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A New Substituted Bis(*vic*-dioxime) of Its Mono- and Dinuclear Complexes

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9,10-Bis(hydroxyimino)-4,8,11,15-tetra-aza-1,2,17,18-O-di-iso-propylideneoctadecane (H_2L) was synthesized by the reaction of 1,2-O-iso-propylidene-4-aza-7-aminoheptane and *anti*-dichloroglyoxime in ethanol, containing an excess of $NaHCO_3$ as a buffer to neutralize the HCl formed. The mononuclear metal complexes of this ligand have been synthesized with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) salts. H_2L forms mononuclear complexes $[(HL)_2M]$ with a metal ligand ratio of 1:2 with M = Co(II) · $2H_2O$, Ni(II) and Cu(II). Zn(II) and Cd(II) form with H_2L complexes $[(H_2L)(Cl)_2M]$, which have a metal-ligand ratio of 1:1 and a dinuclear complex with UO_2(VI). H_2L forms the dinuclear complex $[(HL)_2(OH)_2M_2]$ with a metal ligand ratio of 1:1 with M = UO_2(VI). Structures of the ligand and its metal complexes were identified by elemental analyses, IR, ^1H and ^{13}C NMR spectra and thermogravimetric analyses (TGA).

Key words: *vic*-dioxime, cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), and uranyl(VI) complexes

Because of importance, the chemistry of transition metal complexes with *vic*-dioxime ligands has been intensively investigated [1]. Some oximes are widely used for various purposes in organic, inorganic, bioinorganic, pigment, analytical, dyes and medical chemistry [2–4]. *Vic*-dioximes, containing mildly acidic hydroxyl groups and slightly basic nitrogen atoms, are amphoteric and their transition metal complexes have been widely investigated as analytical reagents [5] and models for biological systems [6], such as vitamin B_{12}. *Vic*-dioximes and their derivatives may exist in three isomers, which are the *syn*, *anti*, and *amphi* forms, depending on the position of the -OH groups in the molecule. Usually, the stability order of these is *anti* > *amphi* > *syn* configuration, but there are some exceptions [7]. The *anti*- and *amphi*-forms of these isomers give two different colored complexes with the same metal, but the *syn*-form does not form complexes [8]. Metals and their known compounds have antimicrobial effect. These are all highly toxic. Many structural analogs of them have been prepared, in an attempt to lower their toxicity and to enhance their biological activity as antimicrobial agents.

In our previous studies we have investigated the synthesis and characterization of various transition metal complexes of novel *vic*-dioxime [9–13].

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EXPERIMENTAL

The preparation of *anti*-dichloroglyoxime has been described previously [14]. All the reagents used were purchased from Merck or Fluka or Sigma Companies and are chemically pure.

Physical measurements: Elemental analyses (C, H, N) were performed on a LECO-932 CHNSO elemental analyses apparatus. IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q FT-NMR and Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometers. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temprature using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. The melting points were determined on a Gallenkamp melting point apparatus. The metal contents of the complexes were determined with an ATI Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposition of the compounds in conc. HCl and conc. HNO_3 (3:1) solutions followed by dilution in water. TGA curves were recorded on a Shimadzu TG-50 thermobalance.

Synthesis of 1-chloro-2,3-O-iso-propylidenepropane (1): 15–20 drops of borontrifluoride etherate were added dropwise to purified acetone (58.00 g, 1.00 mole) in (100 mL) carbon tetrachloride. Then epichlorohydrine (23.00 g, 0.25 mole) was added dropwise over a period of 3 h at temperature below 15–20°C. After the reaction was completed, the mixture was stirred for an additional 5 h at the same temperature. The catalyst $BF_3 \cdot OEt_2$ was then destroyed by addition of triethylamine (3 mL). The mixture was washed with water and dried over anhydrous potassium carbonate. The liquid products were distilled at 64–70°C and 27 mm-Hg. Yield: 26.73 g (71%); IR bands (NaCl cell, cm^{-1}): 757 υ(C–Cl), 1089 δ(C–O–C), 3004–2902 υ(C–H)$_{\text{aliph.}}$; ^{1}H NMR (DMSO-d_6, δ ppm, 90 MHz): 1.40–1.50 (s, 6H, CH_3), 3.40 (m, 2H, CH_2–O), 3.80 (m, 2H, CH_2–Cl), 4.00 (m, 1H, CH–O); ^{13}C NMR (DMSO-d_6, δ ppm, 90 MHz): 26.30 (C_2), 27.00 (C_1), 46.10 (C_6), 64.00 (C_4), 72.60 (C_5), 115.05 (C_3).

Synthesis of 1,2-O-iso-propylidene-4-aza-7-aminoheptane (2): 1,3-diaminopropane, (6.93 mL, 0.05 mole), triethylamine (16.70 mL, 0.20 mole) and absolute xylene (60 mL) were mixed in a reaction flask filed with a $CaCl_2$ drying tube and a dropping funnel and heated to 80°C. To this mixture, a solution of 1-chloro-2,3-O-iso-propylidenepropane (7.50 g, 0.05 mole) in (30 mL) absolute xylene was added, refluxed for 40 h and cooled to room temperature. The mixture was filtered and the filtrate was evaporated to remove the excess of 1,3-diaminopropane. The compounds were distilled at 100–110℃ at 4 mm-Hg. Yield: 6.09 (65%); IR bands (NaCl cell, cm^{-1}): 3412 υ(-NH); ^{1}H NMR (DMSO-d_6, δ ppm, 90 MHz): 1.35 (s, 3H, $NH_{\text{deuterium exchangeable}}$), 1.45 (s, 6H, CH_3), 2.75 (m, 6H, N–CH_2-), 3.55 (m, 2H, CH_2–O), 3.90 (m, 1H, CH–O); ^{13}C NMR (DMSO-d_6, δ ppm, 90 MHz): 25.80 (C_2), 26.70 (C_1), 35.30 (C_9), 41.20 (C_8), 45.90 (C_6), 48.60 (C_7), 64.00 (C_4), 71.15 (C_5), 114.20 (C_3).

Synthesis of the ligand H_2L (3): A solution of triethylamine (6.06 g, 60.00 mmole) was added to a solution of 1,2-O-iso-propylidene-4-aza-7-aminoheptane (6.96 g, 40.00 mmole) in absolute THF (70 mL), then a solution of *anti*-dichloroglyoxime (3.14 g, 20.00 mmole) in absolute THF (50 mL), synthesized by the method described previously [14], was added dropwise to the mixture at –10℃ over 5 h. The mixture was filtered and THF was removed by evaporation. The oily product was dissolved in chloroform and precipitated in *n*-hexane (1/10). Obtained product was filtered off, washed with diethyl ether several times and dried *in vacuo* for 12 h. The compound found to be soluble in acetone, EtOH, $CHCl_3$, DMSO and DMF and insoluble in benzene, diethyl ether and *n*-hexane. The analytical and physical data, characteristic IR bands and ^{1}H NMR data are given in Tables 1–3. The characteristic ^{13}C NMR peaks are: (DMSO-d_6, δ, 400 MHz): 25.08–25.48 (C_2 and C_{19}), 26.53–26.80 (C_1 and C_{20}), 33.00–33.64 (C_8 and C_{13}), 37.40–37.78 (C_9 and C_{12}), 41.65–41.80 (C_7 and C_{14}), 48.95–49.06 (C_6 and C_{15}), 61.49–62.16 (C_4 and C_{17}), 70.04–71.59 (C_5 and C_{16}), 107.50–108.08 (C_3 and C_{18}), 148.32–151.12 (C_{10} and C_{11}) ppm.

Synthesis of the Co(II) complex (4): The ligand (0.46 g, 1.00 mmol) was dissolved in absolute ethanol (15 mL). A solution of $CoCl_2 \cdot 6H_2O$ (0.12 g, 0.50 mmole) in absolute ethanol (15 mL) was added dropwise to the ligand solution with continuous stirring at 50°C. The colour of the solution immediately turned brown; the pH dropped to 3.95 and was raised to 5.5 by addition of a 1 M NaOH solution in ethanol. The reaction mixture was kept stirring at this temperature for 3 h, filtered and the precipitate washed with ethanol and diethyl ether and dried *in vacuo* at 60°C. The complex is soluble in water, $CHCl_3$, EtOH, MeOH, THF, DMF and DMSO and insoluble in toluene, diethyl ether and *n*-hexane. The analytical and physical data, and characteristic IR bands are given in Tables 1 and 2.

Synthesis of the Ni(II) complex (5): Red **5** was prepared following the same procedure as that described for **4**, starting from **3** (0.46 g, 1.00 mmol) and $NiCl_2 \cdot 6H_2O$ (0.12 g, 0.50 mmol). The analytical and physical data, characteristic IR bands and ^1H NMR data are given in Tables 1–3.

Synthesis of the Cu(II) complex (6): Dark green **6** was prepared following the same procedure as that described for **4**, starting from **3** (0.46 g, 1.00 mmol) and $CuCl_2 \cdot 2H_2O$ (0.10 g, 0.50 mmol). The analytical and physical data, and characteristic IR bands are given in Tables 1 and 2.

Synthesis of the Zn(II) complex (7): 0.46 g, (1.00 mmole) of the ligand was dissolved in absolute methanol (10 mL). Asolution of $ZnCl_2$ (0.136 g, 1 mmole) in absolute methanol (5 mL) was added dropwise to the ligand solution with continuous stirring. The mixture on a water bath at 50°C was further stirred for 1 h in order to complete precipitation. The colour of the solution immediately turned light yellow. The precipitate was filtered, washed with diethyl ether and dried *in vacuo* at 60°C. The analytical and physical data, characteristic IR bands and ^1H NMR data are given in Tables 1–3.

Synthesis of the Cd(II) complex (8): Yellow **8** was prepared following the same procedure as that described for **4**, starting from **3** (0.46 g, 1.00 mmol) and $CdCl_2 \cdot H_2O$ (0.20 g, 1.00 mmol). The analytical and physical data, characteristic IR bands and ^1H NMR data are given in Tables 1–3.

Synthesis of the UO_2(VI) complex (9): When a solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.42 g, 1.00 mmol) in absolute ethanol (60 mL) was added to a solution of **3** (0.46 g, 1.00 mmol) in absolute ethanol (30 mL), an orange complex precipitated. The mixture was stirred on a water bath for another half hour and filtered while hot. The product was washed with water, then ethanol and dried with diethyl ether. The complex is soluble in dioxan, CH_2Cl_2, EtOH, DMF and DMSO and insoluble in toluene, diethyl ether and *n*-hexane. The analytical and physical data, characteristic IR bands and ^1H NMR data are given in Tables 1–3. Elemental analyses confirmed the compositions of the above synthesized compounds.

RESULTS AND DISCUSSION

A novel (E,E)-dioxime 9,10-bis(hydroxyimino)-4,8,11,15-tetra-aza-1,2,17,18-O-di-iso-propylideneoctadecane (H_2L) has been synthesized from the reaction of *anti*-dichloroglyoxime and 1,2-O-iso-propylidene-4-aza-7-aminoheptane **(2)**, which has been prepared from 1-chloro-2,3-O-iso-propylidenepropane **(1)** and 1,3-diaminopropane. The structure of H_2L was determined by a combination of elemental analyses, IR, ^1H and ^{13}C NMR spectra and thermogravimetric analyses (TGA), as shown in Tables 1–3.

In IR spectrum of H_2L, characteristic peaks are observed at 3460 cm^{-1} υ(O–H), 3361 cm^{-1} υ(N–H), 1658 cm^{-1} υ(C=N), 1066 cm^{-1} υ(C–O–C) and 997 cm^{-1} υ(N–O), in agreement with the values reported for similar compound [12,15,16]. In the ^1H NMR spectrum, since the (-OH) protons of these oximes are equivalent in the (E,E) form, two peaks are present for the protons [17]. In the H_2L, chemical shifts for (=N-OH) protons were observed at 9.00–9.60 ppm as singlet. Also, chemical shifts for (-NH) protons were observed at 5.70–5.78 ppm [18–22]. These bands are easily identified by deuterium exchange. In the ^{13}C NMR, carbon resonance of dioxime groups (C_{10} and C_{11}) were observed at 148.32–151.12 ppm as expected for (E,E) dioxime [9,13]. The most characteristic signal for $C_{3(ipso)}$ is at 107.50–108.08 ppm.

Scheme 1

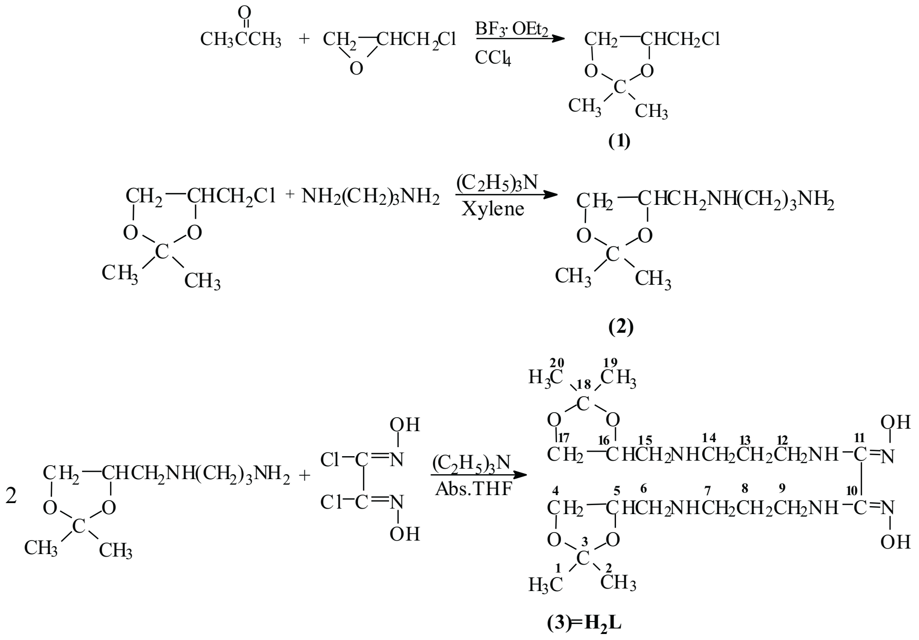

Table 1. Analytical and physical data of the ligand and its complexes.

	Compounds	F.W. g/mol	Colour	M.p. (°C)	Yield (%)	μ_{eff} (B.M.)	% Metal calc. (found)
	H_2L						
(3)	$C_{20}H_{40}N_6O_6$ $[(HL)_2Co\cdot 2H_2O]$	460.66	dirty white	192	61	–	–
(4)	$C_{40}H_{82}N_{12}O_{14}Co$ $[(HL)_2Ni]$	1014.27	brown	205	60	3.90	9.86 (10.21)
(5)	$C_{40}H_{78}N_{12}O_{12}Ni$ $[(HL)_2Cu]$	977.99	red	224	62	dia	6.00 (5.74)
(6)	$C_{40}H_{78}N_{12}O_{12}Cu$ $[(HL)_2(Cl)_2Zn]$	982.84	dark green	148	67	1.97	6.46 (6.18)
(7)	$C_{20}H_{40}N_6O_6Cl_2Zn$ $[(HL)_2(Cl)_2Cd]$	596.95	light yellow	166	54	dia	10.95 (11.33)
(8)	$C_{20}H_{40}N_6O_6Cl_2Cd$ $[(UO_2)_2(HL)_2(OH)_2]$	643.97	yellow	196	66	dia	17.45 (17.81)
(9)	$C_{20}H_{80}N_{12}O_{18}U_2$	1493.38	orange	202	72	dia	–

The *vic*-dioxime **3** forms mononuclear complexes with Co(II) **(4)**, Ni(II) **(5)**, Cu(II) **(6)** with a metal:ligand ratio of 1:2 and Zn(II) **(7)** and Cd(II) **(8)** with a metal:ligand ratio of 1:1 and a dinuclear complex with UO_2(VI) **(9)** with a metal:ligand ratio of 1:1 (Figs. 1–3).

Table 2. Characteristic IR bands of the ligand and its complexes as KBr pellets (in cm^{-1}).

Compounds	υ(O–H)	υ(N–H)	υ(C–H)	υ(N–O)	υ(C=N)	υ(O···H–O)
H_2L	3460	3361	2945–2987	997	1658	–
$[(HL)_2Co\cdot 2H_2O]$	–	3325	2945–2987	975	1620	1710
$[(HL)_2Ni]$	–	3323	2945–2987	980	1619	1707
$[(HL)_2Cu]$	–	3320	2945–2987	965	1638	1695
$[(H_2L)(Cl)_2Zn]$	3440	3368	2871–2987	977	1625	–
$[(H_2L)(Cl)_2Cd]$	3440	3366	2871–2987	989	1630	–
$[(UO_2)_2(HL)_2(OH)_2]$	3337	3290	2940–2980	972	1635	–

(H_2O) = 3500 cm^{-1} for $(HL)_2Co\cdot 2H_2O$ and (O=U=O) = 920 cm^{-1} for $(UO_2)_2(HL)_2(OH)_2$.

Table 3. ^{1}H NMR data of the ligand and its complexes (in DMSO-d_6).

Comp.	H_2L	$[(HL)_2Ni]$	$[(H_2L)(Cl)_2Zn]$	$[(H_2L)(Cl)_2Cd]$	$[(UO_2)_2(HL)_2(OH)_2]$
N–H^{a}	5.70–5.78 (4H)^{s}	5.83–5.94 (8H)^{s}	5.84–6.04 (4H)^{s}	5.90–6.00 (4H)^{s}	5.95–6.05 (8H)^{s}
N–CH_2	2.95–3.31 (12H)^{m}	2.86–3.30 (24H)^{m}	2.98–3.30 (12H)^{m}	3.00–3.34 (12H)^{m}	2.90–3.40 (24H)^{m}
-CH_2-	1.56–1.80 (4H)^{m}	1.50–1.86 (8H)^{m}	1.60–1.88 (4H)^{m}	1.58–1.90 (4H)^{m}	1.64–1.92 (8H)^{m}
-CH_3	1.33–1.42 (12H)^{m}	1.30–1.40 (24H)^{m}	1.30–1.40 (12H)^{m}	1.30–1.45 (12H)^{ms}	1.27–1.38 (24H)^{m}
-CH–O	3.66–3.88 (2H)^{m}	3.69–4.00 (4H)^{m}	3.70–4.05 (2H)^{m}	3.65–4.00 (2H)^{m}	3.60–3.90 (4H)^{m}
-CH_2–O	3.40–3.55 (4H)^{m}	3.40–3.60 (8H)^{m}	3.35–3.62 (4H)^{m}	3.30–3.60 (4H)^{m}	3.45–3.55 (8H)^{m}
N–OH^{a}	9.00 (1H)^{s}	–	9.17 (1H)^{s}	9.25 (1H)^{s}	10.15 (1H)^{s}
N–OH^{a}	9.60 (1H)^{s}	–	9.84 (1H)^{s}	9.94 (1H)^{s}	10.92 (1H)^{s}
others	–	14.99 (2H)^{s} (O···H–O)^{a}	–	–	4.45 (2H)^{s} (-OH-)

^{a}Disappears on D_2O exchange, s: singlet, m: multiplet.

The IR spectra of the complexes **4**, **5** and **6** exhibit C=N absorptions at 1620 cm^{-1} for **(4)**, 1619 cm^{-1} for **(5)** and 1638 cm^{-1} for **(6)**. These values are lower than for the free ligand (1658 cm^{-1}), suggesting that **3** is coordinated only by the N,N atoms of the *vic*-dioxime. At the same time, the band observed at 997 cm^{-1} in the free ligand, which assigned to the N–O, is shifted to lower frequency after complexation. It shows the characteristic features of *vic*-dioxime complexes. The colors of the complexes are in accordance with those of previously reported *vic*-dioxime complexes [23,24]. On the other hand, a band not seen in the free ligand, which is assigned to hydrogen bridge (O···H–O), is observed at 1710 cm^{-1} for **(4)**, 1707 cm^{-1} for **(5)**, 1695 cm^{-1} for **(6)** [23–28,31–35]. The absorptions indicate that the oxime group takes part in complexation of **4** with two coordinated water molecules. In the case of compound **4** the coordinated H_2O groups are identified by a broad OH absorption at 3500 cm^{-1}, that keeps its intensity even after heating at 110°C for 24 h. The ^{1}H NMR spectrum of the diamagnetic complex **5** shows the disappearance of OH at 9.00–9.60 ppm belonging to the neighboring oxime group. The existence of intra-molecular H-bridge protons is observed by a new signal at lower field, 14.99 ppm, in addition to NH protons at 5.83–5.94 ppm very near to oxime group. NH protons and intra-molecular binding

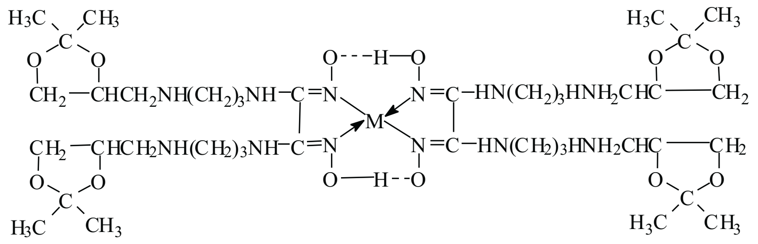

Figure 1. Suggested structure of the octahedral Co(II)(H_2O)$_2$ and square-planar Ni(II) and Cu(II) complexes of the ligand.

O· · · H–O protons in **5** observed at 5.83–5.94 and 14.99 ppm disappear after addition of D_2O [25–27].

The **5** complex is diamagnetic, whereas the **4** and **6** complexes are paramagnetic and their magnetic susceptibilities are 3.90 and 1.97 B.M. [28–30]. For these complexes, additional physical and analytical data are given in Tables 1–3. According to these results, the **4** complex has an octahedral geometry and **5** and **6** complexes have a square-planar structure. The suggested structures of the complexes are shown in Fig. 1.

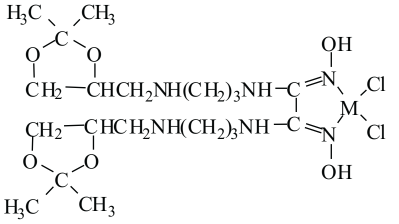

Figure 2. Suggested structure of the tetrahedral Zn(II) and Cd(II) complexes of the ligand.

The complexes of H_2L with **7**, and **8** have a 1:1 metal:ligand ratio. In these complexes, two of four coordination sites on the metals are occupied by the two atoms of the dioxime molecule; the elemental analytical results show the presence of one ligand molecule and two chloride ions for each metal ion (Fig. 2). The ^{1}H NMR and IR spectra indicate that hydroxyl ions play also the role of a ligand. Therefore in the IR spectrum of the **7,** and **8** complexes, the stretching band of v(C=N), appearing at 1658 cm^{-1} in H_2L, is shifted to 1625 cm^{-1} for **(7)** and 1630 cm^{-1} for **(8)**. There is no O· · · H–O peak, as expected for complexes of formula shown in Fig. 2. The **8,** and **9** complexes are diamagnetic as expected for a d^{10} electronic configuration. The ^{1}H NMR spectrum of **7** and **8** complexes shows the presence of a N-coordinated oxime (N–OH) proton at 9.17–9.84 for **(7)** and 9.25–9.94 ppm for **(8)**. To elucidate the structures of the complexes, elemental analyses IR, NMR and TGA have been used. For these complexes, additional physical and analytical data are given in Tables 1–3. Taking into consideration the observations given above, the usual tetrahedral structures for **(7),** and **(8)** complexes can be proposed, Fig. 2 [31–33].

The uranyl complex **9** exhibits a different structure. The elemental analysis of the complex indicates that the metal:ligand ratio is 1:1. Uranyl complexes of *vic*-dioximes with this metal:ligand ratio is uncommon, although we have reported a dinuclear complex with μ-hydroxo bridges [34]. In the IR spectrum, the $UO_2(VI)$ shows a band at 920 cm^{-1}, which is assigned to O=U=O and there is not an $v(O\cdots H–O)$ band. The band observed at 920 cm^{-1} is characteristic for O=U=O stretches and OH stretching vibrations of the oxime group still appear at 3337 cm^{-1} as a broad band. The ^1H NMR spectrum of the uranyl complex shows a signal for a deuterium exchangeable N–OH proton at 10.15–10.92 ppm; the shift can be attributed to the magnetic anisotropy of the uranyl ion, as discussed in relation to some amine complexes [35]. It is known, that the uranyl ion enhances the chemical shift difference between non-equivalent protons. This effect is equivalent to increasing the ^1H NMR observing frequency by few orders of magnitude [36]. These spectral data lead us to a binuclear μ-hydroxo-bridged non-planar structure for the uranyl complex of **3.** The suggested structure of **9** is shown in Fig. 3.

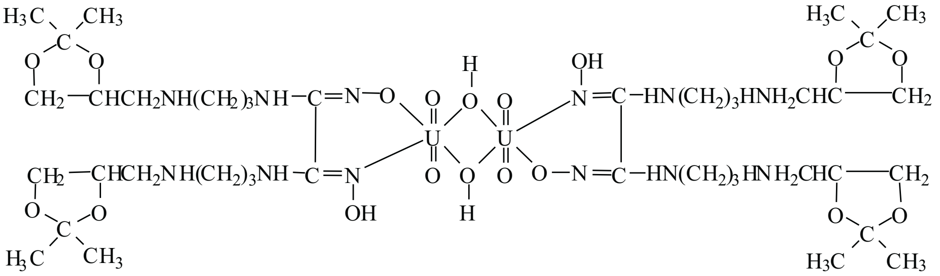

Figure 3. Suggested structure of the dinuclear $UO_2(VI)$ complex of the ligand.

The metal contents were determined by FAAS and the TGA curves for the ligand and its complexes were obtained at a heating rate of 10℃/min in a nitrogen atmosphere over the temperature range of 25–800℃. The decomposition of **3** starts at 211℃ and finishes around 685°C [37]. The complex **4** is stable up to 148°C, and its decomposition starts at 148℃ and is completed at 689°C. The **4** decompose to CoO (residue: 8.34%) in three steps in the temperature ranges 188–350, 350–522 and 522–689°C. In the decomposition process of **4,** the mass losses correspond to two water molecules and were observed at 148℃ (4.08%) [38]. The complexes **5** and **6** decompose and produce NiO (residue: 8.11%) and CuO (residue: 7.73%) in two steps in the temperature ranges at 190–485 and 485–774 for **5** and 154–521 and 521–737℃ for **6**. Thermal studies show that the complexes **7** and **8** are stable up at 160°C for **7** and 185°C for **8**. Complexes **7**, **8** and **9** undergo a complete decomposition to the corresponding thermodynamically stable metal oxides, ZnO (residue: 14.35%), CdO (residue: 20.57%) and U_3O_8 (residue: 57.06%).

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