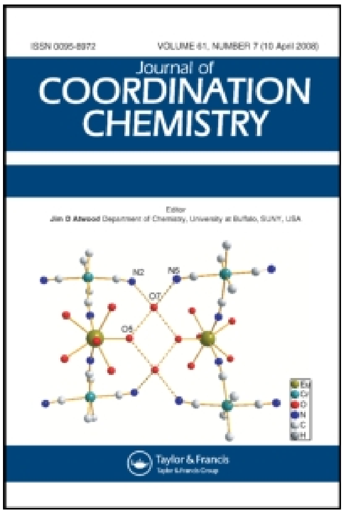

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THE SYNTHESIS AND Co(II), Co(III), Cu(II), Ni(II) AND UO_2(VI) COMPLEXES OF A NEW SYMMETRICAL *vic*-DIOXIME CONTAINING 1,3-DIOXOLANE

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THE SYNTHESIS AND Co(II), Co(III), Cu(II), Ni(II) AND UO_2(VI) COMPLEXES OF A NEW SYMMETRICAL *vic*-DIOXIME CONTAINING 1,3-DIOXOLANE

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9,10-bis(hydroxyimino)-4,8,11,15-tetraaza-1,2,17,18-O-dibenzal octadecane (LH_2) was synthesized starting from 1,2-O-benzal-4-aza-7-aminoheptane, which was prepared from reaction of 1-chloro-2,3-O-benzal propane and dichloroglyoxime. The structure of this novel vicinal (*vic*) dioxime has been determined as the (*E*, *E*) form by ^{1}H NMR, ^{13}C NMR and IR data. Mononuclear complexes with a metal–ligand ratio of 1:2 have been prepared with Co(II), Cu(II) and Ni(II). In the case of uranyl, UO_2(VI) salt was used and the metal–ligand ratio was found to be 1:1. In addition, a Co(III)(py)Cl complex of the ligand was prepared with pyridine (py) and chloride as axial ligands. The structures of the ligand and its complexes are proposed based on elemental analysis, IR, ^{1}H NMR and ^{13}C spectra, magnetic susceptibility measurements, thermogravimetric analyses (TGA) and differential thermal analyses (DTA).

Keywords: *vic*-Dioxime; 1,3-dioxolane; cobalt(II and III); copper(II); nickel(II)

INTRODUCTION

Oxolane bearing molecules are used as solvents, additive compounds and as corrosion retardants. Polymers containing the 1,3-dioxolane group exhibit semiconducting behavior. Polymers and co-polymers of 1,3-dioxolane exhibit herbicidic and perfume activity.[1,2] On the other hand, oximes are compounds having effective complexing capability with many transition metals. With the increasing use of coordination compounds in analytical,

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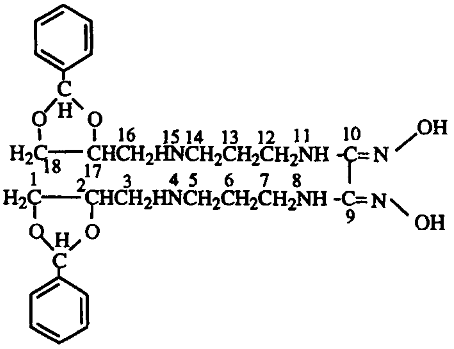


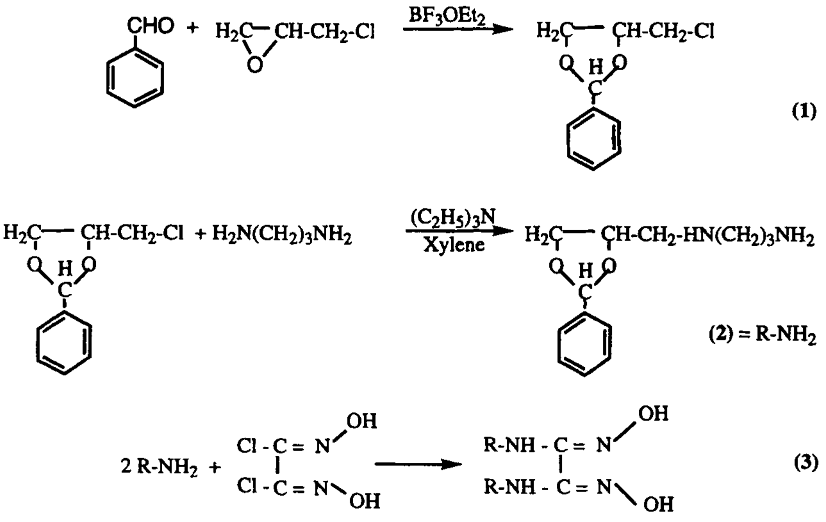
FIGURE 1 9,10-bis(hydroxyimino)-4,8,11,15-tetraaza-1,2,17,18-O-dibenzal octadecane.

biological pigment and medicinal chemistry, many scientists have studied this type of compound, especially, the important role of complexes of 1,2-dioximes in coordination chemistry.[3,4] Also, transition metal complexes of *vic*-dioximes have been of particular interest as biological model compounds.[5] Substitution of the *vic*-dioxime moiety affects the structure and stability of the complexes.[6] Coordination compounds of *vic*-dioximes have also been widely investigated in macrocyclization reactions.[7,8] The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make *vic*-dioximes amphoteric ligands which form corrin-type square-planar,[9] square-pyramidal and octahedral complexes with transition metal ions such as Cu(II), Ni(II), Pd(II), Co(II) and Co(III) as central atoms.[10–12]

In the present paper, as a part of our study to determine the coordination and semiconductor properties of various dioximes attached by the oxolane groups to transition metal ions, we have synthesized five new complexes of 9,10-bis(hydroxyimino)-4,8,11,15-tetraaza-1,2,17,18-O-dibenzal octadecane (Figure 1) with Co(II), Co(III), Cu(II), Ni(II) and UO_2(VI). As far as we know, this is the first report on this ligand.

RESULTS AND DISCUSSION

The steps for synthesis of LH_2 are given in Scheme 1. The first step is synthesis of 1-chloro-2,3-O-benzal propane (**1**) from reaction 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-benzal propane and 1,3-diamino propane reacted to give 1,2-O-dibenzal-4-aza-7-aminoheptane (**2**) (abbreviated as $R{-}NH_2$). In the third step, 9,10-bis(hydroxyimino)-4,8,11,15-tetraaza-1,2,17,18-O-dibenzal octadecane was obtained from reaction of dichloroglyoxime, which was obtained from the procedure published previously,[13] and 1,2-O-benzal-4-aza-7-aminoheptane (Scheme 1).



SCHEME 1

For the structural characterization of (**1**)–(**3**), IR, ^{1}H NMR and ^{13}C NMR were used and the data are given in the experimental section. Additional analytical data are given in Tables I–IV.

In the IR spectrum of (**1**) the most characteristic absorptions are at 1095 cm^{-1} υ(C–O–C) and 745 cm^{-1} υ(C–Cl); characteristic ^{1}H NMR peaks are given in the experimental section.

In the IR spectrum of (**2**), the characteristic peaks are at 3361 and 3285 cm^{-1}, assigned to υ(–NH) and υ(–NH_2), and at 1095 cm^{-1}, assigned to the υ(C–O–C) group. There is no C–Cl stretch in the IR spectrum of (**2**). In the ^{1}H NMR spectra of (**2**), resonances appear at 2.4–3.2 ppm for N–CH_2– and at 1.75 ppm for, broad, –NH– and –NH_2. These peaks (–NH– and –NH_2) disappear with addition of D_2O. On the other hand, in the ^{13}C NMR spectrum of (**2**), each carbon atom namely, C_2, C_3, C_4, C_5, C_6 and C_7, has double resonances at 131.78 and 132.00, 129.44 and 129.73, 134.7 and 135.3, 107.18 and 108.06, and 75.09 and 74.97 ppm, respectively, indicating that compound (**2**) has *cis–trans* isomers.[14] The isomer ratios were found to be 56% *cis* and 44% *trans* from the ^{1}H NMR and ^{13}C NMR data.

The characterization of the ligand was carried out by elemental analysis, IR, ^{13}C and ^{1}H NMR, thermogravimetric analyses (TGA) and differential thermal analyses (DTA).

TABLE I The colors, formulas, formula weights, melting points, magnetic susceptibilities, yields and elemental analyses of the ligand and the complexes

Compounds	*F.W.* g/mol	*Color*	*M.p.* (*dec*) °C	*Yield* %	μ_{eff} (*B.M*)	*Elemental analyses % calculated* (*found*)		
						C	*H*	*N*
Ligand, LH_2 $C_{28}H_{40}N_6O_6$	556.7	Gray	113	74	—	60.42 (59.98)	7.24 (6.90)	15.10 (14.90)
$Co(LH)_2{\cdot}2H_2O$ $C_{56}H_{82}N_{12}O_{14}Co$	1204.9	Brown	193	49	4.56	55.77 (56.07)	6.80 (6.74)	13.94 (14.58)
$Co(LH)_2(py)Cl{\cdot}H_2O$ $C_{61}H_{85}N_{13}O_{13}ClCo$	1301.4	Light brown	186	35	Dia	56.24 (56.59)	6.53 (6.31)	13.98 (14.06)
$Cu(LH)_2$ $C_{56}H_{78}N_{12}O_{12}Cu$	1173.5	Green	143	38	1.78	57.26 (57.62)	6.65 (6.34)	14.31 (14.56)
$Ni(LH)_2$ $C_{56}H_{78}N_{12}O_{12}Ni$	1168.7	Red	229	35	Dia	57.49 (57.19)	6.67 (6.62)	14.37 (14.17)
$(UO_2)_2(LH)_2(OH)_2$ $C_{56}H_{80}N_{12}O_{18}U_2$	1684.0	Orange	213	47	Dia	39.90 (39.75)	4.75 (4.66)	9.98 (9.78)

TABLE II Characteristic IR bands (cm^{-1}) of the ligand and complexes as KBr pellets

Compounds	*O–H*	*N–H*	*Aliph. C–H*	*C–O–C*	*N–O*	*C=N*	*Ar–CH*	*Others*
$R{-}NH_2$	—	3285–3361	2953–2876	1095	—	—	3055, 3080	—
LH_2	3285	3387	2953–2876	1100	978	1649	3080	—
$Co(LH)_2{\cdot}2H_2O$	3234	3361	2953–2876	1105	989	1614	770, 700	1695(O···H–O)
$[Co(LH)_2(py)Cl]{\cdot}H_2O$	3300	3412	2953–2876	1104	999	1612	769, 711	1728(O···H–O) 1580(C_5H_5N)
$Cu(LH)_2$	—	3259	2953–2876	1105	978	1614	770–700	1695(O···H–O)
$Ni(LH)_2$	—	3300	2953–2876	1095	1001	1613	3055, 3080	1741(O···H–O)
$(LH)_2(UO_2)_2(OH)_2$	3259	3361	2953–2876	1105	985	1614	770, 700	910(O=U=O)

TABLE III TGA and DTA data of the ligand and the complexes

Compounds	*TGA*			*DTA*	
	I step	*II step*	*Weight loss* (%)	*Exo peaks*	*Endo peaks*
LH_2	98–448	464–583	98	208, 524, 850	113
$Co(LH)_2{\cdot}2H_2O$	158–515	526–694	91	193, 363, 547	256, 463
$[Co(LH)_2(py)Cl]{\cdot}H_2O$	150–500	505–685	93	186, 610	97, 449
$Cu(LH)_2$	164–495	499–666	94	143, 359, 492, 584	—
$Ni(LH)_2$	186–450	455–700	87	229, 429, 494	—
$(UO_2)_2(LH)_2(OH)_2$	153–460	500–571	62	229, 278, 417, 435	—

TABLE IV ^{1}H NMR spectra of the ligand and some complexes in DMSO-d_6 and $CDCl_3$ in δ (ppm)

Compound	*R–NH$_2$*	*LH$_2$*	*(LH)$_2$Co(py)Cl*	*(LH)$_2$Ni*	*Uranyl complex*
OH	—	8.6–10.8 (2H)^s	—	—	10.2 (1H)^s 10.83 (1H)^s
N–H	1.75 (3H)^s	6.0–6.5 (4H)^s	5.90 (4H)^s 7.00 (4H)^s	6.1–6.6 (4H)^s 6.75 (4H)^s	6.4–7.5 (8H)^s
ϕ–CH$\langle$	5.60, 5.75 (1H)^s	5.72, 5.90 (2H)^s	5.73, 5.88 (4H)^s	5.72, 5.84 (4H)^s	5.72–5.83 (4H)^s
Ar-CH–	7.42 (5H)^m	7.1–7.8 (10H)^m	7.01–7.51 (20H)^m	6.88–7.54 (20H)^m	6.36–7.54 (20H)^m
–CH–O–	4.00–4.50 (1H)^m	4.01–4.05 (1H)^m 4.19–4.21 (1H)^m	4.36 (4H)^m	4.20–4.39 (4H)^m	4.23 (4H)^m
–O–CH$_2$–C	3.7–4.1 (2H)^m	3.71–3.73 (2H)^m 3.84–3.88 (2H)^m	4.36 (4H)^m	3.90–4.13 (8H)^m	4.01 (8H)^m
N–CH$_2$	2.4–3.2 (6H)^m	3.01–3.39 (12H)^m	2.90–3.56 (24H)^m	2.98–3.60 (24H)^m	2.86–3.41 (24H)^m
–CH$_2$–^{10}	2.08 (2H)^m	1.71–1.81 (4H)^m	1.50–2.00 (8H)*	1.68–1.90 (8H)^m	1.53–1.90 (8H)^m
Others	—	—	18.3 (2H)^s (O–H···O) 8.34 (3H)^s, 8.63 (2H)^s C_5H_5N	14.92 (2H)^s (O–H···O)	—

^{m} Multiplet; ^{s} singlet; ^{t} triplet; $^\bullet$ broad bands; ^{i} deuterium exchangeable; ^{10} denotes position of carbon atom (see Figure 2); ϕ–CH$\langle$: oxolane.

Note: As can be seen in Table III, the most stable complex is the Ni(II) complex. All these complexes undergo complete decomposition to the corresponding metal oxides, CoO, CuO, NiO or U_3O_8.

In the IR spectrum of LH_2, characteristic bands appear at $3387\,cm^{-1}$ υ(-NH), $3285\,cm^{-1}$ υ(O-H), $1649\,cm^{-1}$ υ(C=N), $1100\,cm^{-1}$ υ(C-O-C) and $978\,cm^{-1}$ υ(N-O) as expected for a substituted *vic*-dioxime.[4] In the ^1H NMR spectrum, since the OH protons of the oxime are equivalent in the (*E*, *E*) form, a peak was observed at 8.6-10.8 ppm as a broad band and the -NH protons at 6.0-6.5 ppm as a singlet. ^1H NMR signals observed for the protons in N-OH and N-H disappeared upon addition of D_2O to the solution. In the ^{13}C NMR, carbon resonances of dioxime groups (C_{12} and C_{13}) were observed at 151.94 ppm as expected for (*E*, *E*) dioxime.[15,16] C_5(ipso) carbon resonances are at 104.28 and 105.18 ppm. The deuterium exchangeable protons of N-OH groups show a chemical shift at 8.6-10.8 ppm as a singlet also consistent with an (*E*, *E*) structure for the dioxime.[17,18] In the ^{13}C NMR spectrum, C_2, C_3, C_4, C_5, C_6, C_7, C_8 and C_9 carbons are double resonances, while in the ^1H NMR spectrum, each of ϕ–CH$\langle$, C–CH–O and O–CH_2–C groups exhibit two resonances. This is consistent with *cis–trans* isomerism of the oxolane ring of the molecule, LH_2. According to the elemental analysis, IR, ^{13}C and ^1H NMR results, the structure of the ligand is as shown in Figure 2.

The ligand LH_2, on reaction with Co(II), Cu(II) and Ni(II) salts yields complexes corresponding to the general formula $(LH)_2M$ (in the case of Co(II), $(LH)_2M{\cdot}2H_2O$). For the Co(III) complex having pyridine and chloride ligands, the formula is $(LH)_2Co(py)Cl$. The uranyl complex has the composition, $(UO_2)_2(LH)_2(OH)_2$. The analytical data for all complexes are presented in Tables I–IV.

The metal–ligand ratio for the Co(II), Cu(II) and Ni(II) complexes was found to be 1 : 2, but the Co(II) complex has two coordinated water molecules, in addition to the two ligand molecules. The infrared band observed near $1649\,cm^{-1}$, assigned to the υ(C=N) frequency in the free ligand, is shifted to lower frequencies after complexation ($1614-1612\,cm^{-1}$), due to N,N-metal coordination.[4,11] The band observed at $978\,cm^{-1}$ in the

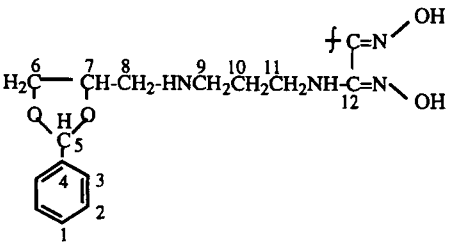


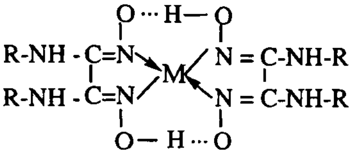
FIGURE 2 The structure of the ligand LH_2.

free ligand, assigned to the ν(N–O), is shifted to higher frequencies after complexation. On the other hand, the band not seen in the free ligand but present in the complexes was assigned to ν(O···H–O),[19,20] and observed at 1695 cm^{-1} for $(LH)_2CO{\cdot}2H_2O$, 1728 cm^{-1} for $(LH)_2Co(py)Cl$, 1695 cm^{-1} for $(LH)_2Cu$ and 1741 cm^{-1} for $(LH)_2Ni$. These indicate that the oxime group takes part in complexation.

In the ^1H NMR spectrum of the Ni(II) complex, there is no OH peak as expected for the formula in Figure 3, but there is a band at 14.92 ppm which is assigned to the (O···H–O).[4,11] The Ni(II) complex is diamagnetic as expected for a d^8 electronic configuration. The Cu(II) and Co(II) complexes are paramagnetic and their magnetic susceptibility values are 1.78 and 4.56 B.M., respectively. These results indicate a square-planar geometry for the Ni(II) and Cu(II) complexes and an octahedral geometry for the Co(II) complex.[21–23] The suggested structure of the complexes is shown in Figure 3.

In the IR spectrum of $(LH)_2Co(py)Cl$, characteristic peaks appear at 3412 cm^{-1}, 1728 cm^{-1}, 999 cm^{-1}, 1612 cm^{-1} and 1580 cm^{-1} which are assigned to ν(N–H), ν(O···H–O), ν(N–O), ν(C=N) and pyridine (C_5H_5N vibration) respectively. On the other hand, characteristic ^1H NMR peaks are at 18.3 ppm for (O···H–O)[19,20] and 8.34–8.63 ppm for pyridine protons[24] as expected for the formula shown in Figure 3. The octahedral structure of the $(LH)_2Co(py)Cl$ complex is shown in Figure 3.

The uranyl complex exhibits a different structure. In the IR spectrum, the UO_2(VI) complex shows a band at 910 cm^{-1} which is assigned to ν(O=U=O)[23] and there is no O···H–O band. The band observed at 910 cm^{-1} is characteristic for (O=U=O) stretches and OH stretching vibrations of the oxime group still appear as a broad band. The ^1H NMR spectrum of the uranyl complex shows two chemical shifts for the deuterium exchangeable N–OH (10.2 and 10.83 ppm) and –NH protons (6.4 and 7.5 ppm). These spectral data lead us to a binuclear μ-hydroxo-bridged nonplanar structure for the uranyl diamagnetic complex of LH_2.[11] The suggested structure of the complex is shown in Figure 4.



M = Co(II)·$2H_2O$
Co(III)(py)Cl
Cu(II)
Ni(II)

FIGURE 3 Suggested structure of the square-planar and octahedral complexes of the ligand LH_2.

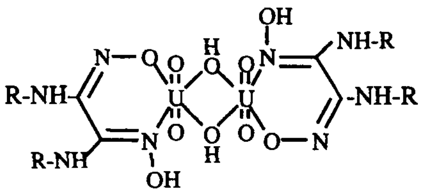


FIGURE 4 Suggested structure of the uranyl complex of the ligand LH_2.

EXPERIMENTAL

Benzaldehyde and epichlorohydrin were purchased from Merck (Pure) and used without further purification. Dichloroglyoxime was synthesized by the method described in the literature.[3]

The elemental analysis was carried out in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey), IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets, ^{13}C and ^{1}H NMR spectra were recorded on Bruker GmbH Dpx-400 MHz High Performance Digital and JEOL FX 90Q FT-NMR Spectrometers. 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.[25] TGA and DTA curves were recorded on a Shimadzu TG-50 thermobalance.

Synthesis of 1-Chloro-2,3-O-benzalpropane (1)

This substance was synthesized according to the method described in the literature,[26] but some modifications were made on the synthesis as follows. 15–20 drops of boron trifloride etherate were added dropwise to 106.0 g (1.0 mol) benzaldehyde. Then 28 g (0.30 mol) of epichlorohydrin was added dropwise to the reaction mixture at 10–20°C with continuous stirring. The reaction mixture was then further stirred for 3 h at 20°C. The product obtained was distilled at 130–133°C at 4 mmHg in *vacuum*. Yield: 40 g (66%). The density of the product was found to be $d_4^{20} = 1.2169$. Elemental analysis for $C_{10}H_{11}O_2Cl$, calculated (found): C: 66.40 (66.20), H: 5.58 (5.66). Characteristic IR bands (NaCl cell, cm^{-1}): 2953–2876 (aliphatic C–H), 3055–3080 (aromatic C–H), 1095 υ(C–O–C), 745 υ(C–Cl). Characteristic ^{1}H NMR bands (CCl_4, TMS, δ ppm): 7.27 (5H, aromatic), 5.70 and 5.87 (1H, –CH⟨), 4.20 (1H, C–CH–O), 4.10 (2H, –O–CH_2–C), 3.50

(2H, $-CH_2-Cl$). Characteristic ^{13}C NMR bands (CCl_4, TMS, δppm): C_1 (128.66), C_2 (126.20 and 126.50), C_3 (129.27 and 129.58), C_4 (138.20 and 138.51), C_5 (104.65 and 105.87), C_6 (69.56 and 70.18), C_7 (76.64 and 76.95), C_8 (45.24 and 45.55).

Synthesis of 1,2-O-Benzal-4-aza-7-aminoheptane (2)

29.6 mL (350 mmol) of 1,3-diamino propane, 10.0 mL (72 mmol) triethylamine and 100 mL absolute xylene were mixed in a reaction vessel and the temperature was raised to 90°C with continuous stirring. To this solution, a solution of 14.3 g (72 mmol) of (**1**) in 50 mL absolute xylene was added dropwise. The mixture was refluxed for 38 h more. After cooling to room temperature the mixture was filtered and the filtrate was distilled at 140–145°C at 2 mm Hg. Yield: 13.0 g (76%), the density and the refractive index of the product were found to be $d_4^{20} = 1.0837$ and $n_D^{20} = 1.5398$ respectively. Elemental analysis, calculated (found) % for $C_{13}H_{20}N_2O_2$, C: 66.10 (66.35), H: 8.47 (8.50), N: 11.86 (11.58). Characteristic IR bands (NaCl cell, cm^{-1}): 3285–3361 υ(–NH, $-NH_2$), 2953–2876 υ(C–H), 1095 υ(C–O–C) Characteristic ^1H NMR bands ($CDCl_3$, TMS, δppm) are in Table IV. Characteristic ^{13}C NMR bands ($CDCl_3$, TMS, δppm): C_1 (131.20), C_2 (131.78 and 132.0), C_3 (129.44 and 129.73), C_4 (134.7 and 135.3), C_5 (107.18 and 108.06), C_6 (75.09 and 74.97), C_7 (82.50 and 82.08), C_8 (54.17), C_9 (59.15), C_{10} (40.01), C_{11} (58.57).

Synthesis of the Ligand (LH_2)

A solution of 4.72 g (20 mmol) of 1,2-O-benzal-4-aza-7-aminoheptane in 25 mL absolute THF was added to a solution of 2.8 mL (20 mmol) triethylamine in 10 mL absolute THF. This mixture was cooled to −10 to −15°C and kept at this temperature, and a solution of 1.57 g (10 mmol) of dichloroglyoxime in 25 mL absolute THF was added dropwise under a nitrogen atmosphere with continuous stirring. Addition of dichloroglyoxime solution was carried out over 1.5 h. The mixture was stirred 1 h more and the temperature raised to 0°C. Precipitated triethylammonium chloride was filtered off and the filtrate was evaporated to 15 mL. The product that precipitated with the addition of cold diethyl ether was filtered, washed with cold diethyl ether twice and dried in *vacuum* at 40°C. Yield: 4.1 g (74%), m.p. 113°C (dec). Characteristic ^1H NMR bands ($CDCl_3$, TMS, δppm) are in Table IV. Characteristic ^{13}C NMR bands ($CDCl_3$, TMS, δppm): C_1 (129.52), C_2 (127.60 and 127.74), C_3 (130.33 and 130.42), C_4

(138.95 and 139.44), C_5 (104.28 and 105.18), C_6 (68.94 and 69.24), C_7 (75.60 and 76.08), C_8 (52.92 and 54.54), C_9 (46.72 and 45.64), C_{10} (30.92), C_{11} (39.16), C_{12} (151.94).

Synthesis of the Co(II), Co(III), Cu(II), Ni(II) and UO_2(VI) Complexes

A quantity of 0.400 g (0.719 mmol) of the ligand was dissolved in 10 mL absolute ethanol. A solution of 0.36 mmol metal salt $CoCl_2 \cdot 6H_2O$ (0.086 g), $CuCl_2 \cdot 2H_2O$ (0.061 g) and $NiCl_2 \cdot 6H_2O$ (0.086 g) in 5 mL absolute ethanol was added dropwise with continuous stirring. The pH of the solutions which decreased to about 3.0–3.5 was adjusted to 5.0–5.5 by the addition of a 1% triethylamine solution in ethanol, then the mixture was cooled to room temperature and with the addition of 25 mL diethyl ether, the complexes precipitated. The complex crystals obtained were filtered, washed with diethyl ether, water and cold ethanol. Crystals were dissolved in 10 mL of CH_2Cl_2 and 100 mL of *n*-hexane was added to precipitate the compound. The product obtained was filtered, washed with *n*-hexane and dried in *vacuum* at 70°C. In the case of Co(II), since precipitation did not occur, the excess of ethanol was evaporated in a rotary evaporator. The brown complex was dissolved in 10 mL of CH_2Cl_2 and 100 mL of *n*-hexane was added to precipitate the compound. The precipitate was filtered, washed with *n*-hexane and dried in *vacuum* at 70°C. In the case of uranyl complex, to a solution of 0.200 g (0.359 mmol) of LH_2 in 10 mL ethanol, a solution of 0.153 g (0.359 mmol) of $UO_2(CH_3COO)_2 \cdot 2H_2O$ in 10 mL ethanol was added. The orange complex which formed immediately was stirred 30 min more and filtered, washed with diethyl ether and ethanol. The crystals were dissolved in 10 mL of THF and 100 mL of diethyl ether was added to precipitate the compound. The crystals obtained were filtered, washed with diethyl ether and dried in *vacuum* at 30°C.

In the synthesis of $(LH)_2Co(py)Cl$, a solution of $CoCl_2 \cdot 6H_2O$ (0.064 g, 0.269 mmol) in 10 mL THF was added to a solution of the ligand (0.300 g, 0.539 mmol) in 25 mL THF. Pyridine (0.085 g, 1.078 mmol) in 5 mL THF was added to the mixture and O_2 was bubbled through the solution for 3 h while heating at 55°C. A light brown color was formed. The mixture was evaporated to 10 mL. The complex was precipitated with the addition of 20 mL diethyl ether. The precipitate was filtered, washed with diethyl ether, water and cold methanol. To obtain a high purity compound, the precipitate was dissolved in 10 mL of absolute THF and 100 mL of diethyl ether was added to precipitate the compound. The compound obtained was filtered, washed with diethyl ether and dried in *vacuum* at 50°C.

Thermal Studies

The TGA and DTA curves, which were obtained at a heating rate of $10°C\,min^{-1}$ in a nitrogen atmosphere over the temperature range of 20–900°C, show that copper and nickel complexes are thermally stable up to 164°C and 186°C, respectively, whereas the $Co(LH)_2{\cdot}2H_2O$ and $Co(LH)_2(py)Cl$ complexes are thermally stable up to 158°C and 150°C, respectively. The uranyl complex has a weight loss between 153°C and 571°C. The ligand, LH_2 is stable up to 98°C and its decomposition starts at 98°C and is completed at 583°C. On the other hand, the DTA curve of the ligand shows three exo peaks and one endo peak. As can be seen in the TGA data (Table III), all the complexes and the ligand decompose in two steps at different temperature ranges. The DTA data show that the $Co(LH)_2{\cdot}2H_2O$ and $Ni(LH)_2$ complexes have three exo peaks, while $(LH)_2(UO_2)_2(OH)_2$ and $Cu(LH)_2$ complexes exhibit four exo peaks. The weight losses have been found to be approximately the same as the percentages estimated stoichiometrically from their chemical formulas given in Table I. In the TGA curve of $Co(LH)_2(py)Cl$, 1.5% weight loss was observed at 97°C. This shows that the complex has one mole of crystalline water per molecule. This water content was also identified by the elemental analysis.

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References

[1] H. Kamogawa, Y. Haramoto, T. Nakazawa, H. Sugiura and M. Nanasawa, *Bull. Chem. Soc. Jpn.*, **54**, 1577 (1981).
[2] K. Oguchi, K. Sanui and N. Ogata, *Polymer Engineering and Science*, **30**, 449 (1990).
[3] A. Gül and Ö. Bekaroğlu, *J. Chem. Soc. Dalton Trans.*, 2537 (1983).
[4] V. Ahsen, F. Gökçeli and Ö. Bekaroğlu, *J. Chem. Soc. Dalton Trans.*, 1827 (1987).
[5] A. Chakravorty, *Coord. Chem. Rev.*, **1**, 13 (1974).
[6] G. İrez and Ö. Bekaroğlu, *Synth. React. Inorg. Met.-Org. Chem.*, **13**, 781 (1983).
[7] G. N. Schrauzer, *Angew. Chem. Int. Ed. Engl.*, **15**, 47 (1976).
[8] K. A. Lance, K. A. Goldsby and D. H. Busch, *Inorg. Chem.*, **29**, 4537 (1990).
[9] P. A. Smith, *The Chemistry of Open-Chain Organic Nitrogen Compounds*, Vol. II, W. A. Benjamin, New York, 1966.
[10] A. S. Abusaimleh, P. J. Chimiclewski, P. R. Warburton, L. Morales, N. A. Stephenson and D. H. Busch, *J. Coord. Chem.*, **23**, 91 (1991).
[11] A. Gül and Ö. Bekaroğlu, *J. Chem. Soc. Dalton Trans.*, 2537 (1983).
[12] Y. Gök, S. Z. Yıldız and M. Tüfekçi, *J. Coord. Chem.*, **28**, 237 (1993).
[13] H. Britzingen and R. Titzmann, *Ber. Dtsch. Chem. Ges.*, **85**, 345 (1952).
[14] J.-C. Soutif, L. Ouchatar, D. Courret and J.-C. Brosse, *Macromol. Chem.*, **187**, 561 (1986).

[15] Y. Gök and H. Kantekin, *Chem. Ber.*, **123**, 1479 (1990).
[16] Y. Gök and H. Kantekin, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 1085 (1990).
[17] Y. Gök, H. B. Şentürk, U. Ocak and H. Kantekin, *J. Chem. Res.* (*S*), 258 (1994).
[18] Y. Gök, S. Karaböcek and H. Kantekin, *Trans. Met. Chem.*, **20**, 234 (1995).
[19] H. C. Sevindir, R. Mirzaoğlu, E. Özcan, S. Kurtul and E. Güler, *Synth. React. Inorg. Met.-Org. Chem.*, **24**, 613 (1994).
[20] A. Nakamura, A. Konushi and S. Otsuka, *J. Chem. Soc. Dalton Trans.*, 488 (1979).
[21] V. Ahsen and Ö. Bekaroğlu, *Synth. React. Inorg. Met.-Org. Chem.*, **15**, 61 (1985).
[22] Y. Gök and E. Özcen, *Trans. Met. Chem.*, **16**, 393 (1985).
[23] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Edition, A Wiley-Interscience Publication, 1988, pp. 725–743.
[24] Y. Gök, S. Karaböcek, N. Karaböcek and Y. Atalay, *New J. Chem.*, **19**, 1275 (1995).
[25] A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, London, 1968, p. 4.
[26] P. Cai-Yuan and W. Zhen, *J. Poylmer Sci. Part C: Polymer Letters*, **25**, 243 (1987).