar extinction coefficient (L mol^{-1} cm^{-1})

complexes is proposed[21,22]. The suggested structures of the complexes are shown in Fig. 3. Since all the metal complexes are paramagnetic, their ^1H NMR spectra could not be obtained.

The electronic spectra of the complexes contain intense $n\rightarrow\sigma^*$ bands around 287-300 nm, absorptions due to the ligand, and weak d-d transitions for the Co(II), Ni(II), and Cu(II) complexes at 640, 480; 605, 475; and 610 nm, respectively.

The uranyl complex exhibits a different structure. In the IR spectra[22,23], the $UO_2(VI)$ complex shows a band at 910 cm^{-1} which is assigned to $\upsilon(O{=}U{=}O)$ and there is a N-H (3200; 1600 cm^{-1}) band. The band observed at 910 cm^{-1} is



M	Cu(II)	Ni(II)	Co(II)
n	-	-	2

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

characteristic for υ(O=U=O) stretches and the N-H stretching vibration of the amino group still appear as a broad band because of hydrogen bonding. Two oxygens in the uranyl ion are axial and two μ–hydroxo bridges are equatorial[18]. The acetate carbonyl of the uranyl complex shifted to the lower energy side (1548 cm^{-1}) because the C=O bond electrons are strongly attracted by the uranyl group[20]. Whereas υ(C=O) of acetic acid is seen at 1720 cm^{-1}. The ^{1}H NMR spectrum of the uranyl complex shows three resonances for the deuterium-exchangeable N-H protons (6.95 ppm) and μ–hydroxo bridge protons (7.50 and 7.70 ppm)[24,25]. The μ–hydroxo bridge protons of the uranyl complex last shifted to the low-field side (7.50 and 7.70 ppm) because the O-H bond electrons are strongly attracted by the uranyl group. In the ^{1}H NMR spectra of the UO_2(VI) complex, the bands at 7.50 and 7.70 ppm are assigned to a μ–hydroxo bridge in a non-planar structure. At the same time, this complex is diamagnetic. The UO_2(VI) complex has a broad charge transfer band between 330-345 (ε = 7300) and

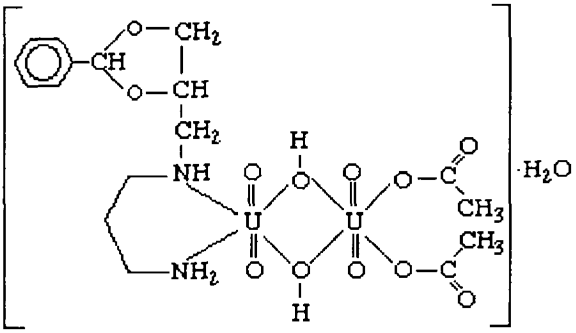


Fig. 4. Suggested Structure of the Uranyl Complex of the Ligand L

425-450 nm (ε = 3500)[24,26]. There are not any processes 5f→5f or 5f→6d because UO_2(VI) has a $5f^0$ $6d^0$ $7s^0$ electronic configuration[18]. A suggested structure of the complex is shown in Fig. 4.

The complexes are non-electrolytes as shown by their molar conductivity (Λ_M) measurements in absolute ethanol, which are in the range[27] 4-6 Ω^{-1} cm^2 mol^{-1}.

EXPERIMENTAL

Reagent grade chemicals were used. Benzaldehyde and epichlorohydrin were purchased from Merck (Pure) and used without further purification. 1,2-O-Benzal-4-aza-7-aminoheptane was synthesized as described in the literature[33].

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}C and ^1H 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 $Hg[Co(SCN)_2]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants.[28] 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-benzalpropane (1)

In a three-necked flask with a thermometer, a $CaCl_2$ drying tube and a dropping funnel, 106.0 g (1.0 mole) benzaldehyde and 15-20 drops of boron trifluoride ethyl ether complex were mixed. This mixture was cooled to 10 to 15° C. While maintaining 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 under nitrogen atmosphere. The product obtained distilled 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^{-1} υ(Ph-C-H), 1700-2000, and 706-782 cm^{-1} υ(arom. mono substitution), 2978-2876 cm^{-1} υ(aliph. C-H), 1114 cm^{-1} υ(C-O-C), 745 cm^{-1} υ(C-Cl). Characteristic ^1H NMR signals (CCl_4, TMS, δ 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, $-O-CH_2-$), 3.50 (2H, t, J = 6.24 Hz, $-CH_2-Cl$) Characteristic ^{13}C NMR resonances (CCl_4, TMS, δ ppm): C_a (128.66), C_b (126.20 and 126.50), C_c (129.27 and 129.58), C_d (138.20 and 138.51), C_e (104.65 and 105.87), C_1 (69.56 and 70.18), C_2 (76.64 and 76.95), C_3 (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 1,2-O-Benzal-4-aza-7-aminoheptane (2)

In a reaction flask containing a thermometer, a $CaCl_2$ drying tube and a dropping funnel, 29.6 mL (350 mmole) of 1,3-diaminopropane, 10.0 mL (72 mmole) of triethylamine and 60 mL absolute xylene were mixed and heated at 90° C for 15 min. To this solution, a solution of 14.3 g (72 mmole) of 1-chloro-2,3-O-benzalpropane in 50 mL xylene was added dropwise in a 30 min period with continuous strirring. After this, the mixture was further refluxed for 38 h and cooled down to room temperature under nitrogen atmosphere. The precipitated triethylammonium salt was filtered and the filtrate was evaporated to remove the excess 1,3-diaminopropane. The compound was distilled at 140-145° C at 2 mm Hg. Yield: 13.0 g (76 %), $d_4^{20} = 1.0837$, $n_D^{20} = 1.5398$. Characteristic IR bands (NaCl cell, cm^{-1}): 3285-3361; 1641 cm^{-1} υ(-NH, and $-NH_2$), 3055-3080 cm^{-1} υ(arom. C-H), 1700-2000 and 706-782 cm^{-1} υ(arom. mono substituted), 2953-2876 cm^{-1} υ(aliph. C-H), 1114 cm^{-1} υ(C-O-C). Characteristic ^1H NMR peaks ($CDCl_3$, TMS, δ ppm): 7.42 (5H, m, aromatic), 5.60 (56 % cis-isomer) and 5.75 (44 % trans-isomer) (1H, as two singlet peaks, Ph-CH<), 4.00-4.50 (1H, m, -O-CH-), 3.7-4.1 (2H, m, $-O-CH_2-$), 2.4-3.2 (6H, m, $-N-CH_2-$), 2.08 (2H, m, $-CH_2-$), 1.75 (3H, s, exchangeable, -NH and $-NH_2$). Characteristic ^{13}C NMR bands ($CDCl_3$, TMS, δ ppm): C_a (131.20), C_b (131.78 and 132.0), C_c (129.44 and 129.73), C_d (134.7 and 135.3), C_e (107.18 and 108.06), C_1 (75.09 and 74.97), C_2 (82.50 and 82.08), C_3 (54.17), C_5 (59.15), C_6 (40.01), C_7 (58.57). 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_2(VI) Complexes

The ligand (0.236 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 metal salt [$CoCl_2$ (0.0648 g), $NiCl_2 \cdot 5H_2O$ (0.1098 g) and $CuCl_2$ (0.0672 g)] in 5 mL absolute ethanol was added dropwise in a 15 min period with continuous stirring at room temperature. The reaction mixtures were then further stirred for 24 h at room temperature. The resulting precipitates were filtered and washed with absolute ether. The products were dissolved in chloroform and precipitated with n-hexane (1/5). The resulting crystals were filtered and were dried at room temperature. Yields of the complexes were found to be 0.23 g (72.83 %) for Co(II), 0.12 g (39.88 %) for Ni(II) and 0.26 g (85.75 %) for Cu(II).

For the UO_2 complex a quantity of 0.236 g (1.0 mmole) of the ligand was dissolved in 15 mL absolute ether in a 50 mL round bottom flask. A solution of 0.5 mmole (0.1940 g) of $UO_2(CH_3COO)_2$ in 10 mL absolute ether was added dropwise in a 15 min period with continuous stirring at room temperature. The reaction mixture was then further stirred for 24 h at room temperature. The yellow precipitate was filtered and washed with absolute ether. The product was dissolved in chloroform and precipitated with n-hexane (1/5). The resulting crystals were filtered and dried at room temperature. Yield of the complex 0.19 g (80.37 %). Characteristic ^{1}H NMR resonances ($CDCl_3$, TMS, δ ppm): 7.50 and 7.70 (2H, s, exchangeable with D_2O, μ–hydroxo bridge), 7.45 (5H, m, aromatic), 6.95 (3H, s, exchangeable with D_2O, -NH- and $-NH_2$), 5.86 (1H, s, Ph-CH<), 4.22 (1H, m, -O-CH-), 4.10 (2H, m, $-O-CH_2-$), 3.30 (6H, m, $-NCH_2$), 3.20 (2H, br, exchangeable with D_2O, H_2O), 1.60 (2H, m, $-CH_2-$), 1.20 (6H, s, CH_3COO^-). This complexes 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 nitrogen atmosphere over the temperature range of 20-949.9° C. The copper and nickel complexes are thermally stable up to 152.0° C and 121.0° C, respectively, whereas the $[(UO_2)_2(L)(OH)_2\ (CH_3COO)_2]\cdot H_2O$ and $[Co(L)_2Cl_2]\cdot H_2O$ complexes are thermally stable up to 100.0° C and 105.3° C, respectively. The DTA data show that all of the complex have five exothermic peaks. In addition, the complexes, except $[(UO_2)_2(L)(OH)_2(CH_3COO)_2]\cdot H_2O$, have also five endothermic peaks (Table III). In the TGA curve of the $[Co(L)_2Cl_2]\cdot H_2O$ complex, 5.70 % weight loss was observed at 105.3° C. In the TGA curve of the $[(UO_2)_2(L)(OH)_2\ (CH_3COO)_2]\cdot H_2O$ complex, 1.90 % weight loss was observed at 100.0° C. This shows that the complexes contain one or two 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 3225-3464 cm^{-1} due to the υ(O-H) frequency of water of crystallization[29]. This water content was also identified by the elemental analyses. As can be seen in Table IV, the most stable complex is $Cu(L)_2Cl_2$. The weight losses have been found to be approximately the same, when expressed as the percentages calculated from their chemical formulas given in Table I. The decomposition temperature and the weight losses of the complexes were calculated from the TGA data. The weight losses have been found to be approximately the same as the percentages estimated stoichiometrically from their chemical formulas given in Table I and IV. All these complexes undergo complete decomposition to the corresponding metal oxides, CuO, NiO, CoO or U_3O_8[30,31,32].

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