

Research Article

Synthesis and Spectral Characterization of Homo Binuclear $\text{UO}_2(\text{VI})$, $\text{Th}(\text{IV})$, $\text{ZrO}(\text{IV})$ and $\text{VO}(\text{IV})$ Complexes with Schiff-base Monohydrazone Derivatives

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Abstract

A series of homo binuclear complexes of the type $[\text{M}_2(\text{L}/\text{L}')(\text{NO}_3)_n].m\text{H}_2\text{O}$, [where $\text{M}=\text{UO}_2^{2+}$, Th^{4+} , ZrO^{2+}] and $[(\text{VO})_2(\text{L}/\text{L}')(\text{SO}_4)_2].2\text{H}_2\text{O}$, $\text{L}=1,18\text{-dihydroxy-}1,4,5,8,11,14,15,18\text{-octaaza-}2,3,16,17\text{-tetramethyl-}6,7,12,13\text{-tetraphenyl octadec-}1,3,5,7,11,13,15,17\text{-octene}$ or $\text{L}'=9:10\text{-benzo-}1,18\text{-dihydroxy-}1,4,5,8,11,14,15,18\text{-tetraaza-}2,3,16,17\text{-tetramethyl-}6,7,12,13\text{-tetraphenyl octadec-}1,3,5,7,11,13,15,17\text{-octene}$ $n=4$ for UO_2^{2+} , ZrO^{2+} $n=8$ for Th^{4+} $m=3, 2, 1$ respectively, have been synthesized in template method from ethylenediamine/orthophenylene diamine, benzil monohydrazone and diacetyl

monoxime and characterized on the basis of elemental analysis, thermal analysis, molar conductivity, magnetic moment, electronic, infrared, $^1\text{H-NMR}$ studies. The results indicate that the $\text{VO}(\text{IV})$ ion is penta co-ordinated yielding paramagnetic complexes; $\text{UO}_2(\text{VI})$, $\text{ZrO}(\text{IV})$ ions are hexa co-ordinated where as $\text{Th}(\text{IV})$ ion is octa co-ordinated yielding diamagnetic complexes of above composition.

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1. Introduction

Schiff base compounds are widely studied and used, attracting wide range of applications in organic synthesis and metal ion complexation [1]. The conventional synthesis of such compounds is still very common along with modern synthetic approaches [2]. One major topic of interest is to develop homo-multimetallic complexes because they exhibit distinct reactivity pattern as compared to corresponding monometallic complexes [3]. The magnetic interactions and coupling between the metal ions present in such complexes play key role in both natural and synthetic catalysts [4]. As a result, the synthesis and characterization of homo bimetallic complexes continue to attract attention [5].

Following all these observations and as a part of our continuing research on the coordination chemistry of multidentate ligands [6-10], we report here the synthesis and structural studies of some unknown homo binuclear macrocyclic complexes from the reaction of ethylenediamine/orthophenylene diamine, benzil

monohydrazone and diacetyl monoxime in presence of UO_2^{2+} , ZrO^{2+} , Th^{4+} and VO^{2+} ions.

2. Materials and methods:

All the chemicals used of AR grade. The solvents were purified before use by standard procedures.

2.1 Preparation of benzilmonohydrazone:

The analytical monohydrazones were synthesized according to literature method [11]. As the isolation of Schiff base ligand proved futile, all the metal complexes were synthesized (in an identical method) *in situ* by taking different amount of metal salts, ethylene diamine/orthophenylene diamine, benzilmonohydrazone and diacetyl monoxime.

2.2 Preparation of the complexes of the type $[\text{M}_2(\text{L})(\text{NO}_3)_n].m\text{H}_2\text{O}$, $\text{M}=\text{UO}_2^{2+}$, ZrO^{2+} , Th^{4+} and $[(\text{VO})_2(\text{L})(\text{SO}_4)_2].2\text{H}_2\text{O}$

An ethanolic solution of hydrated $\text{UO}_2(\text{VI})/\text{Th}(\text{IV})/\text{ZrO}(\text{IV})$ nitrates /vanadyl sulphate (1 mmol in 10 mL) was added to a hot ethanolic solution of the mixture of ethylene diamine (1 mmol in 10 mL) and benzil monohydrazone (2 mmol in 20 mL). The resulting mixture was refluxed on a water bath for 2-3 hours during which a coloured complex was precipitated out in each case. The ethanolic suspensions of the complexes were treated with diacetyl monoxime (2 mmol in 20 mL), which is followed by the corresponding metal salts (1 mmol in 10 mL EtOH). The mixture was again refluxed for 3-4 hours on a water bath during which the metal complexes of different colour than the precursor complexes were obtained (Table-1). The progress of the reaction was signaled by colour change of the resulting solution. These were filtered off, washed several times with ethanol followed by ether and finally dried in vacuo over anhydrous CaCl_2 (fused).

2.3 Preparation of the complexes of the type $[\text{M}_2(\text{L}')(\text{NO}_3)_n].m\text{H}_2\text{O}$, $\text{M} = \text{UO}_2^{2+}$, ZrO^{2+} , Th^{4+} and $[(\text{VO})_2(\text{L}')(\text{SO}_4)_2].2\text{H}_2\text{O}$

Same procedure was adopted for preparation of $[\text{M}_2(\text{L}')(\text{NO}_3)_n].m\text{H}_2\text{O}$ and $[(\text{VO})_2(\text{L}')(\text{SO}_4)_2].2\text{H}_2\text{O}$ by taking orthophenylene diamine instead of ethylene diamine.

Analysis and Physical Measurements

The metal contents in the complexes were determined gravimetrically following standard procedures [12]. A weighed quantity of the compound (0.2-0.3 g) was treated with a few drops of concentrated H_2SO_4 and 1 cc. of concentrated HNO_3 . It was heated till all the organic matter decomposed and sulphur trioxide fumes came out. The same process was repeated two to three times to decompose the substance completely. Then it was dissolved in water and the resulting solution was used for analysis of metal ions. Uranium, thorium, zirconium and vanadium were precipitated as ammonium diuranate, thorium oxalate, zirconium mandelate and ammonium vanadate followed by subsequent ignition to their respective oxides as U_3O_8 , thoria (ThO_2), zirconia (ZrO_2) and V_2O_5 . Sulphur was determined as BaSO_4 [12]. Room temperature magnetic susceptibilities were measured by Gouy method [13] using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. The molar conductance measurements were carried out at room temperature with a Toshniwal conductivity Bridge (Model CL-01-06, cell constant 0.5 cm^{-1}) using $1 \times 10^{-3} \text{ M}$ solution of the complexes in DMSO. Carbon, hydrogen and nitrogen contents of the complexes were determined by using a MLW-CHN microanalyser. FTIR spectra in KBr pellets were recorded on a Varian FTIR spectrophotometer, Australia. The electronic spectra of the complexes in DMSO were recorded on a Perkin Elmer spectrophotometer. Thermogravimetric analysis was done by Netzch-429 thermoanalyser. The $^1\text{H-NMR}$ spectra of the complexes were recorded in DMSO- d_6 medium on Jeol GSX-400 model equipment.

Results and discussion

The complexes were formulated from the analytical data and molar conductance data support the suggested formulae (Table 1). The complexes are highly coloured and insoluble in water and common organic solvents such as ethanol, methanol, acetone, CCl_4 , CHCl_3 , benzene and ether but moderately soluble in highly coordinating solvents such as DMF and DMSO. They are non-hygroscopic, highly stable under normal conditions and all of them decompose above 250°C . The molar conductance data in DMSO for the complexes indicate them to be non-electrolyte in nature. However, the conductivity value is higher than as expected for non-electrolytes probably due to partial solvolysis of the complexes in DMSO medium [14].

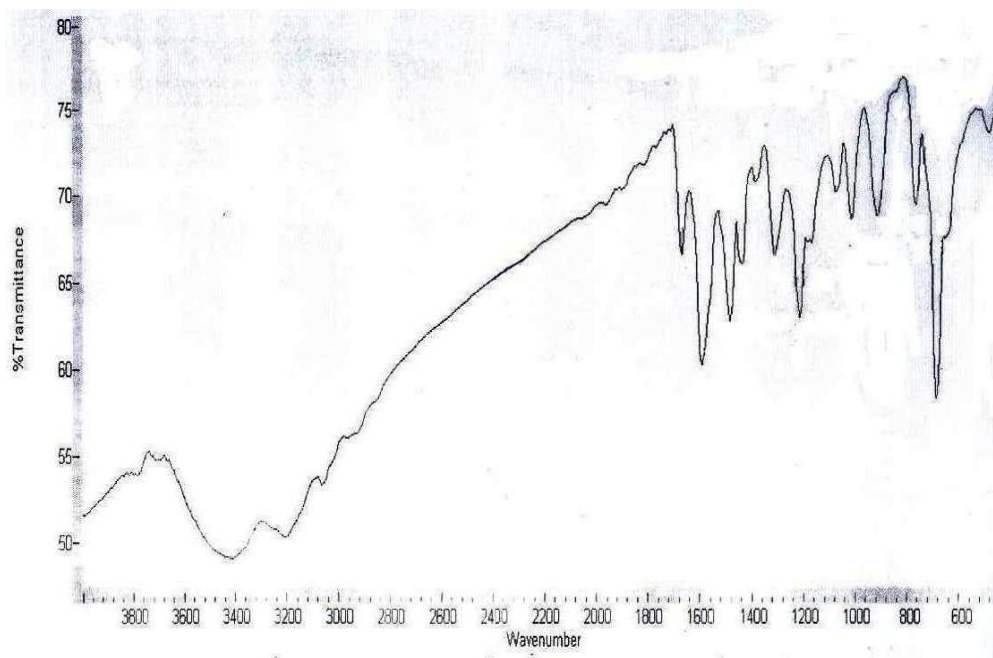
IR spectra:

As the Schiff base ligands could not be isolated, the spectra of the complexes were compared with spectra of the starting materials and other related compounds. Ethylene diamine/ orthophenylene diamine exhibit a pair of strong bands precisely located at ~ 3310 , ~ 3275 and $\sim 1600 \text{ cm}^{-1}$ which may be assigned to asymmetric, symmetric and deformation mode of vibration of NH_2 group respectively. Diacetyl monoxime exhibits strong band in the region $\sim 3350 \text{ cm}^{-1}$ attributed to $\nu\text{N-OH}$. Apart from these, a band system at ~ 1620 and 1720 cm^{-1} are observed in the above compound which may be attributed to azomethine $\nu\text{C=N}$ and carbonyl $\nu\text{C=O}$ vibration respectively. The characteristic $\nu\text{C=O}$, $\nu\text{C=N}$, $\nu\text{N-N}$ and νNH_2 bands of benzilmonohydrazone occur at ~ 1700 , ~ 1615 , ~ 1050 and $\sim 3300 \text{ cm}^{-1}$ respectively.

The IR spectra of the complexes show strong bands appearing at 1625 and $\sim 1070 \text{ cm}^{-1}$ assignable to azomethine $\nu\text{C=N}$ and $\nu\text{N-N}$. The position of the former band at comparatively lower frequency region than usual free $\nu\text{C=N}$ value [15] and that of later band at comparatively higher frequency region than that of free N-N [16] leads us to suggest that azomethine nitrogen atom has taken part in complexation as evidenced from the appearance of band in the region $\sim 475 \text{ cm}^{-1}$ due to $\nu(\text{M-N})$ [17]. The occurrence of N-N band at higher frequency in the IR spectra of the complex is due to reduction of the repulsion between the lone pair of nitrogen atoms as a result of coordination via azomethine nitrogen atoms. It is to be noted that though two $\nu\text{C=N}$ bands are expected due to their presence in different chemical environment, only one band due to $\nu\text{C=N}$ occurs in these complexes. The band due to $\nu\text{N-OH}$ intramolecularly hydrogen bonded continues to appear in the range 3370 cm^{-1} . Consequently the band occurring at $\sim 1245\text{-}1310 \text{ cm}^{-1}$ due to $\nu\text{C-N}$, in case of ligand containing orthophenylene diamine is blue shifted to 1480 cm^{-1} while that in case of ethylene diamine, it practically remains unaltered. This is because C-N assumes a partial double bond character on coordination to the metal ion through resonance in the former case.

Table 1 Analytical and physical data of the complexes

Sl. no.	Compounds	Colour	Yield (%)	Λ_m^a	Found(calc.)%				
					C	H	N	S	M
1	$[(UO_2)_2(L)(NO_3)_2]3H_2O$	Lemon yellow	64	19.34	30.77 (30.81)	2.95 (2.97)	11.32 (11.35)	-	32.13 (32.16)
2	$[(UO_2)_2(L')(NO_3)_2]3H_2O$	Tint yellow	61	18.35	32.91 (32.94)	2.94 (3.00)	10.94 (10.98)	-	31.07 (31.11)
3	$[(Th)_2(L)(NO_3)_4]H_2O$	Cream	62	26.59	26.09 (26.14)	2.38 (2.40)	19.22 (19.26)	-	26.55 (26.60)
4	$[(Th)_2(L')(NO_3)_4]H_2O$	Cream	68	22.67	30.95 (30.99)	2.55 (2.58)	10.31 (10.33)	-	28.49 (28.53)
5	$[(ZrO)_2(L)(NO_3)_2]2H_2O$	Daffodil	65	23.50	35.14 (35.18)	3.22 (3.24)	12.93 (12.96)	-	14.01 (14.04)
6	$[(ZrO)_2(L')(NO_3)_2]2H_2O$	Daffodil	63	20.41	42.46 (42.49)	3.67 (3.70)	14.14 (14.16)	-	15.29 (15.34)
7	$[(VO)_2(L)(SO_4)_2]2H_2O$	Green	57	12.74	43.31 (43.34)	4.24 (4.26)	11.33 (11.38)	6.45 (6.50)	10.33 (10.36)
8	$[(VO)_2(L')(SO_4)_2]2H_2O$	Chocolate	59	11.54	48.70 (48.74)	4.22 (4.25)	10.81 (10.83)	6.14 (6.18)	9.81 (9.86)

**Figure 1** IR spectra of $[(UO_2)_2(L)(NO_3)_2]3H_2O$

The uranyl complexes exhibit a strong band at $\sim 950\text{--}930\text{ cm}^{-1}$ and the medium intensity band at $\sim 830\text{--}815\text{ cm}^{-1}$ assignable to $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$ and $\nu_{\text{s}}(\text{O}=\text{U}=\text{O})$ mode respectively [18]. The co-ordination of nitrate ions in unidentate manner has been indicated by the appearance of additional band at the region $\sim 1480\text{ cm}^{-1}$ and $\sim 1380\text{ cm}^{-1}$ corresponding to the ν_4 and ν_1 modes of the vibration respectively, of coordinating nitrate ion under C_{2v} symmetry [19]. The magnitude of $\Delta\nu = (\nu_4 - \nu_1) = 100\text{ cm}^{-1}$ shows the unidentate coordination of the nitrate ion. The zirconyl complexes exhibit one strong band in the region $890\text{--}870\text{ cm}^{-1}$ which can be attributed to the $\nu(\text{Zr}=\text{O})$ as reported earlier [20] indicating the presence of $(\text{Zr}=\text{O})^{2+}$ moiety in these complexes. In the oxovanadium polychelates strong bands at $\sim 955\text{ cm}^{-1}$ are assigned to $\nu(\text{V}=\text{O})$ modes [21,22]. However, these bands are absent in the complexes of Th(IV). However in vanadyl complexes, an additional series of four bands appeared at $\sim 1160, \sim 1115, \sim 875$ & $\sim 650\text{ cm}^{-1}$ indicating the coordination of sulphate group in unidentate manner through oxygen atom [23]; the symmetry being lowered from T_D to C_{3v} upon coordination. Besides the bands observed at $\sim 3450\text{ cm}^{-1}$ may be assigned to $\nu(\text{O-H})$ of coordinated or lattice water. However all the complexes lost water when heated to $\sim 100^\circ\text{C}$ indicating the presence of lattice water molecules which has been confirmed by thermal analysis. The representative spectra of $[(\text{UO}_2)_2(\text{L})(\text{NO}_3)_2]3\text{H}_2\text{O}$ complex is shown in Fig. 1.

Thermal analysis:

All these complexes follow the same pattern of thermal decomposition. The complexes remain almost unaffected

upto $\sim 40^\circ\text{C}$. After this a slight depression upto $\sim 100^\circ\text{C}$ is observed. The weight loss at this temperature range is equivalent to one water molecule for the complexes (3) and (4), two water molecule for the complexes (5), (6), (7) and (8) three water molecule for the complexes (1) and (2) indicating them to be lattice water in conformity with our earlier observations from analytical and IR spectral investigations. The anhydrous complexes remain stable upto $\sim 340^\circ\text{C}$ then the complexes show rapid degradation presumably due to decomposition of organic constituents of the complex molecules as indicated by the steep fall in the percentage weight loss. The decomposition continues upto $\sim 650^\circ\text{C}$ and reaches to a stable product in each complex as indicated by the consistency in weight in the plateau of the thermogram. The decomposition temperature varies for different complexes as shown in Table 2. The representative thermogram of $[(\text{VO})_2(\text{L})(\text{SO}_4)_2]2\text{H}_2\text{O}$ complex is shown in Fig. 2.

The thermal stability of the complexes decreases in the order:

(L) complexes: $\text{ZrO(IV)} > \text{UO}_2(\text{VI}) > \text{VO(IV)} > \text{Th(IV)}$

(L') complexes: $\text{UO}_2(\text{VI}) > \text{ZrO(IV)} > \text{Th(IV)} > \text{VO(IV)}$

In the complexes, weight loss was encountered at $\sim 40^\circ\text{C}$ to $\sim 100^\circ\text{C}$ with a broad endothermic peak at the same temperature corresponding to one, two and three molecules of water of crystallization [24].

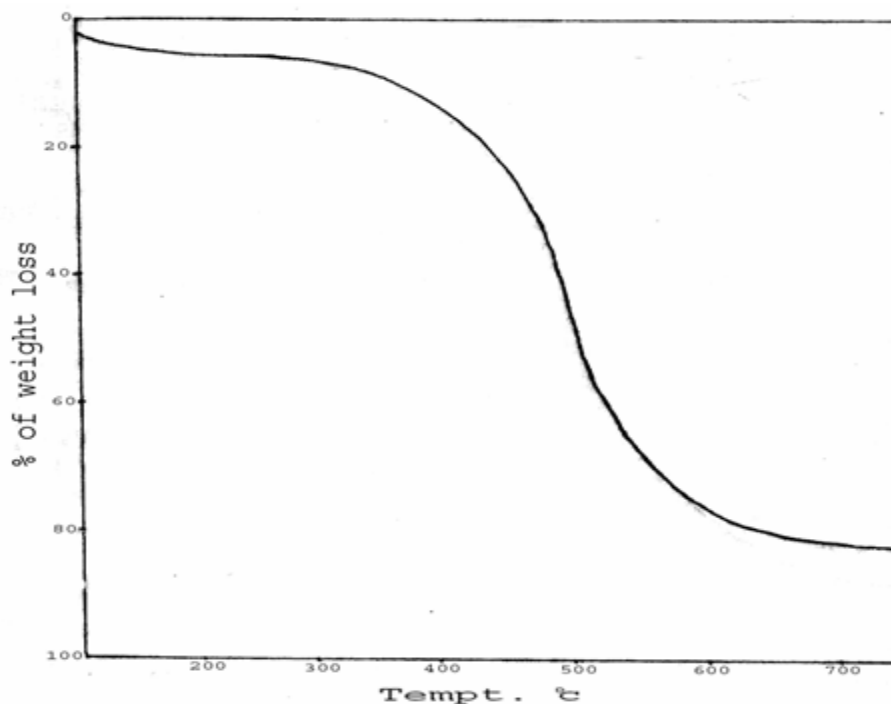


Figure 2 Thermogram of $[(\text{VO})_2(\text{L})(\text{SO}_4)_2]2\text{H}_2\text{O}$

Table 2 Important features of thermo gravimetric analysis (TGA)

Sl. no.	Total wt. for TG(mg)	Temp. range of water loss (0C)	% of water loss Found (calcd.)	Decomposition temperature (°C)	% weight of residue Found (calcd.)	Composition of the residue
1	97	40-110	3.62 (3.64)	390-615	37.42 (37.47)	U ₃ O ₈
2	102	50-100	3.48 (3.52)	395-630	36.21 (36.25)	U ₃ O ₈
3	94	50-110	1.00 (1.03)	365-635	30.24 (30.27)	ThO ₂
4	95	50-100	1.07 (1.10)	360-615	29.40 (29.43)	ThO ₂
5	93	40-110	3.11 (3.16)	400-650	21.61 (21.65)	ZrO ₂
6	96	40-110	2.99 (3.03)	380-610	20.69 (20.74)	ZrO ₂
7	91	40-105	3.61 (3.65)	375-660	18.46 (18.49)	V ₂ O ₅
8	87	50-115	3.25 (3.28)	330-670	17.56 (17.60)	V ₂ O ₅

Electronic spectra:

The electronic spectra of the UO₂(VI) complexes are quite similar. The complexes display mainly one weak band at ~450 nm and a highly intense band at ~270-280 nm, which may be due to $^1\Sigma_g^+ \rightarrow ^3\Pi_u$ transitions and charge transfer transitions respectively [25]. It may be noted that the band occurring at 360 nm is due to uranyl moiety because of apical oxygen $\rightarrow f^0(U)$ transition is being merged with the ligand band due to $n \rightarrow \Pi^*$ transition as evident from broadness and intensity. The electronic spectra of ZrO(IV) complexes exhibit only one extra highly intensive band in the region 350-380 nm which may be due to charge transfer band besides the ligand bands. However the electronic spectra could not provide structural details of these complexes. The electronic spectra of VO(IV) complexes show three bands at ~12330, ~18480 and ~25860 cm⁻¹ corresponds to transitions, $d_{xy}(b_2) \rightarrow d_{xz}d_{yz}(e)$, $d_{xy}(b_2) \rightarrow d_{x^2-y^2}(b_1)$ and $d_{xy}(b_2) \rightarrow d_z^2(a_1)$ respectively, indicating the complexes to be in distorted octahedral environment under C_{4v} symmetry [26].

¹H NMR spectra:

The ¹H-NMR spectra of the diamagnetic complexes are recorded in DMSO-d₆ medium. The complexes do not show any signal attributed to amino protons, suggesting that the proposed skeleton has been formed by condensation reactions. The complexes show a broad multiplet at δ 6.96-7.34 ppm corresponding to aromatic (C₆H₅-C=N; 20H) protons of four phenyl groups and a signal appear in the region δ 2.03-2.45 ppm corresponding to imine methyl (CH₃-C=N; 12H) protons [27,28]. In L complexes an additional peak at δ ~3.4 ppm is observed corresponding to (NCH₂CH₂N; 4H) protons [29].

Magnetic moment

All the complexes except VO(IV), are diamagnetic consistent with their d⁰ and f⁰ electronic configuration. The magnetic moment values for the oxovanadium(IV) complexes (7) and (8) lie in the range 2.36-2.48 BM. These values are less than spin-only value required for

two unpaired electrons indicating spin-spin coupling in the solid state between unpaired electrons belonging to different VO(IV) ions in the same structural unit [30].

Conclusion

Based on the foregoing observations the following tentative structures have been proposed for the present complexes.

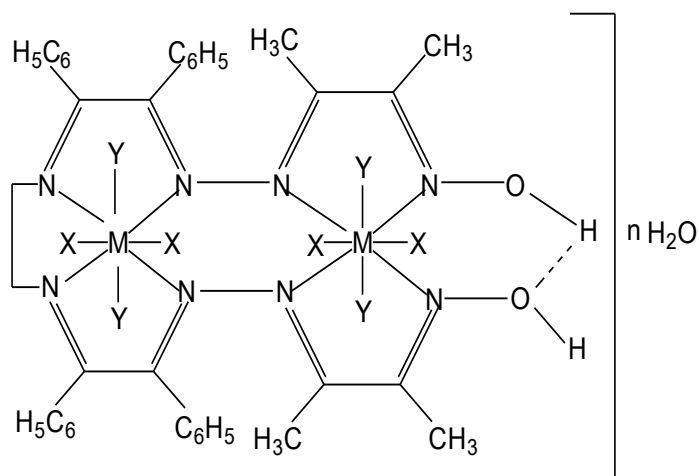


Figure 3 Complexes with L ligand

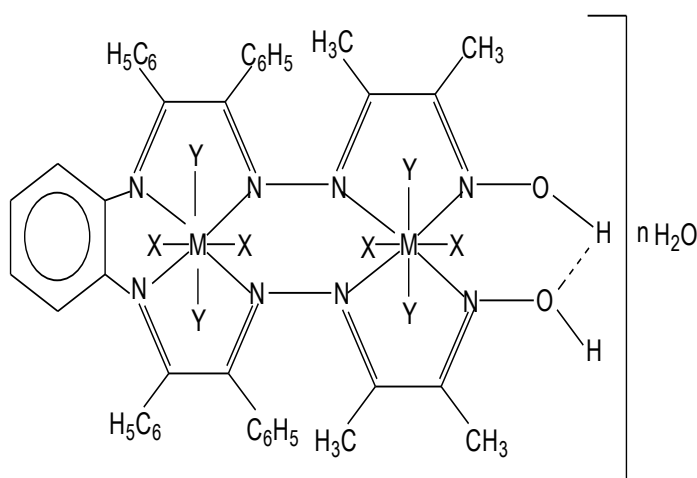


Figure 4 Complexes with L' ligand

$M = M' = \text{UO}_2(\text{VI}), \text{ZrO}(\text{IV})$ and $\text{Th}(\text{IV})$

$X = \text{NO}_3^-$ for $\text{Th}(\text{IV})$

$X = \text{O}$ for $\text{UO}_2(\text{VI})$ and $\text{ZrO}(\text{IV})$

$Y = \text{NO}_3^-$

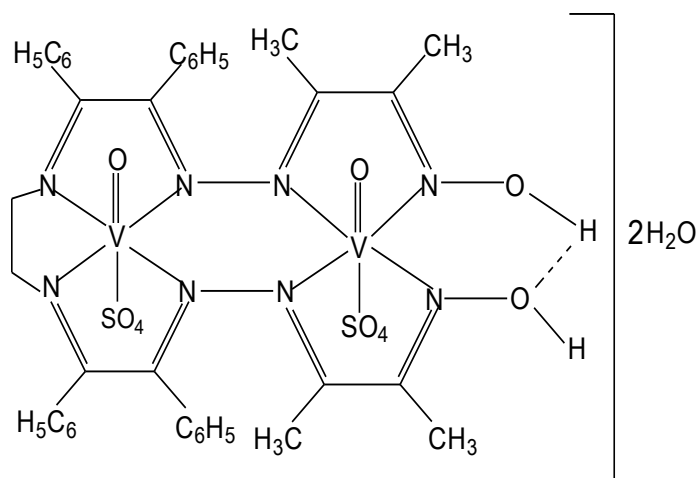


Figure 5 $[(\text{VO})_2(\text{L})(\text{SO}_4)_2]2\text{H}_2\text{O}$

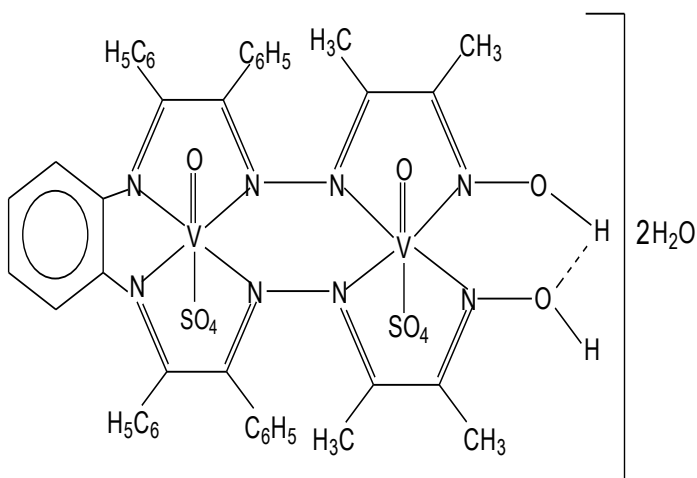


Figure 6 $[(\text{VO})_2(\text{L}')(\text{SO}_4)_2]2\text{H}_2\text{O}$

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