Study of the ternary complexes of Fe(III) and Uo_2(II) with O-Tolidine derivatives with 2-aminopyridine and oxalic acid in the solid state

N.G. El-Kholy

Chemistry Department, Faculty of Science (Girl's), Al-Azhar University, Nasr City, Cairo, Egypt
amerahobiana2012@yahoo.com

Abstract : The ternary complexes of Fe(III) and Uo_2(II) with three Schiff base ligands, -4,4-N,N-bis (furfuryllidene) O -Tolidine,- 4,4-N,N-bis (methyl-2-thienylidene)O-Tolidine, and 4,4-N,N-bis (4-hydroxy-3-methoxy benzylidene) O-Tolidine, (L^1,L^2 and L^3) respectively with 2-aminopyridine (2-Ampy) and oxalic acid (OX) have been studied in solid state.The mixed ligand complexes have been isolated and characterized based on elemental microanalysis, molar conductance, thermal analysis and mass spectroscopy as well as spectral (UV-Vis, IR, ^{1}HNMR, mass and magnetic moment measurements. The molar conductance measurements reveal that the complexes are non-electrolytic 1:1, and 1:2 electrolytic nature of the metal complexes. Bonding of the ligands with the metal ions is deduced from IR spectra. The ligands are coordinated to the metal ions in ternary (terdendate) manar with ONO donor sites of the carbonyl oxygen, azomethine nitrogen and phenolic oxygen. Thermal studies indicate weight loss associated with water molecules. All synthesized compounds were screened for their antimicrobial activity against gram positive, gram negative bacteria and fungi. The biological evaluation study showed low to high bacterial activity compared with the ligands and their iron and uranyl metal complexes.

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1- Introduction

Schiff base ligands have been in the chemistry catalogue for over 150 year (1). Schiff bases are compounds containing the azomethine group (R–CH=N–) and are usually formed by condensation a primary amine with an active carbonyl compounds(2-6).

The chemistry of biological science has produced a number of compounds that are now employed as antibacterial agents. Such type of compounds revealed great promise in this area is the Schiff bases(7).

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions(8). Transition metal compounds containing Schiff base ligands have also been of great interest for many years(9). A great deal of work has been done not only from an inorganic and biological point of view(10-12), but also in catalysis(13-14). Schiff base complexes have acquired special significance due to their interesting magnetic properties(15,16), spectroscopic characteristics as well as important biological application (17-19) and catalytic activities.

Schiff bases are reported to exhibit antibacterial(20-22), antifungal activity(23) and antitumor activity(24). In a continuation of our earlier studies on the ligating properties of Schiff base(25-27). The polydentate ligands 2,5 N,N-bis (dimethyl-1-phenyl-4-pyrazoline-5-one) furanidine, 2,5-N,N-bis (pyridine)furanidine and 2,5-N,N-bis (2-thiophenol) furanidine have been prepared and identified. The chemical behaviour of these ligands towards some metal cation such as Co(II), Cd(II), Hg(II), Fe(III) and Uo_2(II) was studied(28).

Herein we report synthesis and structure studies of Fe(III) and Uo_2(II) complexes of heterocyclic ligands of 4,4-N,N-bis (furfurylidene)-O-Tolidine (L^1)-4,4-N,N-bis(methyl-2-thienylidene) O-Tolidine (L^2)-4,4-N,N-bis (4-hydroxy-3-methyl benzylidene) O-Tolidine (L^3).

The structural chemistry of the ligands and their complexes is the aim of this manuscript in addition to test whether any of synthesized compounds would prove to be effective in controlling the growth of a new important bacteria and fungi in attempt to understand the influence of metal ion/ligand nature on the biological properties.

2- Experimental

- Reagents

All chemicals were of reagent grade which used without further purification and obtained from BDH, Merck Aldrich, sigma and Fluka. They include $Fe(NO_3)_3.9H_2O$; $Uo_2(NO_3)_2.6H_2O$–O-Tolidine; oxalic acid; 2-aminopyridine; furfuraldehyde; 2-methyl thienyl ketone; 4-hydroxy-3-methoxybenzaldehyde; diethyl ether; dimethyl formamide (DMF)' dimethyl sulphoxide (DMSO); ammonia solution; Variamine blue; ethylene-diaminetetraactic acid disodium salt (EDTA); ethyl alcohol was analytical grade and was purified by standard method prior its use(29). Concentrated nitric acid and perchloric acid are reagent grade and used as supplied.

Physical measurements

Elemental analysis (C,H,N,S) were carried out using Perkin–Elmer 2408 CHN analyzer at the microanalytical center, Cairo University, Gizza, Egypt. Metal content were determined complexometrically(30) by standard EDTA titration. Melting or decomposition points of the prepared compounds were measured by electronic melting point apparatus: Giffin & George made in Britain.

Mass spectra

Mass spectra were recorded at 70 ev and 300°C on a Hewlett-Packard mass spectrometer model MS 5988 at the microanalytical center, Cairo University, Giza, Egypt.

Electronic spectra

Electronic spectra of solutions of ligand, and its metal complexes on DMF and the solid reflectance spectra were recorded on a Jasco model V-550 UV-Vis spectrophotometer.

IR spectra

IR spectra of the prepared compounds were recorded as KBr discs using a Perkin – Elmer 437 IR spectrometer (400-4000cm^{-1}).

^{1}H-NMR

^{1}H-NMR spectra were recorded using Brucker ARX-300 spectrometer using DMSO-d_6 as a solvent. Magnetic susceptibilities of the metal complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alpha product, model MKI magnetic susceptibility balance. The effective magnetic moments were calculated using the relation $\mu_{eff} = 2.828\ (X_m, T)^{1/2}$ B.M. where X_m is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds.

Thermogravimetric analysis

A thermogravimetric analyzer TGA-50 SHIMA, VZU and DTA, TA50 Shimadzu, at the micro Analytical Center, Mubarak City for Scientific Research, Borg El-Arab, Alexandria, Egypt and at the Microanalytical Center, Cairo, University, Giza, Egypt, were used to record simultaneously the TG curves, the experiments were carried out in dynamic nitrogen atmosphere (20 ml min^{-1}) with a heating rate 10°C min^{-1} in the temperature range 20-1000°C using platinium crucibles.

Molar conductance

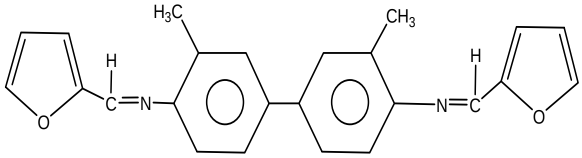
Highly sintered α-Al_2O_3 was used as a reference. The molar conductance measurements were measured in solution of the complexes in DMF (10^{-3}M) using JEN WAY 4510 conductivity meter.

Antibacterial activity

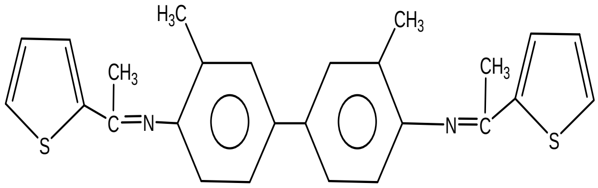
Antibacterial activity of all prepared compounds, free ligands and their ternary complexes were tested using the diffusion agar method(31). The chosen strains were *Staphylococcus aureus* (ATCC 25923), *Streptococcus pyogenes* (ATCC 19615) as Gram-positive bacteria, *Pseudomonas phase olicola* (GSPB 2828) *Pseudomonas* fluorescens (Sa7) as Gram-negative bacteria and *Fusarium oxysporum*, *Aspergillus fumigatus* as fungi. The antibiotic chloramphencol was used as standard reference in the case of Gram-negative bacteria. Cephalothin was used as standard reference in the case of Gram-positive bacteria, cycloheximide was used as standard antifungal reference, and potato dextrose agar (PDA) as a medium.

Synthesis of Schiff base ligands :

The three Schiff base ligands L^1-L^3 (Fig. 1) were prepared by condensation of O-Toluidine with aldehyde or ketone [e.g. furaldehyde, methyl-2-thienyl ketone and 4-hydroxy-3-methoxy-benzaldehyde] with continuous stirring in 1:2 molar ratio, respectively in ethanolic solution for 3hr on water bath then cooled. After cooling, the product was filtered off, recrystallized from ethanol, washed with diethyl ether and finally dried in a desiccator over anhydrous calcium chloride to give orange yellow powder of Schiff base ligand (L^1) in 80.2% yield or brown powder of Schiff bas ligand (L^2) in 75.8% yield and yellow powder of Schiff base ligand (L^3) in 83.7% yield. The proposed structure of the ligands, (Fig. I) is in a good agreement with the stoichiometry calculated from their analytical data (Table 1).

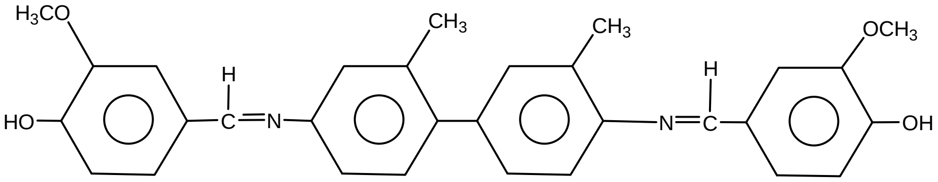


L^1[4,4-N,N bis (furfurylidene)-O-Tolidine $C_{24}H_{20}N_2O_2$ (M.wt=368.46)



L^2(4,4-N,N-bis (methyl-2-thienylidene)o-toluidine $C_{26}H_{24}N_2S_2$

(M.wt. = 428.66)



L^3 (4,4-N,N-bis (4-hydroxy-3-methoxy benzylidene)o-tolidine $C_{30}H_{28}N_2O_4$ (M. wt. 480.60)

Fig. 1. Structure, name and abbreviation of ligands, L^1-L^3

Synthesis of the ternary complexes

A general method has been adopted to prepared the ternary (mixed) ligand complexes in which the prepared Schiff base ligands L^1–L^3 act as primary ligands and the secondary ligand was 2-amino pyridine or oxalic acid. A hot ethanolic solution (30 ml) of the appropriate metal nitrate salt namely, ($Fe(NO_3)_3$. $9H_2O$) and ($Uo_2(NO_3)_2.6H_2O$ (0.02 mol) was added dropwise to a mixture of the Schiff base ligands (L^1–L^3) (0.01 mol) and 2-aminopyridine (0.01 mol) or oxalic acid (0.01 mol) with stirring. The mixture was heated under reflux for three hours on the water bath, during this period, the precipitation was completed from, and collected by filtration, then washed with ethanol and diethyl ether and dried in a desiccators over anhydrous calcium chloride. These complexes are soluble in DMF and DMSO while insoluble in most organic solvents. All these (1-12 complexes) were analyzed by using different available techniques which agree well with the suggested molecular formula. The analytical data of the ligands and their metal complexes with their physical properties are summarized in Table 1.

3. Results and Discussion

Condensation of the aldehyde with amine readily give rise to the corresponding imines "Schiff base ligands", "L^1–L^3" (Fig. 1). Their reaction with metal ions Fe(III) and Uo_2(II) afford the ternary complexes (1-12). Table 1- shows the analytical data and some physical properties of the prepared compound. The suggested structure of the prepared compounds were elucidated by elemental analysis (Table 1), mass spectra, magnetic moments, conductance and TGA measurements. Moreover, the antibacterial activity of the free ligands and its ternary complexes were tested against different strains of bacteria at different concentrations.

Infrared spectra

In IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation, all data are listed in Table 2. The band assigned to the azomethine group in all free Schiff base ligands were observed at $\upsilon_{C=N}$ 1628-1588cm^{-1}(32) and shifted to lower or higher wave numbers ranging from (1708-1584) cm^{-1} in the spectra of all complexes. This indicates the participation of the nitrogen atom of the azomethine group in coordination(25, 33). Also, a band was observed at 874cm^{-1} attributed to $\upsilon_{C\text{–}O\text{–}C}$ of heterocyclic ring of furyl ring of ligand (L^1) which shifts to lower frequencies in the spectra of metal complexes (2-4) in the region 824-804cm^{-1}, suggesting the coordination of metal ions through the oxygen atom of furyl ring moiety supported from ^{1}H–NMR data.

The observed band, at 824 cm^{-1} in the spectrum of free ligand (L^2) was assigned to $\upsilon_{C\text{–}S\text{–}C}$ stretching vibration of thiophene moiety(34,35) which shifts to lower frequencies in the spectra of metal complexes (5-8) in the region 815-804cm^{-1}, suggesting the coordination of metal ions through the sulphur atom of thiophene moiety supported from ^{1}H–NMR data.

The presence of IR broad bands of metal complexes are in the range 3442-3206-cm^{-1} indicate the presence of coordinated or/and lattice water molecules supported from thermal analysis(25,36).

The IR spectra of ternary complexes exhibited bands in the range 1668-1500 cm^{-1} due to vibration of pyridine ring suggesting the participation of ring nitrogen in complex formation(37).

The nitrato complexes (1-12) show three bands at 1498-1352cm^{-1}, 1310-1150cm^{-1}and 1092-1020cm^{-1} corresponding to unidentate coordination mode of nitrate group while there are two characteristic bands at 1386-1382cm^{-1} and 808-715cm^{-1} assigned to ionic nitrate(38-40). All these results are consistent with the conductance data. The IR spectra of metal complexes reveal newly medium and/or weak bands at 630-500cm^{-1}, 500-435cm^{-1} and 450-423cm^{-1} assigned to $\upsilon_{M\text{-}O}$, $\upsilon_{M\text{–}N}$ and $\upsilon_{M\text{–}s}$ respectively(41). These new bands indicate a good evidence for the participation of O,N and S donors in complex formation.

The uranyl complexes (2, 4, 6, 8, 10, 12) show strong absorption bands in the region 946-918cm^{-1} assigned to the antisymmetric $\upsilon_{(O=U=O)}$ vibration(8,42,43).

Table (1): Analytical data and some physical properties of the ligands and their metal complexes.

Comp. No.	Empirical formula	Molecular weight found (calcd)[a]	Color	Λm[b]	m.p. (°C)	Elemental analysis, found (calcd.(%)				
						C	H	N	S	M
L^1	$C_{24}H_{20}N_2O_2$	368.20 (368.46)	Yellow	--	230	78.10 (78.23)	5.55 (5.47)	7.80 (7.60)	--	-
1	$[Fe_2(L^1)(2\text{-}ampy)_2(NO_3)_5(H_2O)]NO_3.H_2O$	(1077) (1076.50)	Brown	56	>320	37.60 (37.93)	3.98 (3.37)	15.90 (15.62)	--	10.45 (10.38)
2	$[Uo_2)_2(L^1)(2\text{-}ampy)_2(NO_3)_3(H_2O)_3]NO_3.H_2O$	(1417) (1416.86)	Dark brown	59	>320	28.4 (28.82)	3.04 (2.85)	10.02 (9.89)	--	34.0 (33.6)
3	$[Fe_2(L^1)(OX)(NO_3)_4(H_2O)_2]\frac{1}{2}H_2O$	(858) (861.27)	Brown	22	>320	55.1 (55.63)	3.06 (2.93)	8.99 (9.76)	--	12.77 (12.97)
4	$[Uo_2)_2(L^1)(OX)(NO_3)_2(H_2O)_4]H_2O$	(1211.8) (1210.66)	Page	33	>320	25.3 (25.79)	2.7 (2.5)	4.20 (4.63)	--	39.00 (39.32)
L^2	$C_{26}H_{24}N_2S_2$	428.15 (428.66)	Page	--	160	72.5 (72.85)	5.55 (5.64)	6.30 (6.54)	15.02 (14.96)	--
5	$[Fe_2(L^2)(2\text{-}ampy)_2(NO_3)_5(H_2O)]NO_3\frac{1}{2}H_2O$	(1128) (1127.71)	Dark brown	67	>300	38.1 (38.34)	3.10 (3.49)	14.20 (14.91)	5.99 (5.69)	10.00 (9.91)
6	$[Uo_2)_2(L^2)(2\text{-}ampy)_2(NO_3)_3(H_2O)_3]NO_3$	(1460) 1459.08)	black	74	>320	29.20 (29.63)	3.4 (2.90)	10.01 (9.60)	4.85 (4.39)	32.30 (32.63)
7	$[Fe_2(L^2)(OX)_2(H_2O)_4]2NO_3.1\frac{1}{2}H_2O$	(940) (939.53)	Brown	123	>320	38.06 (38.36)	4.01 (3.76)	6.04 (5.96)	7.01 (6.82)	12.20 (11.89)
8	$[Uo_2)_2(L^2)(OX)(NO_3)(H_2O)_5]NO_3.4\frac{1}{2}H_2O$	1350 1351.95	Pale yellow	91	>320	24.50 (24.87)	3.02 (3.21)	4.6 (4.15)	4.99 (4.74)	35.3 (35.21)
L^3	$C_{30}H_{28}N_2O_4$	(480.60) 480.3	Yellow	--	190	74.50 (74.97)	6.1 (5.87)	6.12 (5.83)	--	--
9	$[Fe_2(L^3)(2\text{-}ampy)_2(NO_3)_6(H_2O)_2]H_2O$	1207 (1206.68)	Black	37	>320	39.4 (39.81)	4.02 (3.84)	13.2 (13.93)	--	10.00 (9.26)
10	$[Uo_2)_2(L^3)(2\text{-}ampy)_2(NO_3)_4(H_2O)_4]H_2O$	1550.2 1547.06	Dark Brown	11	>320	32 (31.05)	3.30 (3.26)	10.1 (9.06)	--	30.20 (30.77)
11	$[Fe_2(L^3)(OX)_2(H_2O)_6]2NO_3.H_2O$	1019 1018.50	Dark brown	132	>300	40.20 (40.09)	4.04 (4.16)	6.0 (5.50)	--	11.30 (10.97)
12	$[Uo_2)_2(L^3)(OX)(H_2O)_8]2NO_3.3H_2O$	1428.8 (1430.92)	Pale yellow	121	>300	26.9 (26.86)	3.30 (3.52)	3.70 (3.92)	--	32.99 (33.27)

[a] Found values obtained from mass spectra

[b] Molar conductance (Ω^{-1} cm^2 mol^{-1}) of 1 x 10^{-3}M solution in DMF at room temperature

Table (2): Characteristic IR bands (cm^{-1}) of the ligands and their metal complexes

Comp. No.	υC=N (azome.)	υ pyridine	υCH (aromatic)	$\upsilon_{C\text{-}O\text{–}C}$ ring	$\upsilon_{C\text{-}S\text{–}C}$ ring	$\upsilon_{M\text{-}O}$	$\upsilon_{M\text{-}N}$	$\upsilon_{M\text{-}S}$	υ_{OH} (phenol/H_2O)	Addition bands
L^1	1628	1560	3124	874	-	-	-	-	-	-
1	1620	1516	3170	824	-	515	445	-	3394	1384,765(ionic NO_3) and 1494, 1170, 1020(coord. NO_3)
2	1624	1550	2931	818	-	530	447	-	3408	1384, 758 (ionic NO_3) and 1494, 1284, 1026 (coord NO_3) and 924 (O=U=O)
3	1708	1668	3185	804	-	546	474	-	3350	1352, 1306, 1092 (coord. NO_3). 1498, 1310, 1030 (coord NO_3) and O=U=O).
4	1685	1632	2974	806	-	520	490	-	3442	1498,1310, 1030 and 946 (O=U=O)
L^2	1620	1565	3066	-	824	-	-	-	-	------
5	1624	1560	2926	-	814	530	485	450	3406	1384, 715, (ionic NO_3)1494, 1298, 1036(coord. NO_3)
6	1624	1558	3162	-	815	506	465	430	3346	1382, 758(ionic NO_3) 1494, 1150, 1030 (coord. NO_3) and 918 (O=U=O)
7	1670	1635	3185	-	804	526	456	433	3318	1386, 735 (ionic NO_3), 1494 1300, 1036 (coord. NO_3)
8	1655	1624	2960	-	808	500	450	423	3438	1384, 730 (ionic NO_3), 1498, 1302. 1035 (coord. NO_3) and 946 (O=U=O)
L^3	1588	1510	2936	-	-	-	-	-	3416	----
9	1584	1500	3152	-	-	630	500	-	3300	1294, 1028 (coord. NO_3)
10	1666	1635	3156	-	-	510	435	-	3335	1498, 1165, 1030 (coord. NO_3) and 930 (O=U=O)
11	1668	1520	3165	-	-	531	480	-	3206	1386, 808 (ionic NO_3) 1498, 1304, 1035 (coord. NO_3)
12	1600	1516	3122	-	-	550	490	-	3420	1382, 804 and 946(O=U=O)

^{1}H-NMR spectra : the proton magnetic resonance of the free Schiff base ligands, L^{-1}–L^3 and their diamagnetic ternary complexes (2,4,6,8,10,12) have been recorded in DMSO-d_5 as solvent (Table 3). The ^{1}H-NMR spectrum of the ligand L^1–L^3 (Fig. 2) displays the following signals: at 8.47-7.21 and 2.57-2.30 ppm that was assigned to azomethine and CH_3 protons respectively. The multiplet signals of free ligands L^1–L^3 at 7.57-7.31 ppm assigned to aromatic protons.

In addition, signals peaks at 6.65-6.96ppm attributed to pyridine protons$^{(44)}$. The spectra of ligand L^2 shows a signal at about 9.87 ppm attributed to CH of thinly ring. Also, the ^{1}H-NMR spectrum of ligand L^3 showed a signals peaks at (3.93-3.40) and (9.80-8.48)ppm that was assigned to OCH_3 protons and OH protons respectively.

The comparison of ^{1}H-NMR data of the free ligands and their Uo_2(II) complexes clarifies the mode of coordination between the ligand and its metal ion. Upon complexation, it was found that the spectra display a significant shift of the signals due to azomethine protons indicating their involvement chelation.

The spectra of the ligand L^1 shows a signal at about δ 9.61ppm attributed to CH of furyl ring, this signal in metal complexes is shifted to upfield from 9.61-9.78 which indicate that the participation occur in this ring, also, in uranyl metal complexes of L^2 (6,8) there is shift to down field in spectra of thinly ring from 9.87-8.21 ppm due to complexation.

Moreover, the spectra of ternary complexes (2,4,6,8) showed signals at (7.62-6.05) ppm due to up field shift which suggest the participation of pyridine nitrogen in coordination to the metal ion(45). Also in metal complexes of L^3 (10, 12) showed signals at (3.99-3.80) ppm and (9.83-8.48) ppm due to up field shift in the spectra of OCH_3 protons and OH proton respectively (Table 3), (Figs. 2-9).

Molar conductivity measurements:

The metal complexes were dissolved in DMF and the molar conductivities of 10^{-3} M of their solutions at room temperature were measured. Table (1) shows the molar conductance values of the metal complexes and it is concluded from the results only the metal (1,2,5,6,8) complexes are found to have molar conductance (91-56 $ohm^{-1}mol^{-1}$ cm^2 indicting that these complexes are 1:1 electrolytic nature. On the other hand, the molar conductivity values of metal complex (7,11,12) are found to be 121-132ohm^{-1} mol^{-1} cm^2 suggesting 1:2 electrolytic nature, while the other metal complexes (3,4,9,10) having conductance values of 11-37 ohm^{-1} mol^{-1} cm^2 indicating that these complexes are neutral (46,47).

Magnetic susceptibility and electronic absorption spectrum:

The room temperature magnetic moments and electronic spectral data of the metal complexes are listed in Table4.

The magnetic moments values for Fe(III) complexes are 5.41-5.92 B.M. these data are closed to that reported for five unpaired electrons. Uo_2(II) complexes are diamagnetic as expected for d^{10} system(4,48,49).

Table (3): ^{1}H-NMR spectral data of Schiff base ligands (L^1–L^3) and their diamagnetic Uo_2(II) complexes (δ, ppm)

Comp. No.	Azomethine protons	Aromatic (and/or) pyridine protons	CH of furyl ring	CH of thinly ring	CH_3 protons	OCH_3 protons	OH protons
L^1	8.37, 7.92	7.57-6.65 [6H]	9.61	-	2.50, 2.35	-	-
2	8.36, 7.94	7.62-6.53[14H]	9.78	-	2.88, 2.57	-	-
4	7.47, 7.10	7.07-6.05[6H]	9.75	-	2.58, 2.31	-	-
L^2	8.47, 7.21	7.31-6.65[6H]	-	9.87	2.30, 2.42	-	-
6	7.94, 7.41	7.16-6.50[14H]	-	9.75	2.80, 2.57	-	-
8	7.58, 7.56	7.55-7.08[6H]	-	8.21	2.57, 2.32	-	-
L^3	7.64, 7.55	7.47-6.96[12H]	-	-	2.57, 2.44	3.93, 3.40	9.80, 8.47
10	7.94, 7.62	7.43-6.52[20H]	-	-	2.90, 2.75	3.99, 3.90	9.77, 8.48
12	8.41, 8.36	8.31-7.01[12H]	-	-	2.57, 2.35	3.89, 3.80	9.83, 8.48

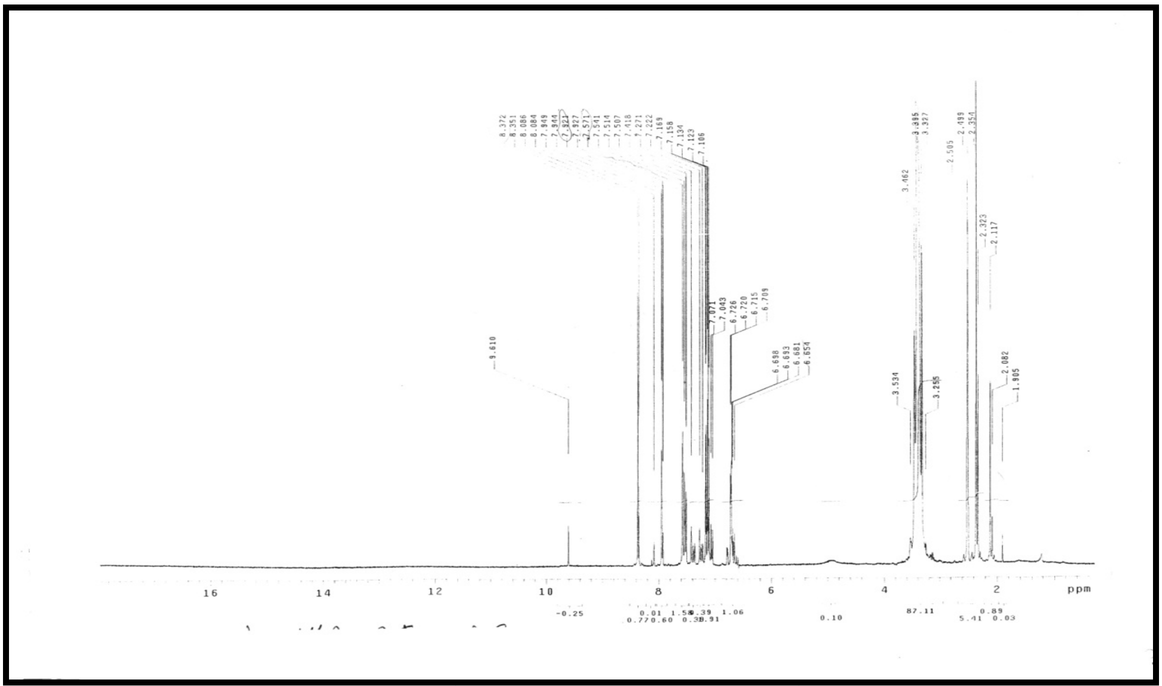


Fig. 2. ^{1}H-NMR spectra of free ligand L^1

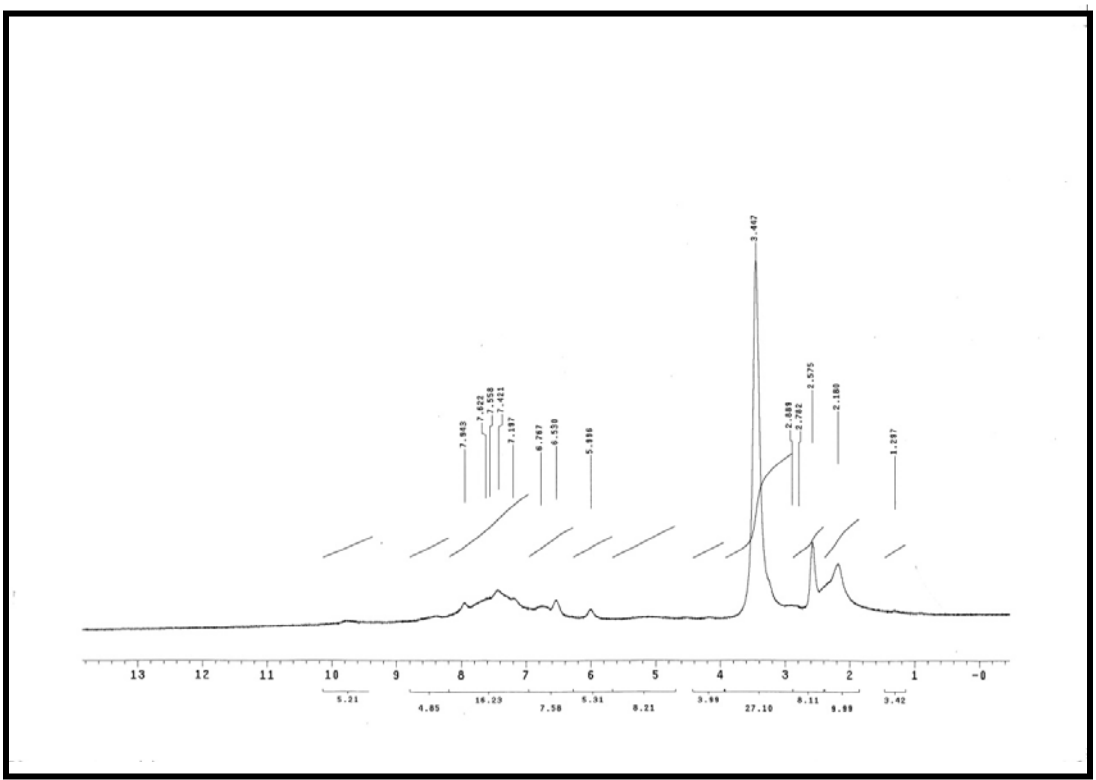


Fig. 3. ^{1}H-NMR uranyl complex (L^1 + Uo_2 + (2 ampy)

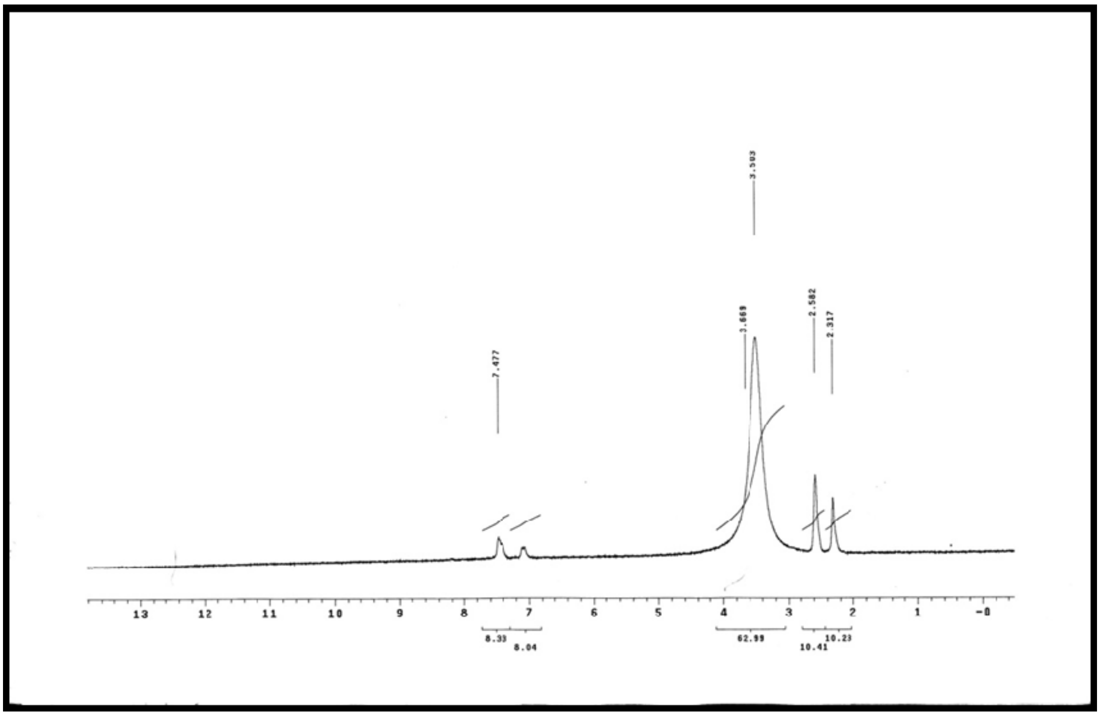


Fig. 4. ^{1}H-NMR uranyl complex (L^1 + Uo_2 + OX)

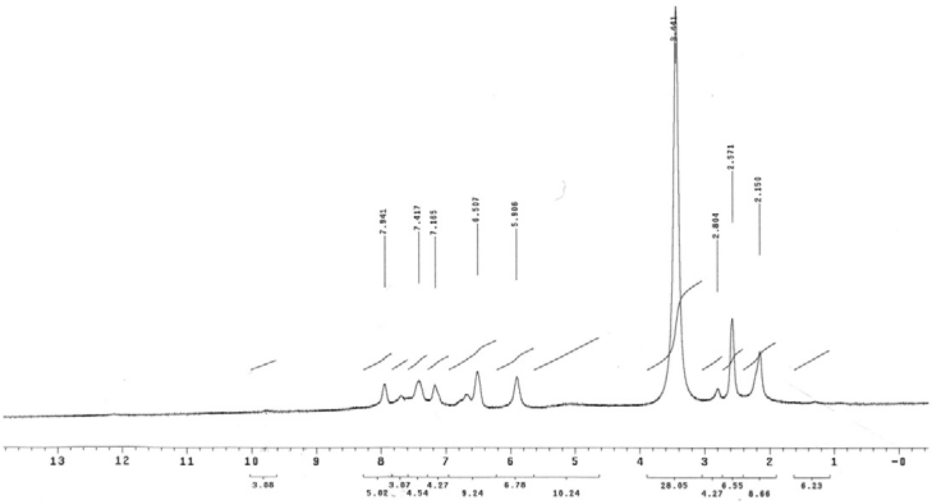


Fig. 5: ^{1}H-NMR of uranyl complex [L^2 + Uo_2 + (2 ampy)]

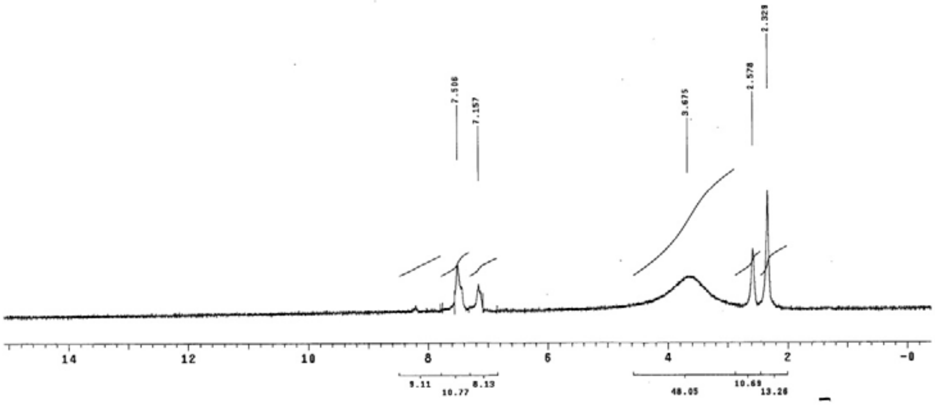


Fig. 6: ^{1}H-NMR of uranyl complex [L^2 + Uo_2 + (OX)

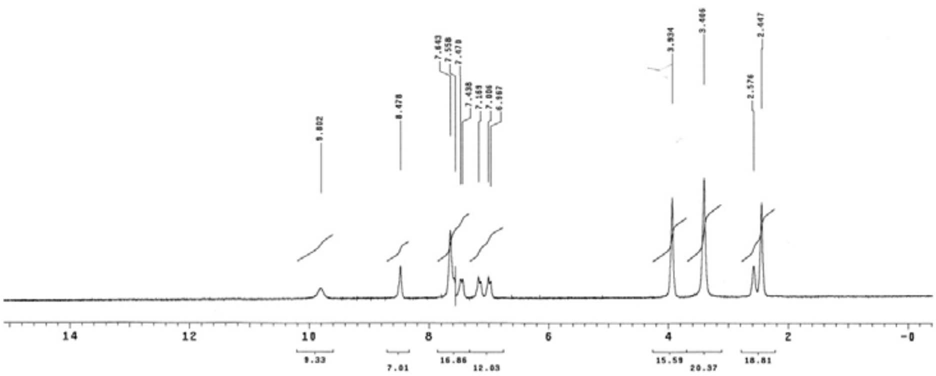


Fig. 7: ^{1}H-NMR of free ligand L^3

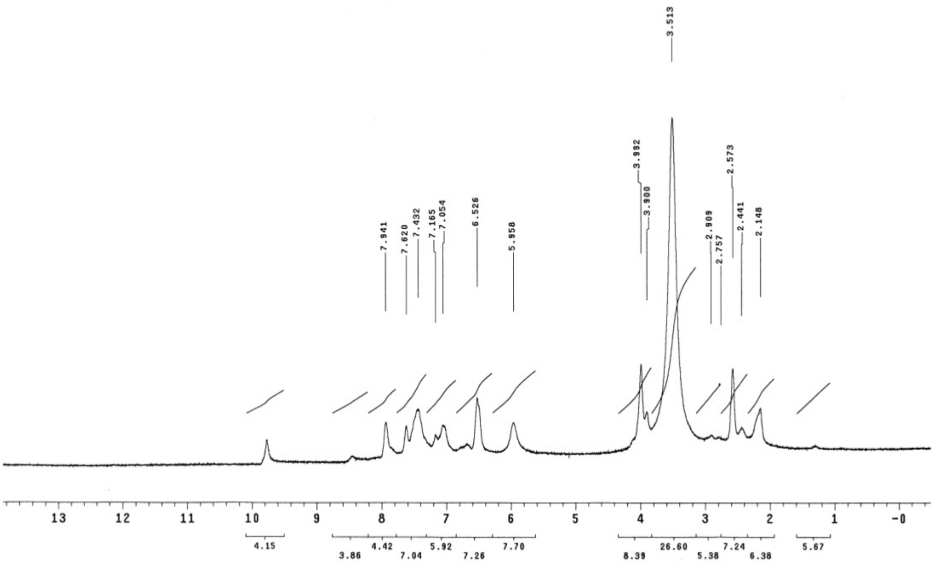


Fig. 8: ^{1}H-NMR of uranyl complex [L^3 + Uo_2 + (2 ampy)

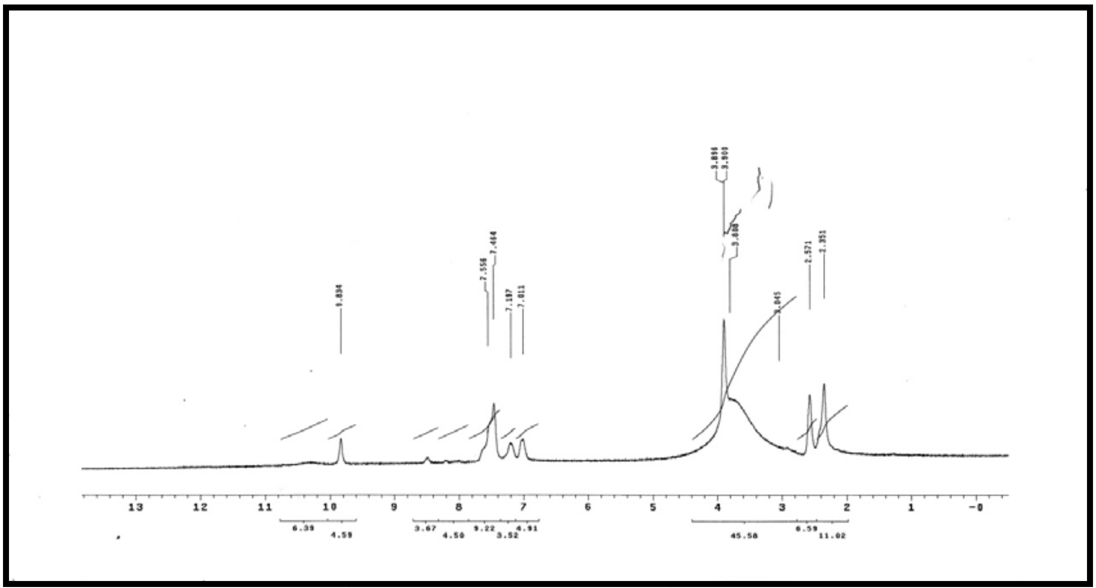


Fig. 9: ^{1}H-NMR of uranyl complex [L^3 + Uo_2 + (OX)

The electronic spectra of the ligands under study and its metal complexes were recorded in DMF at room temperature and all data are given in table 4. In the spectra of the free ligands, three absorption bands were observed in the region 224-359 nm due to π-π* ,n-π* and charge transfer transition respectively due to benzene, thiophene and azomethine (CH=N) function(50). Upon complexation these transition were found to be shifted to lower or higher energy regions compared to the free ligands confirming the coordination of the ligands to the metal ions, in addition to appearance of new band at longer wavelength (435-695 nm) may be assigned to d-d transition.

Table (4): Magnetic moment and electronic spectral data (nm) for the Schiff base ligands (L^1–L^3) and its metal complex

Comp.No.	μ_{eff} (B.M)	π-π* , n-π* and charge transfer transition	d-d transition
L^1	-	224, 253, 295	--
1	5.92	213, 230, 286	489, 562, 691
2	Diamagnetic	222, 240, 287, 489	-
3	5.65	205, 250, 290	485, 526, 620
4	Diamagnetic	215, 245, 280, 469	--
L^2	-	241, 258, 299	--
5	5.41	221, 230, 260	455, 540, 640
6	Diamagnetic	230, 244, 275, 455	--
7	5.74	238, 250, 285	487, 550, 635
8	Diamagnetic	235, 245, 290, 470	--
L^3	--	264, 291, 359	--
9	5.56	250, 266, 340	450, 560, 695
10	Diamagnetic	245, 280, 330, 480	--
11	5.78	230, 255, 325	435, 570, 662
12	Diamagnetic	256, 285, 352, 444	--

Theromograimetric analysis:

In the present investigation heating rates were suitably controlled at 10°C min^{-1} under nitrogen atmosphere and the weight loss was measured from the ambient temperature from 30-800°C. water molecule in complexes are generally of two types lattice water and coordinated water(51,52). All thermal decomposition of metal complexes (1-12) are collected in table 5.

The lattice water is observed at low temperature (26-126°C) where as the loss of coordinated water molecule is observed at high temperature (107-250°C).

During the heating of the metal complexes, the TG-curves undergo a series of thermal changes associated with a weight loss of the samples, and the correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in term of the proposed formula of the complexes (Fig. 10) are is a representative example of thermal analysis of the metal complexes under study.

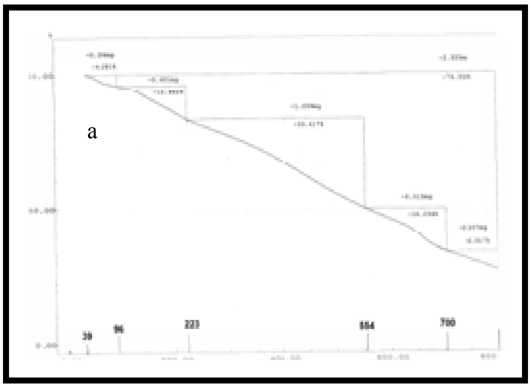
Table (5): Thermal behaviour of metal complexes (1-12) of Schiff base ligands (L^{-1}–L^3)

Complex compounds	Stage	Temperature range (°C)	Loss in weight calcd. (found) %	Evolved moiety	Residue
(1) $[Fe_2(L^1)$ $(2\text{-ampy})_2(NO_3)_5$ $(H_2O)]$ $NO_3.H_2O$	I	30-96	4.55(4.28)	H_2O(cryst.), $\frac{1}{2}$ NO_3	
	II	96-223	13.30(12.66)	$\frac{1}{2}$ NO_3, H_2O (coord.) and (2-Ampy.)	
	III	223-554	34.23(33.42)	L^1	
	IV	554-700	17.39(16.23)	(2-Ampy) and $1\frac{1}{2}$ NO_3	$Fe(NO_3)_3$
	V	700-800	8.07 (6.52)	$\frac{1}{2}$ NO_3 and Fe	
(2) $[Uo_2)_2(L^1)$ $(2\text{-ampy})_2(NO_3)_3(H_2O)_3]$ $NO_3.H_2O$	I	39-100	3.46(3.68)	$1H_2O$ (cryst.), $\frac{1}{2}$ NO_3	
	II	100-309	15.48(15.18)	$\frac{1}{2}$ NO_3 and $(2\text{-Ampy})_2$	
	III	309-570	38.57(37.74)	L^1, $3H_2O$ (coord.) and 2 NO_3	$[(Uo_2)_2\ (NO_3)]$
(3) $[Fe_2(L^1)$ (OX) $(NO_3)_4$ $(H_2O)_2]^{1/2}H_2O$	I	26-107	5.23 (5.13)	$\frac{1}{2}$ H_2O (cryst.) and $2H_2O$ (coord.)	
	II	107-269	24.99(24.79)	$\frac{1}{2}$ NO_3 and $\frac{1}{2}$ L^1	
	III	269-443	24.99 (24.51)	$\frac{1}{2}$ NO_3 and $\frac{1}{2}$ L^1	$[Fe_2(OX)(NO_3)_3]$
(4) $[Uo_2)_2(L^1)$ (OX) $(NO_3)_2$ $(H_2O)_4]H_2O$	I	50-148	7.44 (7.94)	1 H_2O (cryst.) and $4H_2O$ (coord.)	
	II	148-254	7.27 (6.70)	OX	
	III	254-515	20.29(20.46)	$2/3L^1$	$[(Uo_2)_2(\frac{1}{3}\ L^1)$
(5) $[Fe_2(L^2)$ $(2\text{-ampy})_2$ $(NO_3)_6]$ $1\frac{1}{2}$ H_2O	I	43-126	2.40 (2.45)	$1\frac{1}{2}$ H_2O (cryst.)	
	II	126-241	27.69(28.02)	2(2-ampy), $2NO_3$	
	III	241-400	15.12 (14.58)	$2\frac{3}{4}$ NO_3	
	IV	400-580	35.38(34.80)	$1\frac{1}{4}$ NO_3, $\frac{3}{4}$ L^2	$[(Fe)_2(\frac{1}{4}\ L^2)]$
(6) $[Uo_2)_2(L^2)$ $(2\text{-ampy})_2(NO_3)_3$ $(H_2O)_3]$ NO_3	I	39-107	3.19 (3.52)	$\frac{3}{4}$ NO_3	
	II	107-265	9.02(9.30)	$3H_2O$(coord.), $1\frac{1}{4}$ NO_3	
	III	265-490	17.15 (17.42)	2 (2-ampy) , NO_3	$[(Uo_2)_2(L^2)$ $(NO_3]$
(7) $[Fe_2(L^2)$ $(OX)_2$ $(H_2O)_4]$ $2NO_3.$ $1\frac{1}{2}$ H_2O	I	43-107	6.18 (6.12)	$1\frac{1}{2}$ H_2O (cryst.) , $\frac{1}{2}$ NO_3	

	II	107-165	28.98 (28.99)	4H_2O (coord.), $1\frac{1}{2}$ NO_3, $\frac{1}{4}$ L^2	
	III	165-354	13.75 (12.85)	$\frac{1}{4}$ OX,1/4 L^2	[Fe_2 , ($1\frac{1}{4}$ OX)]
	IV	354-720	28.48(27.45)	$\frac{1}{2}$ OX, $\frac{1}{2}$ L^2	
(8) [Uo_2)$_2$(L^2) (OX) (NO_3) (H_2O)$_5$]NO_3. $4\frac{1}{2}$ H_2O	I	46-89	4.67 (4.78)	$3\frac{1}{2}$ H_2O (cryst.)	
	II	89-157	2.48(2.03)	H_2O (cryst.), $\frac{1}{4}$ NO_3	
	III	157-246	17.95(17.82)	5H_2O (coord.), $\frac{1}{2}$ OX, $1\frac{3}{4}$ NO_3	2Uo_2
	IV	246-389	13.82(13.31)	$\frac{1}{2}$ OX, $\frac{1}{3}$ L^2	
	V+VI	389-800	21.14(18.05)	$\frac{2}{3}$ L^2	

Table (5): Continued

Complex compounds	Stage	Temperature range (°C)	Loss in weight calcd. (found) %	Evolved moiety	Residue
(9) [Fe_2(L^3) (2-ampy)$_2$ (NO_3)$_6$(H_2O)$_2$] H_2O	I	44-83	1.49 (1.62)	H_2O (cryst.)	
	II	83-211	11.98(11.93)	2H_2O (coord.), $1\frac{3}{4}$ NO_3	
	III	211-730	60.57(60.47)	NO_3, 2(2-ampy) , L^3	Fe, Fe(NO_3)$_2$
	IV	730-800	60.42(5.98)	$1\frac{1}{4}$ NO_3	
(10) [Uo_2)$_2$(L^3) (2-ampy)$_2$ (NO_3)$_4$ (H_2O)$_4$] H_2O	I	54-131	4.66(4.65)	1H_2O (cryst.), 3H_2O (coord.)	
	II	131-250	7.25(7.35)	1H_2O (coord.), (2-ampy)	
	III	250-530	27.63 (27.39)	$1\frac{1}{2}$ NO_3, (2-ampy), $\frac{1}{2}$ L^3	[Uo_2)$_2$($\frac{1}{2}$ L^3) |(2.5 NO_3)]
(11) [Fe_2(L^3) (OX)$_2$ (H_2O)$_6$] 2NO_3. H_2O	I	39-65	1.33(1.60)	$\frac{3}{4}$ H_2O (cryst.)	
	II	65-124	8.05(8.11)	$1\frac{1}{4}$ NO_3, $\frac{1}{4}$ H_2O (cryst).	[Fe_2($\frac{1}{4}$ L^3)(OX)
	III	124-250	15.18(15.38)	6H_2O (coord.), $\frac{3}{4}$ NO_3	
	IV	250-611	44.03 (44.35)	$\frac{3}{4}$ L^3, OX	
(12) [Uo_2)$_2$(L^3) (OX) (H_2O)$_8$]2NO_3. 3H_2O	I	50-98	5.94(5.48)	3H_2O (cryst.) , $\frac{1}{2}$ NO_3	
	II	98-200	9.02(8.38)	2H_2O (coord.), $1\frac{1}{2}$ NO_3	
	III	200-354	10.18(10.27)	6H_2O (coord.), $\frac{3}{4}$ OX	[(Uo_2)$_2$ ($\frac{1}{4}$ L^3)]
	IV	354-504	47.88(19.06)	$\frac{1}{4}$ OX , $\frac{1}{2}$ L^3	
	V	504-626	8.40(8.54)	$\frac{1}{4}$ L^3	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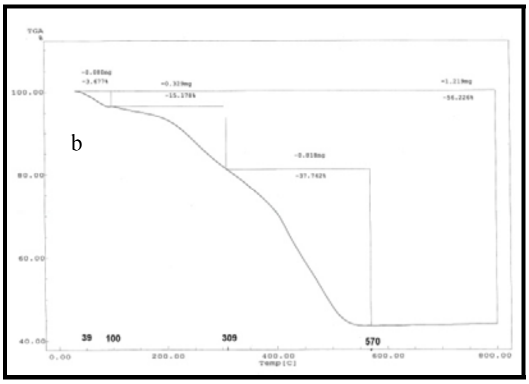
700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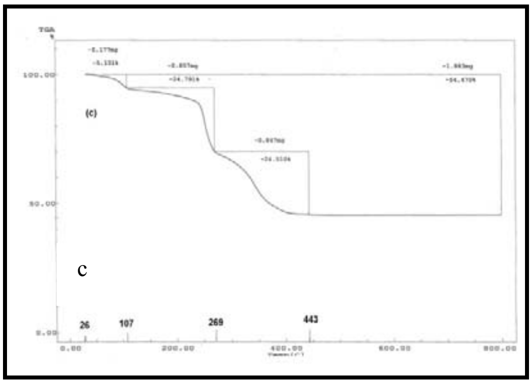
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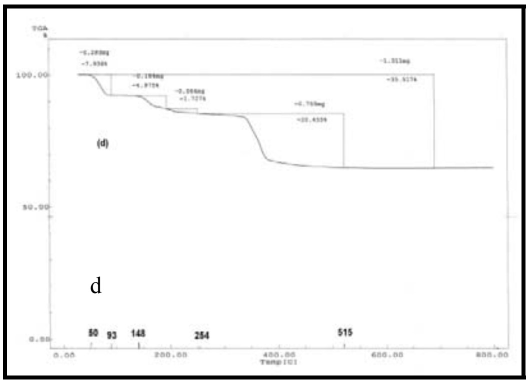
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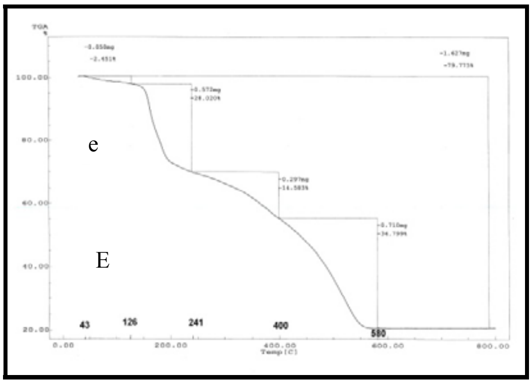
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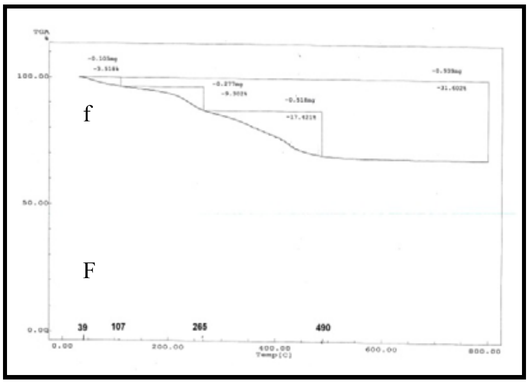
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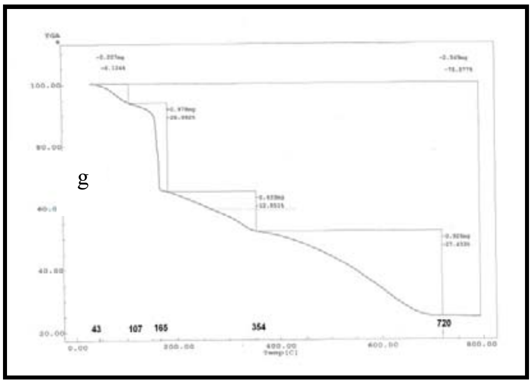
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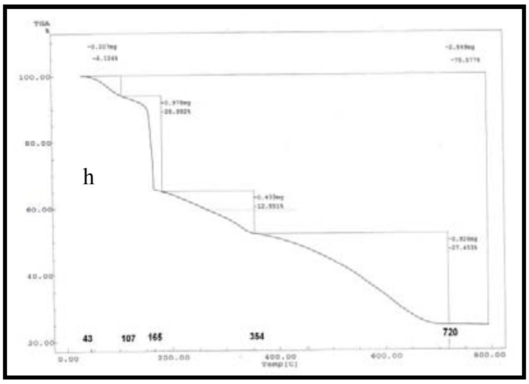
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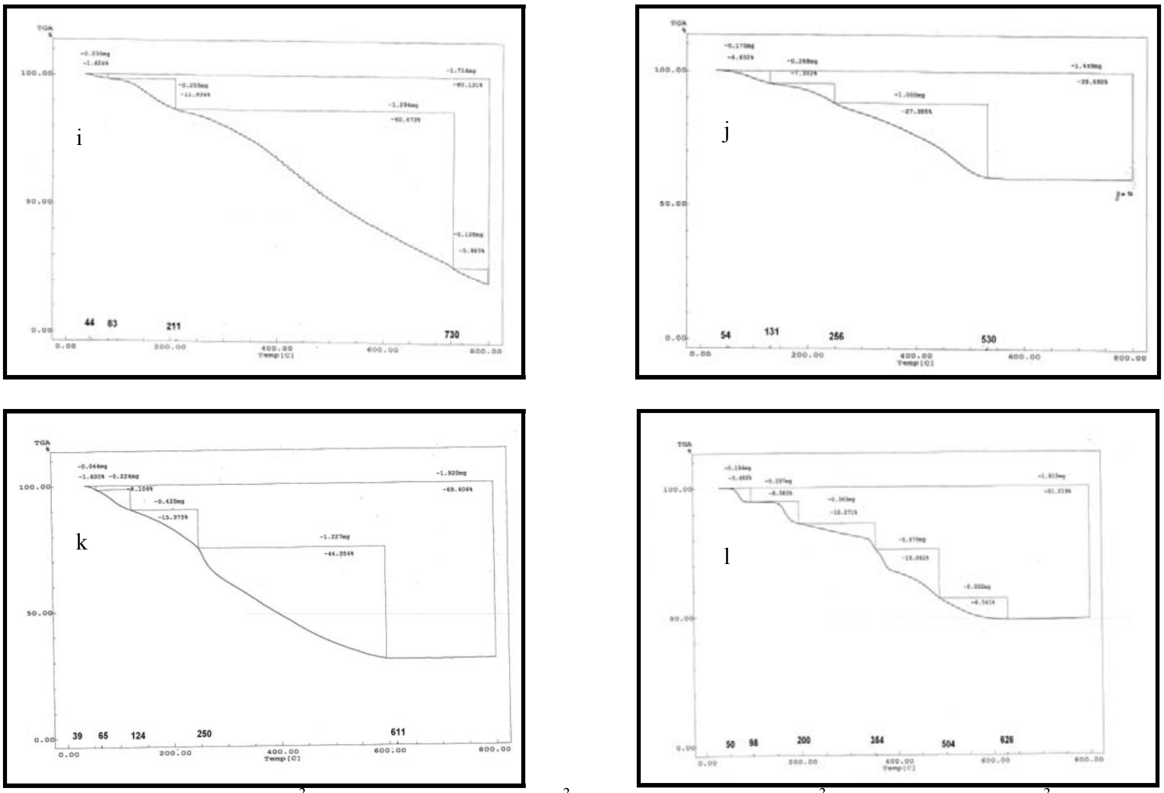
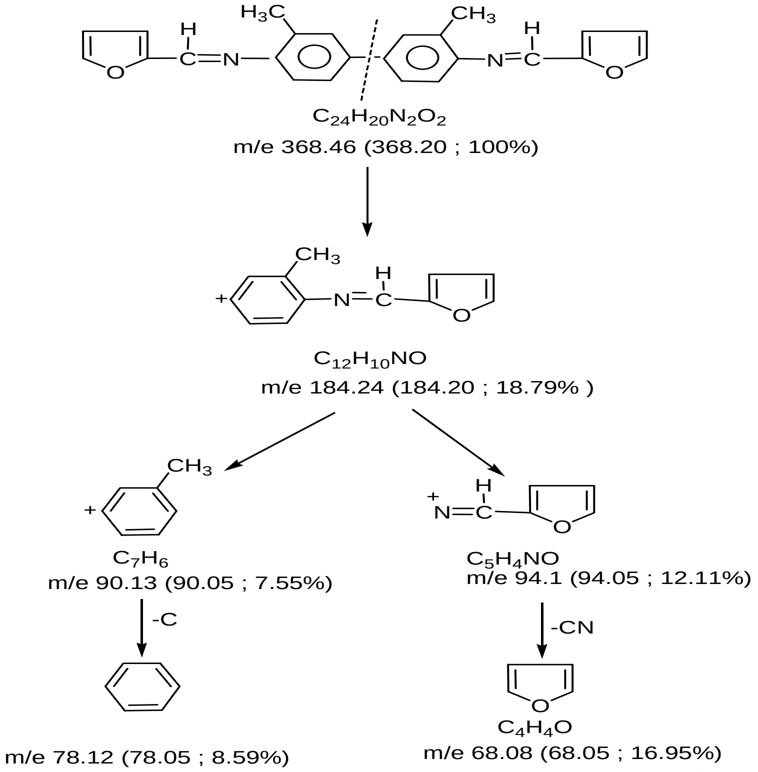
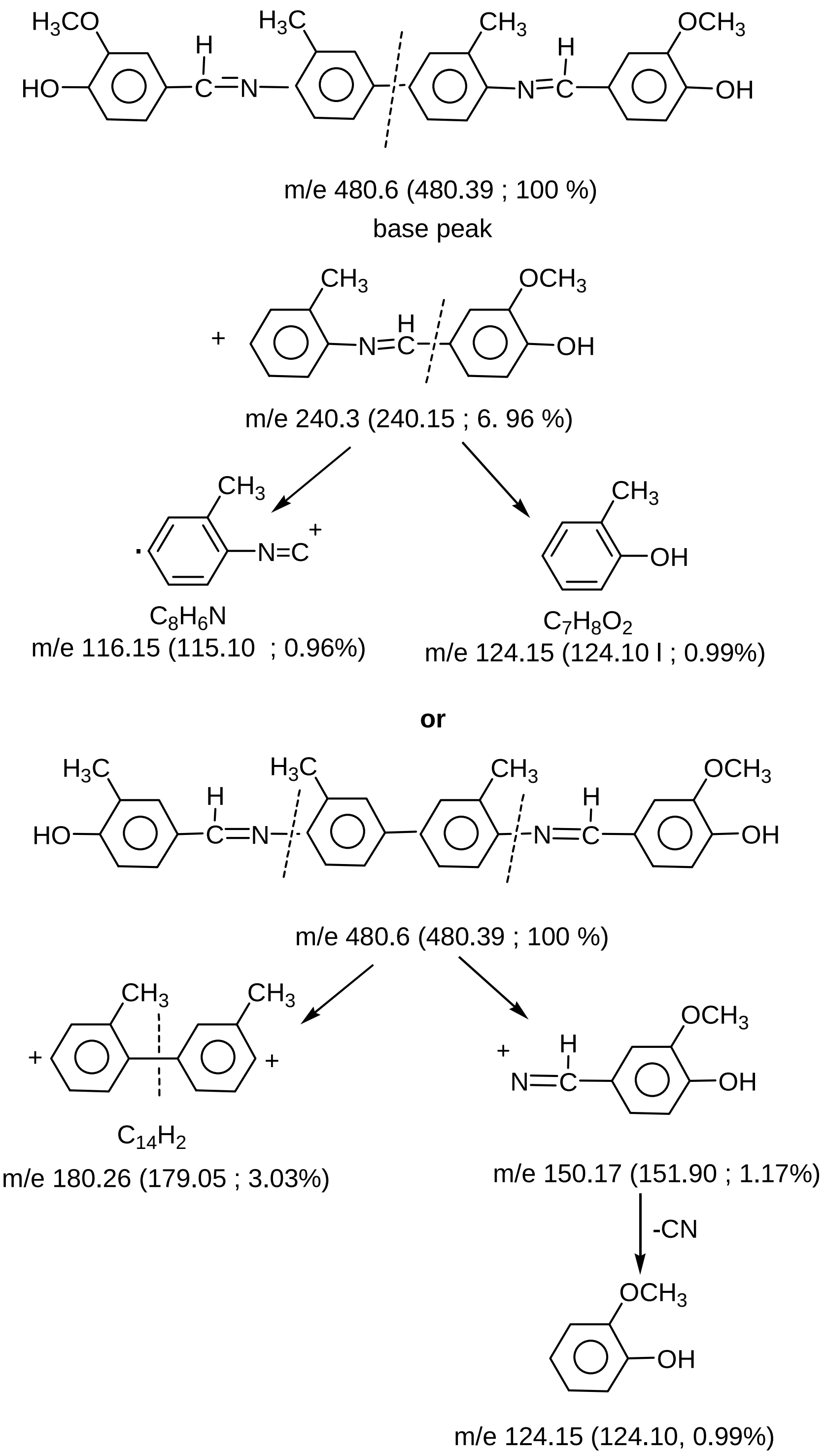


Fig. 10. Cont. (i) Fe + L^3 + (1 ampy) , (j) Uo_2 + L^3 + (2 ampy) , (k) Fe + L^3 + (OX) , (l) Uo_2 + L^3 + (OX)

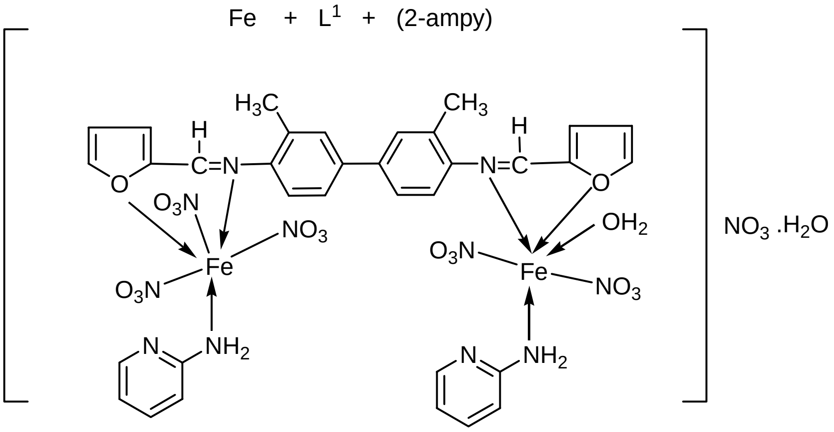


Scheme 1: Mass fragmentation pattern of Schiff base ligand (L^1)



Scheme 2: Mass fragmentation pattern of Schiff base ligand (L^3)

Fe + L^1 + (2-ampy)



[$Fe_2(L^1)(2\text{-ampy})_2(NO_3)_5(H_2O)$] $NO_3.H_2O$
m/z 1076.50 (1077 ; 11.1%)

$\downarrow$ -NO_3 , 1.25 H_2O

$Fe_2(L^1)(2\text{-ampy})_2(NO_3)_5(0.75\ H_2O)$]
m/z 991.96 (992, 100.00%)

$\downarrow$ -NO_3 , 0.75H_2O

[$Fe_2(L^1)$ (2 ampy)$_2$ $(NO_3)_4$]
m/z 916.44 (919 ; 15.5%)

$\downarrow$ -1.25 NO_3 (0.25 (2 ampy)

[$Fe_2(L^1)$ (1.75 2 ampy) (2.5 NO_3)]
m/z 815.40 (815 ; 67.2%)

$\downarrow$ 0.25 NO_3

[$Fe_2(L^1)$(1.75 2 ampy) (2.5 NO_3)]
m/z 799.90 (801 ; 31.4%)

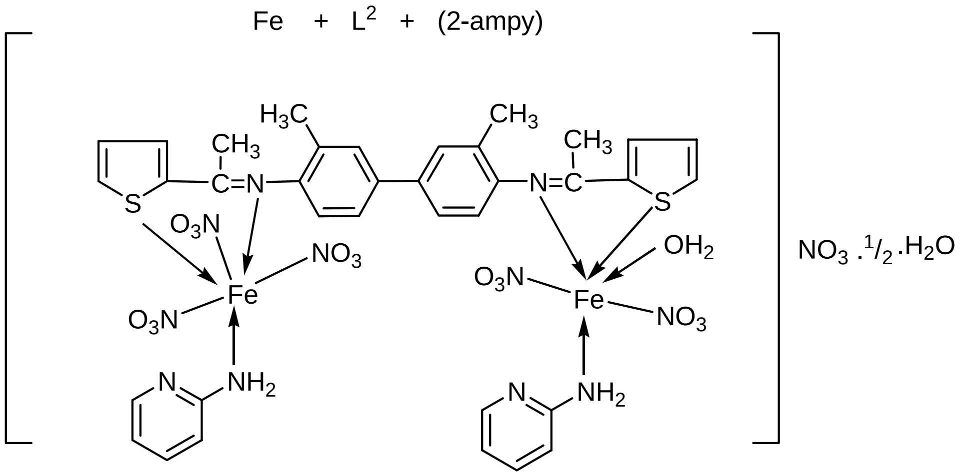
$\downarrow$ -2.5 NO_3, 1.75 (2 amp)

[Fe_2 (L^1)]
m/z 480.15 (481 ; 22.00%)

$\downarrow$ -L^1

Fe
m/z 55.85 (57.00 , 11.9%)

Scheme 3: Mass fragmentation pattern of iron complex (Fe + L^1 + (2 ampy)



$[\,Fe_2(L^2)(2\text{-ampy})_2(NO_3)_5\,(H_2O)]\,NO_{3.}\,1/_2\,H_2O$
m/z 1127.71 (1128.00 ; 16.3%)

$\downarrow$ $-\,0.25\,H_2O,\ NO_3$

$Fe_2(L^2)(2\text{-ampy})_2(NO_3)_{5.}H_2O].\,0.25\,H_2O$
m/z 1061.20 (1061.00 ; 6.3 %)

$\downarrow$ $-1.25\,H_2O,\ NO_3$
m/z 84.54 (85.00 ; 4.4%)

$[Fe_2(L^2)\ (2\ ampy_2\ (NO_3)_4]$
m/z 976.66 (976.00 ; 14.8 %)

$\downarrow$ $-\,L^2\ ,\ NO_3$
m/z 490.67 (491.00 , 10.2%)

$[Fe_3(2\ ampy)_2\ (NO_3)_3]$
m/z 485.99 (485.00 ; 100%)

$\downarrow$ $-(2\text{-ampy})\ NO_3$

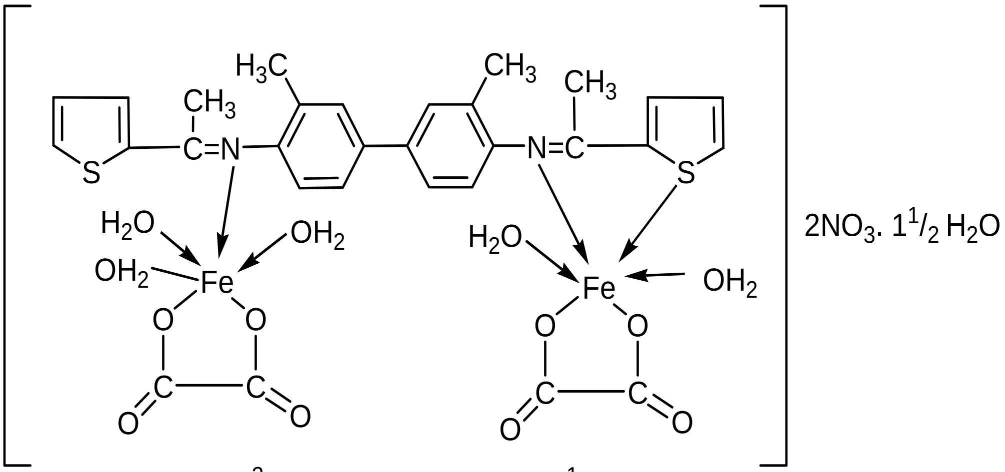
$[Fe_2(2\ ampy)\ (NO_3)_2]$
m/z 329.85 (327.00 ; 20.8%)

$\downarrow$ $-(2\ ampy\ )\ ,\ {}^1/_4\ NO_3\ ,\ Fe$
m/z 165.48 (165.00 ; 13.00%)

$Fe\ (1.75\ NO_3)$
m/z 164.37 (164.00 ; 2.5 %)

Scheme 4: Mass fragmentation pattern of iron complex (Fe + L^2 (2 ampy)

Fe + L^2 + OX



$[Fe_2(L^3)(OX)_2(H_2O)_4]\ 2NO_3.\ 1\ ^1/_2\ H_2O$
m/z 939.53 (939.00 ; 100%)

$-1\ ^3/_4\ H_2O,\ 2\ NO_3$
m/z 155.56 (153.50 ; 7.8%)

$[Fe_2(L^2)(OX)_2(3.75\ H_2O)$

m/z 783.98 (784.00 ; 27%)

$-3.75\ H_2O$, OX

$[Fe_2(L^2)(OX)]$
m/z 628.38 (624.00 ; 26.4 %)

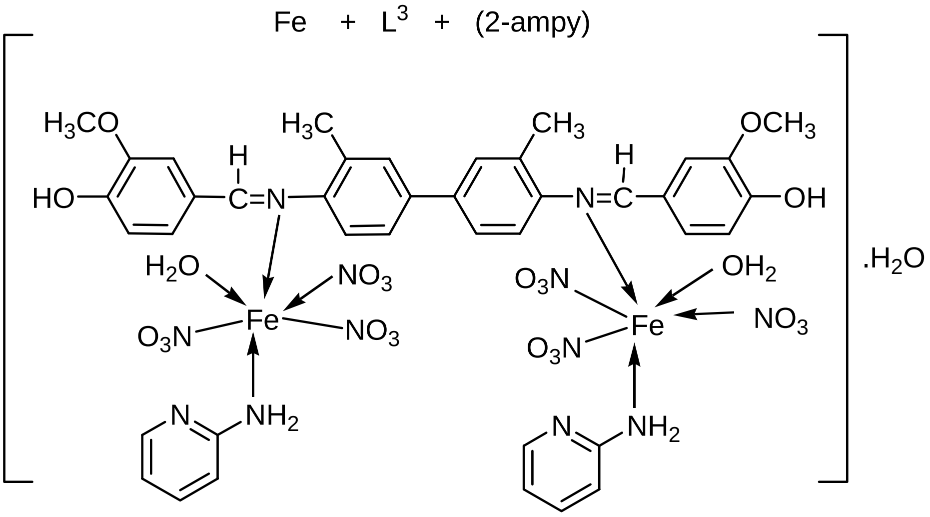
$-\ ^1/_2\ L^2$, Fe
m/z 270.18 (270.50 ; 4%

$[Fe(^1/_2L^2)(OX)$

$-^1/_2\ L^2$, OX
m/z 302.35 (302.00 ; 6.6%)

Fe

Scheme 5: Mass fragmentation pattern of iron complex (Fe + L^2 + (OX)



$[\ Fe_2(L^3)(2\text{-ampy})_2(NO_3)_6\ ]\ (H_2O)_2]H_2O$

m/z 1206.68 (1207.00 ; 31%)

$\downarrow$ $-3H_2O$, $^1/_4\ NO_3$ m/z 69.56 (72.00 ; 44%)

$Fe_2(L^3)(2\text{-ampy})_2(5.75\ NO_3)]$

$\downarrow$ $-5.75\ NO_3$, 2 (2-ampy), Fe m/z 588.45 (590.00 ; 91%)

$[Fe(L^3)]$

$\downarrow$ $-^1/_2\ L^3$ m/z 240.30 (240.00 ; 8.2%)

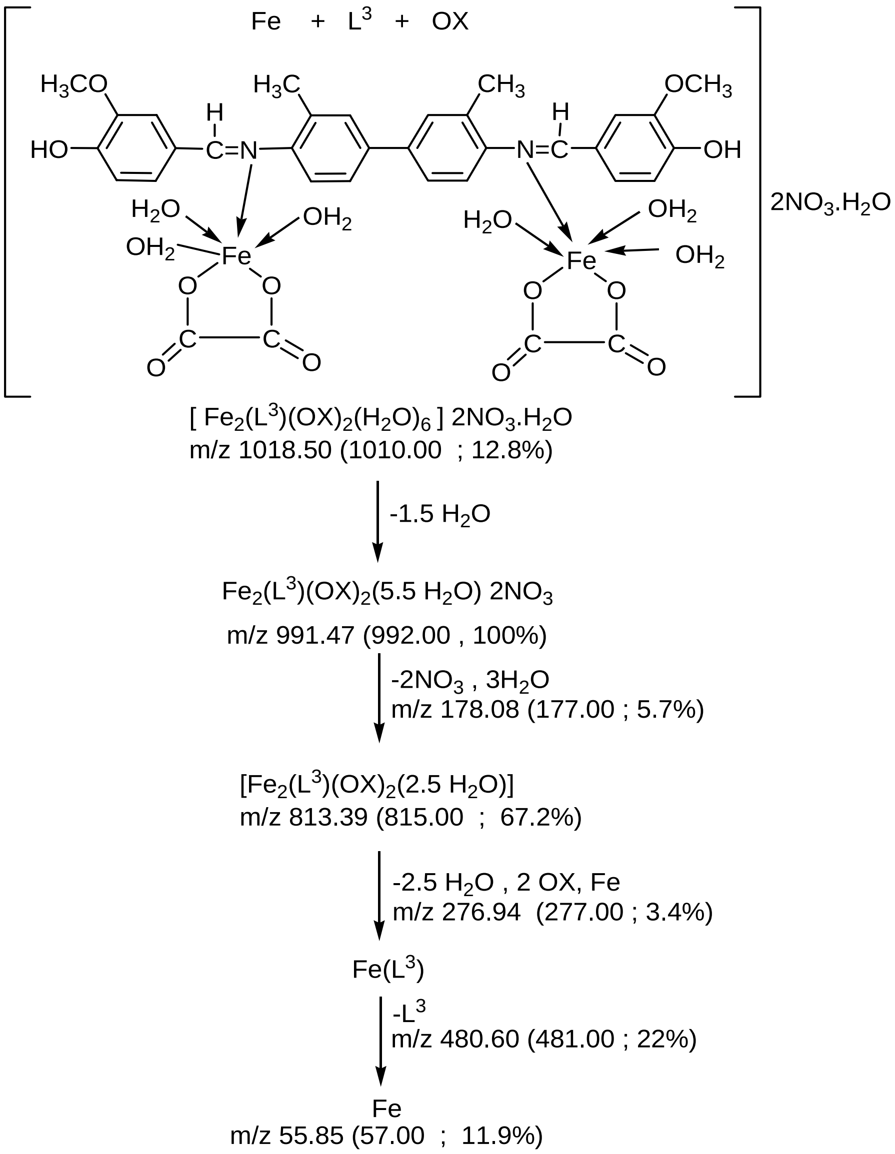
$[Fe(^1/_2\ L^3)]$

$\downarrow$ $^1/_2\ L^3$

Fe

m/z 55.85 (55.00 ; 4.2%)

Scheme 6: Mass fragmentation pattern of iron complex (Fe + L^3 (2 ampy)



Scheme 7: Mass fragmentation pattern of iron complex (Fe + L^3 + (OX)]

Mass spectra:

Mass spectra of complexes provide a vital clue for elucidating the structure of compounds(44). The mass spectra of the ligands used, L^1–L^3 and their Fe(III), Uo_2(II) complexes were performed to determined their molecular weights. The mass spectra of the free ligands confirm the proposed formula by showing the mole peaks corresponding to the molar ion $[M]^+$; $C_{24}H_{20}N_2O_2$, $C_{26}H_{24}N_2S_2$ and $C_{30}H_{28}N_2O_4$, respectively. In the mass spectra of the metal complexes (1-12) (Table 1) showed the molecular ion peak $[M]^+$ corresponding to the molecular weight of the complexes. Scheme (1-7) show the proposed fragmentation pattern steps for the ligands and its iron metal complexes.

Antibacterial and antifungal screening:

The new three Schiff bases and their ternary metal complexes (1-12), were studied against selected types of sensitive organisms *Staphylococcus aureus* and *Streptococcus pyogenes* as Gram positive bacteria, *Pseudomonas fluorescens* and *Pseudomonas phaseolicola* as Gram negative bacteria and the fungi Fusarium oxysporum and *Aspsrgillus fumigatus* in potato dextrose agar media. The tested compounds were dissolved in DMF (which have no inhibition activity to get concentrations of 2mg/ml and 1mg/m. the biological activity data (Table 6) show that the parent Schiff base ligand hadn't any activity while the metal complexes gave high, intermediate and low activities against selected types of bacteria and fungal strain(53,54).

Correlation of all results obtained for the complexes under study gives us information regarding the suggested structure of the complexes to be as in Figs (11-20)

Table (6): Antibacterial and antifungal of ligands and metal complexes against the tested bacteria and fungi

Organisms	**Mean * of zone diameter, nearest whole mm**											
	Gram-positive bacteria				**Gram-negative bacteria**				**Fungi****			
	Staphylococcus aureus **(ATCC 25923)**		***Streptococcus pyogenes*** **(ATCC 19615)**		***Pseudomonas phaseolicola*** **(GSPB 2828)**		***Pseudomonas fluorescens*** **(S 97)**		***Fusarium oxysporum***		***Aspergillus fumigatus***	
Consent. Sample	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**
	2 mg/ml	**1 mg/ml**	**2 mg/ml**	**1 mg/ml**	**2 mg/ml**	**1 mg/ml**	**2 mg/ml**	**1 mg/ml**	**2 mg/ml**	**1 mg/ml**	**2 mg/ml**	**1 mg/ml**
L^1	-	-	-	-	-	-	-	-	-	-	-	-
1	-	-	-	-	-	-	-	-	-	-	-	-
2	21 I	17 I	23 I	17 I	10 L	6 L	8 L	3 L	-	-	-	-
3	5 L	-	-	-	-	-	-	-	-	-	-	-
4	26 I	20 H	-	-	23 I	14 I	20 I	13 I	5 L	3 L	8 L	4 L
L^2	-	-	-	-		-	-	-	-	-	-	-
5	10 L	5L	8 L	5 L	-	-	-	-	-	-	-	-
6	20 I	14 I	21 I	16 I	13 I	9 I	15 I	8 L	-	-	-	-
7	11 L	7 L	9 L	5 L	12 L	6 L	10 L	4 L	-	-	-	-
8	22 I	17 I	21 I	15 I	13 I	9 I	15 I	8 L	12 L	6 L	12 L	5 L
L^3	-	-	-	-	8 L	4 L	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	24 I	17 I	20 I	14 I	11 L	6 L	7 L	4 L	6 L	3 L	6 L	3 L
11	-	-	-	-	-	-	-	-	-	-	-	-
12	23 I	16 I	20 I	15 I	16 I	10 I	16 I	9 L	6 L	4 L	8 L	4 L
Control #	42	28	38	30	36	25	38	30	40	28	40	31

* = Calculate from 3 values.
** = Identified depending on morphological and microscopical characteristics.
- = No effect.
L : Low activity = Means of zone diameter ≤ 1/3 of mean zone diameter of control.
I: Intermediate activity = Mean of zone diameter ≤ 2/3 of mean zone diameter of control.
H: High activity = Means of zone diameter > 2/3 of mean zone diameter of control.
#: Chloramphencol in the case of Gram positive bacteria. Cephalothin in the case of Gram negative bacteria and cycloheximide in the case of fungi.

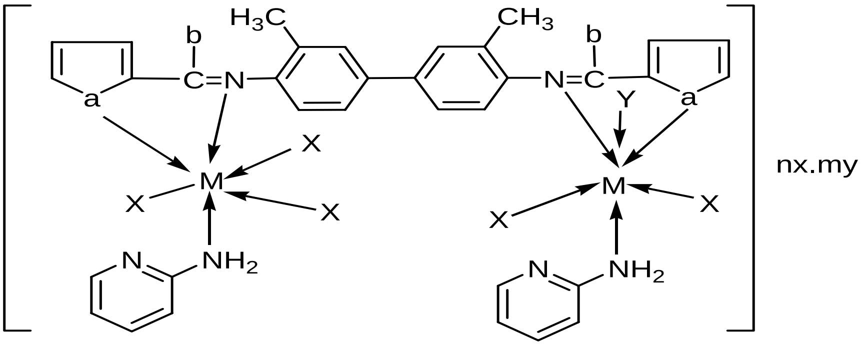


Fig. (11) Suggested structure of iron complexes of ligands L^1, L^2

In complex (1) a = O , b = H, X = NO_3, Y = H_2O n = m = 1

In complex (5) a = S, b = CH_3 , X = NO_3 , Y = H_2O n = 1, $m = \frac{1}{2}$

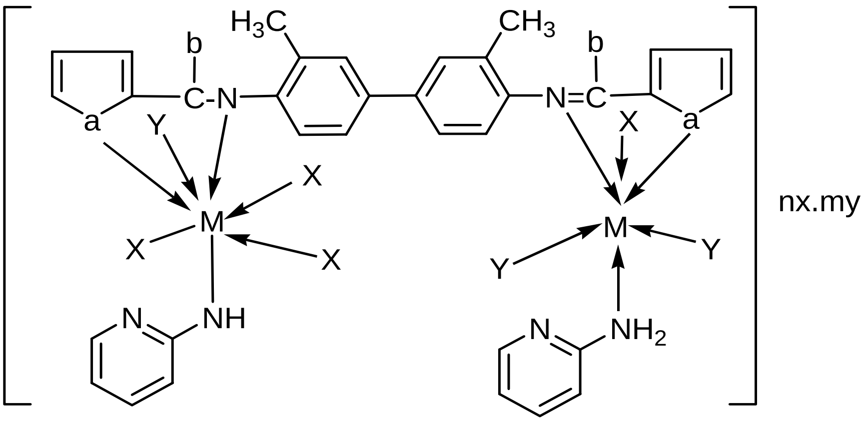


Fig. (12) Suggested structure of vranyl complexes (2,b) of ligands L[1], L[2]

In complex (2) a = O , b = H, X = NO_3, Y = H_2O n = m = 1
In complex (6) a = S, b = CH_3 , X = NO_3 , Y = H_2O n = 1, m = nil

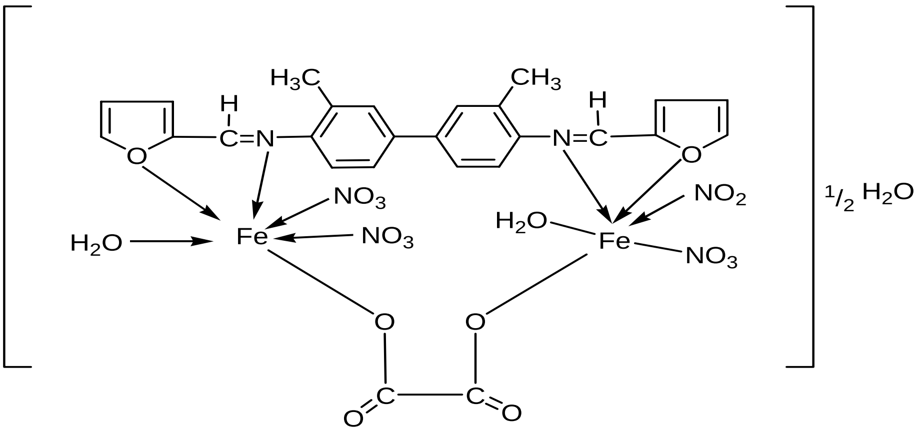


Fig. (13): Suggested structure of complex (3) of ligand L[1]

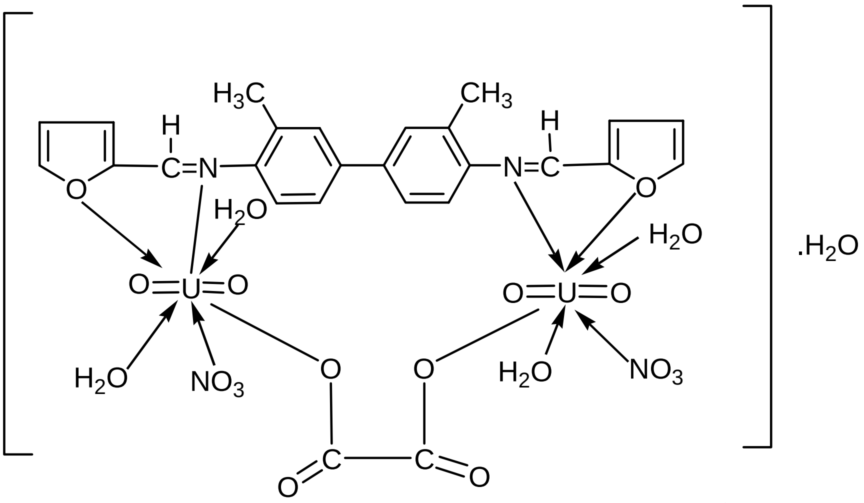


Fig. (14): Suggested structure of complex (4) of ligand L[1]

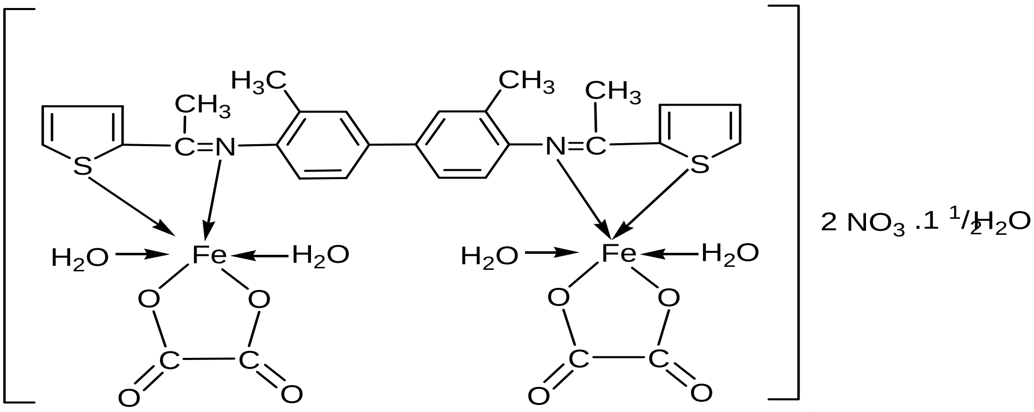


Fig. (15): Suggested structure of complex (7) of ligand L^2

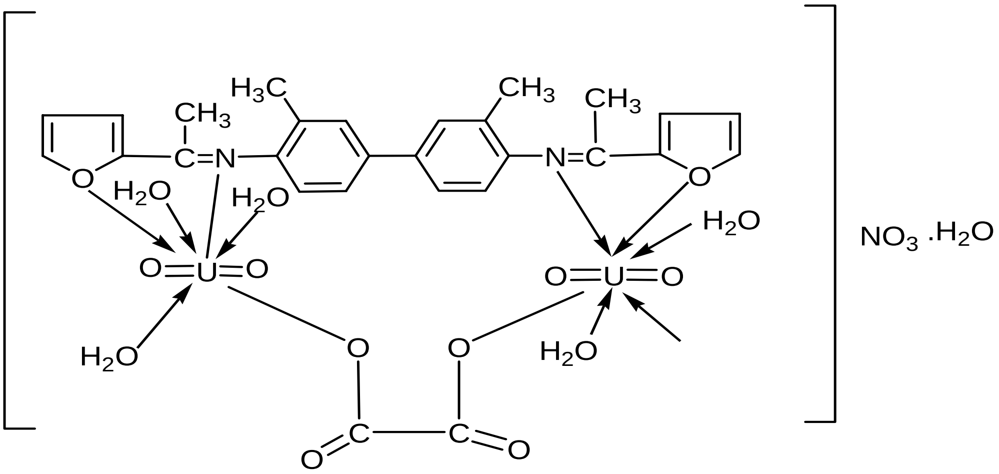


Fig. (16): Suggested structure of complex (8) of ligand L^2

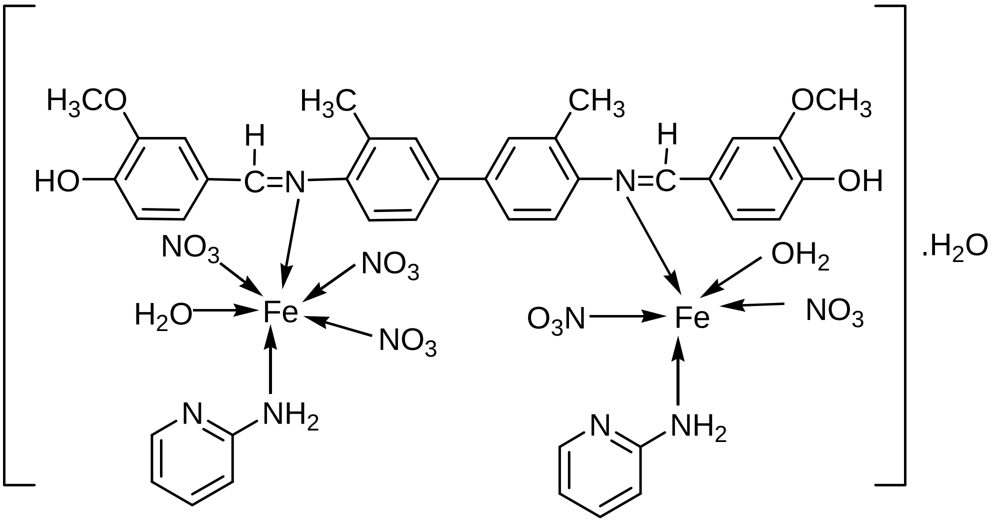


Fig. (17): Suggested structure of iron complex (9) of ligand L^3

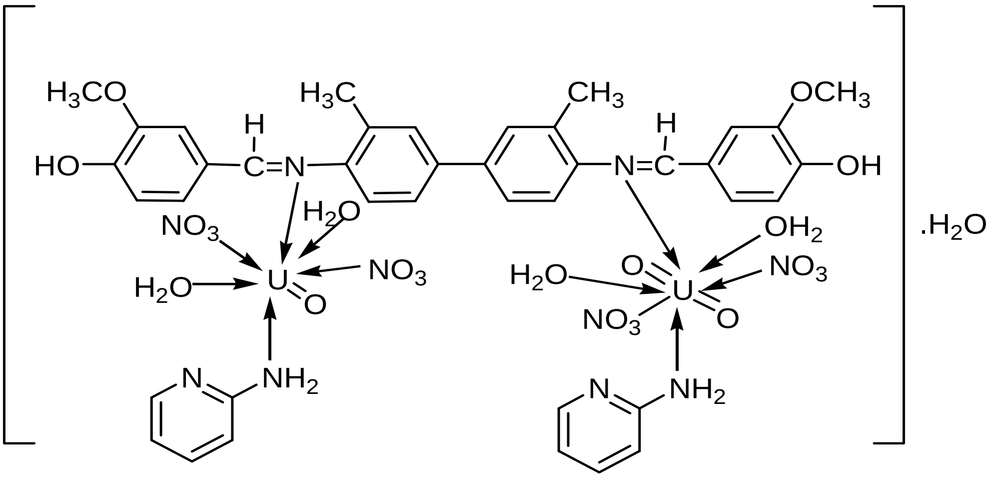


Fig. (18): Suggested structure of uranyl complex (10) of ligand L^3

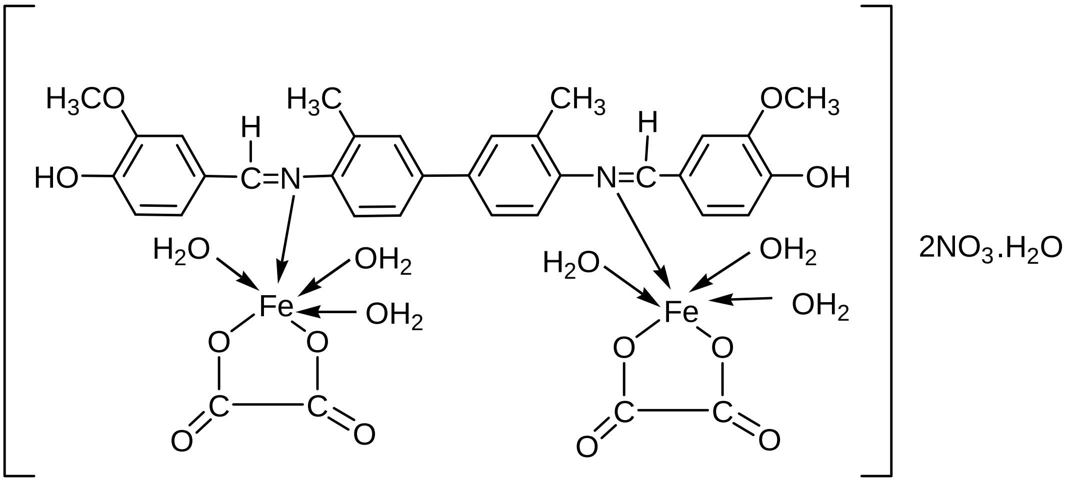


Fig. (19): Suggested structure of iron complex (11) of ligand L^3

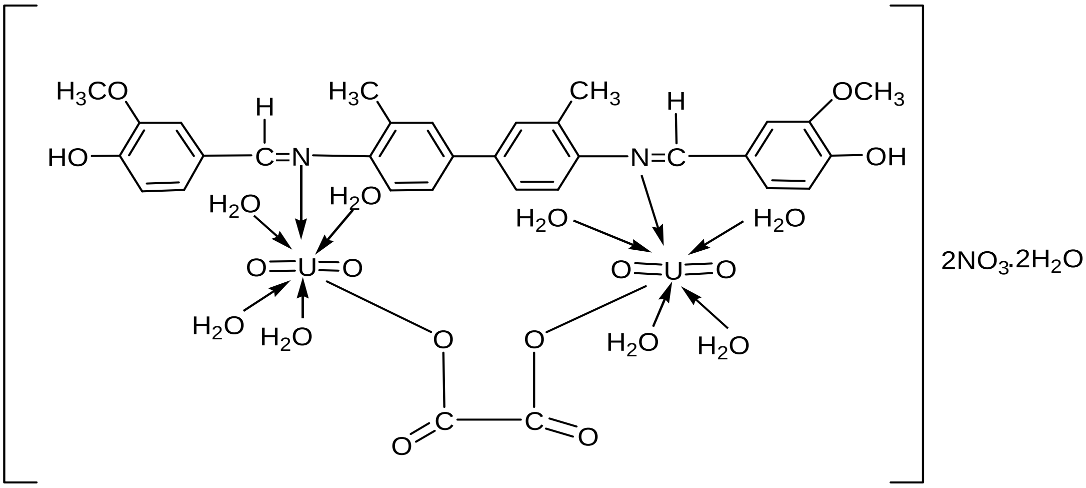


Fig. (20): Suggested structure of uranyl complex (12) of ligand L^3

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