

Synthesis and Studies of Some New Dioxouranium (VI) Complexes with Azoester Ligands

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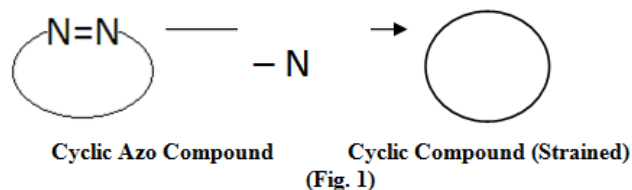
Abstract: Some new complexes of uranyl (VI) metal ion with different anions (viz. Cl^- , I^- , NO_3^- and OAc^-) have been synthesized using azoester ligand. Complexes were characterized by traditional methods viz. melting point measurements, conductivity measurements. These were also characterized by modern spectral methods viz. IR including far IR, UV-vis. spectra. Thermal studies specially DTA studies of representative have also been done and reported. Some of the complexes were also screened against selected microbes to check their antimicrobial activities. Coordination number of these complexes are proposed to be 8, 10 and 12 and tentative structures of the complexes are also reported in the present paper.

Keywords:-Uranyl (VI) metal complexes /azoester ligands /spectral studies/ thermal studies/ antimicrobial studies

I. Introduction

Metal complexes of lanthanides and that of actinides were reported with various organic compounds as ligands¹⁻⁵. Schiff bases are one of the important class among these compounds which are used as ligands for this purpose. So far as the ligands are concerned, compounds which are capable of forming ring structures i.e. chelates are dominating and preferred in this area. As such complex compounds are stable, large in numbers with kinetics as well as thermodynamic stability. In fact, if more compact is the ligands and the smaller is its bite more effective it is in generating higher coordination structures.

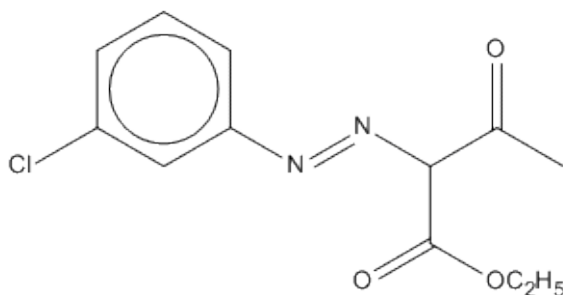
Reactions of azo compounds have been widely studied in which nitrogen molecule is eliminated either thermally or photochemically and two reactive sites remain react to reform a ring (Fig. 1).



The important synthetic application of azo compound decomposition is in synthesis of ring systems with strain. The required azo compounds can be prepared by dipolar cycloadditions of diazocompounds and the cyclic azo-esters so formed can be photochemically or thermally which finally decomposed to strained ring system. Such type of reactions have been developed for pyridazine -3, 6 - dicarboxylate esters; 1,2,4-triazines and 1,2,4,5-tetrazines etc. A large number of metal complexes⁶⁻¹⁰ of Thorium (IV) and dioxo-uranium (VI) have been reported in literature but still a possibility left to report their complexes with azoester ligands.

Keeping this in mind, these studies have been done and this present communication contains such studies related to complexes of dioxouranium(VI) metal with two azoester ligands viz. Ethyl - α - (3 - chloro phenylazo) acetoacetate and Ethyl - α - (4 - bromo phenylazo) acetoacetate.

Ligands used for formation of complexes are reported in figure 2 below.



Chemical Formula: C₁₂H₁₃ClN₂O₃

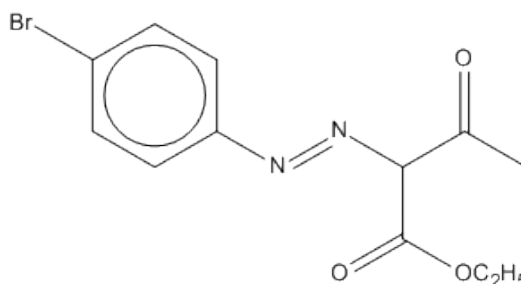
Exact Mass: 268.06

Molecular Weight: 268.70

m/z: 268.06 (100.0%), 270.06 (32.1%), 269.06 (13.7%), 271.06 (4.5%), 270.07 (1.4%)

Elemental Analysis: C, 53.64; H, 4.88; Cl, 13.19; N, 10.43; O, 17.86

Ethyl- α -(3-chloro phenylazo) acetoacetate



Chemical Formula: C₁₂H₁₃BrN₂O₃

Exact Mass: 312.01

Molecular Weight: 313.15

m/z: 312.01 (100.0%), 314.01 (97.4%), 313.01 (13.7%), 315.01 (13.5%), 314.02 (1.4%)

Elemental Analysis: C, 46.03; H, 4.18; Br, 25.52; N, 8.95; O, 15.33

Ethyl- α -(4-bromo phenylazo) acetoacetate

Figure 2

Experimental:

All chemicals which are used for the purpose of preparation of new compounds were obtained in the sealed containers from standard sources e.g. Emerck, Aldrich, CDH and BDH. Uranyl (VI) metal salts viz. dioxouranium (VI) chloride, dioxouranium (VI) nitrate, dioxouranium (VI) acetate, salts were obtained from the RJ (Robbert Johnson Company Ltd.) and BDH (British Drug House), Poole, England. All the chemicals were of AR, AnalR grade. Dioxouranium (VI) iodide was prepared in laboratory by reacting dioxouranium (VI) nitrate with potassium iodide.

Formation of Azo-ester Ligands and their complexes

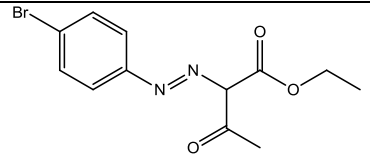
Jolly V. S. et al¹¹⁻¹² have reported the synthesis of many new azo-esters. The complex forming capabilities of some of the azo-esters have been explored in the present investigations against dioxouranium(VI) metal salts. The azo-ester compounds viz. 2-Aceto-2-N (substituted phenyl) azoethylethanoates were prepared as per according to the methods reported in literature¹³⁻¹⁴. All these substituted azo-ester compounds obtained are deeply coloured i.e. reddish brown solids with low melting points and most of them became viscous in the hot summer season of this north central region of Madhya Pradesh where the temperature in this season reaches almost 44-45⁰C. The reported new coordination compounds of dioxouranium (VI) metals were obtained by the reaction of the azoesters with metal salts at the pH ranging from 8 to 10 at the room temperature in water medium containing small amount of alcohol/butanol/mixture of two alcohols. All the new compounds synthesisd were analysed and their analytical studies were reported as reported earlier in related literature⁶⁻¹⁰.

II. Results And Discussions

Analytical data of azoester ligands viz. yield, color, mol. weight etc. are reported in table 1

Table 1: Analytical Data of Azoester Ligands

S.No	Azoester Ligands : Structure & Name	R	Yield	Color	Molecular Formula	Molecular Weight
1.		3-Cl	80%	Dark Brown	C ₁₂ H ₁₃ ClN ₂ O ₃	268.70

	Ethyl - α - (3 - chloro phenylazo) acetoacetate					
2.	 Ethyl - α - (4 - bromo phenylazo) acetoacetate	4 - Br	80%	Light Brown	$C_{12}H_{13}BrN_2O_3$	286

Mass spectral data of these azoester compounds i.e. ligands are also reported in the tables 2,3 and the prominent peaks observed are listed in these tables for these compounds. Base ion peak are marked and shown in the tables for these compounds. Though spectra of azoesters show the peaks related to fragments that may be formed after fragmentation but investigator was not able to record parent ion peak.

Table 2 :Mass Spectral Details of Ethyl – α – (3– chloro phenylazo) acetoacetate

m/z	Relative Abundance (%)
206	5
127	99
112	10
102	15
92	20
75	2
65	35
52	10

Table 3 :Mass Spectral Details of Ethyl – α – (4 – bromo phenylazo) acetoacetate)

m/z	Relative Abundance (%)
207	2
156	45
143	2
129	2
117	2
104	2
77	95
62	2
51	32

Despite of the semi solid physical state of the azo ester ligands during summer season the new complexes of uranyl (VI) metal ion obtained were all crystalline solid with generally high melting points. These were stored in polythene tubes after re-crystallization. The purity of the new compounds was checked by the chromatographic methods. The new complexes prepared are listed below and their analytical data are presented in table 4.

1. [Bis (ethyl- α -(3-chloro phenylazo) acetoacetato) diiodo] Dioxouranium (VI)
2. [Bis (ethyl- α -(3-chloro phenylazo) acetoacetato) dinitro] Dioxouranium (VI)
3. [Bis (ethyl- α -(3-chloro phenylazo) acetoacetato) dichloro] Dioxouranium (VI)
4. [Bis (ethyl- α -(3-chloro phenylazo) acetoacetato) diacetato] Dioxouranium (VI)
5. [Bis (ethyl- α -(4-bromo phenylazo) acetoacetato) diiodo] Dioxouranium (VI)
6. [Bis (ethyl- α -(4-bromo phenylazo) acetoacetato) diacetato] Dioxouranium (VI)
7. [Bis (ethyl- α -(4-bromo phenylazo) acetoacetato) dinitro] Dioxouranium (VI)

Table 4: Analytical Data of The New Metal Complexes of Dioxouranium (VI) Metal Salts with Substituted Azoester Ligands

S. No.	Compound Name	Molecular Formula	Color	Molecular Weight Calculated (Observed)
1.	[Bis (ethyl- α -(3-chloro phenylazo) acetoacetato) diiodo] Dioxouranium (VI)	$C_{24}H_{28}I_2N_4O_8U$	Yellow	992.34 (985)
2.	[Bis (ethyl- α -(3-chloro phenylazo) acetoacetato) dinitro] Dioxouranium (VI)	$C_{24}H_{26}Cl_2N_6O_{14}U$	Deep Yellow	931.43 (927)
3.	[Bis (ethyl- α -(3-chloro phenylazo) acetoacetato) diacetato] Dioxouranium (VI)	$C_{28}H_{32}Cl_2N_4O_{12}U$	Light Yellow	925.51 (918)
4.	[Bis (ethyl- α -(3-chloro phenylazo) acetoacetato) dichloro] Dioxouranium (VI)	$C_{24}H_{26}Cl_4N_4O_8U$	Light Yellow	878.33 (870)

5.	[Bis (ethyl- α -(4-bromo phenylazo acetoacetato) diiodo] Dioxouranium (VI)	C ₂₄ H ₂₆ Br ₂ I ₂ N ₄ O ₈ U	Brown	1150.13 (1145)
6.	[Bis (ethyl- α -(4-bromo phenylazo acetoacetato) dinitro] Dioxouranium (VI)	C ₂₄ H ₂₆ Br ₂ N ₆ O ₁₄ U	Brown	1020.33 (1015)
7.	[Bis (ethyl- α -(4-bromo phenylazo acetoacetato) diacetato] Dioxouranium (VI)	C ₂₉ H ₃₅ Br ₂ N ₄ O ₁₂ U	Brown	1029.44 (1020)

All of these complexes are insoluble in common organic solvents. They were sparingly soluble in DMF and DMSO. Conductivity measurements in DMF for these complexes were too low to account for any disassociation of these complexes in DMF at the concentration of the 10⁻⁵ M. Hence, these complexes may be regarded as non electrolytes.

IR spectral studies

IR spectral analysis of the azoester ligands used for complex formation along with that of the representative complexes are reported in the tables 5-10. The N=N stretching vibration¹⁵ of a symmetrical trans-azo compound is forbidden in the infra red spectrum but absorbs and appears ca 1576 cm⁻¹ region of the Raman spectrum. Unsymmetrical para-substituted azo-benzenes in which the substituent is an electron donating group absorbs ca 1429 cm⁻¹. The bands are weak because of the non-polar nature of the bond. The bands at 1570 cm⁻¹ and 1590 cm⁻¹ due to ν (N=N) undergo batho-chromic shift to 1550 cm⁻¹ in metal complexes clearly indicates that one of the azo nitrogen is bonded to the metal atom.¹⁶⁻¹⁷

Table 5 : IR Absorption frequency (cm⁻¹) of [Bis (Ethyl- α -(3-Chloro phenylazo acetoacetato) dinitro] dioxouranium (VI)

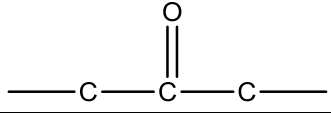
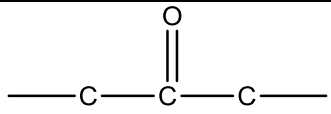
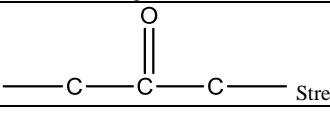
Assignment	Ligand	Complex
Aromatic C – H stretching	3200	3350
C = O Stretching ester	-	-
C – N Stretching	1425	1580
 Stretching vibration	1350	1390
 Bending	1225	-
C – Cl Stretching	1100	1080
Out of place CH vibration	900	-
Out of place C – H Bending	800	890
Out of place C = C Bend	700	710
M – N vibration	-	490

Table 6: IR Absorption frequency (cm⁻¹) of [Bis (Ethyl- α -(3-Chloro phenylazo acetoacetato) diacetato] dioxouranium (VI)

Assignment	Ligand	Complex
Aromatic CH stretching	3100	3350
C = O Stretching ester	1700	1700
C – N Stretching	1425	1500
C – Cl Stretching	1100	1080
Out of place C – H vibration	900	910
Out of place C – C Bending	700	690
M – N vibration	-	490

Table 7 : IR Absorption frequency (cm⁻¹) of [Bis (Ethyl- α -(3-Chloro phenylazo acetoacetato) dichloro] dioxouranium (VI)

Assignment	Ligand	Complex
Aromatic C – H stretching	3100	3300
C = O Stretching ester	1720	1760
C – N Stretching	1425	1500
 Stretching vibration	1350	1400

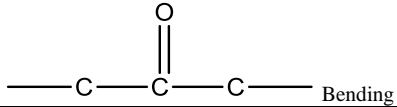
	1225	1200
C - Cl Stretching	1100	1100
Out of plane C - H vibration	900	850
Out of plane C - H Bending	800	800
Out of plane C = C Bend	700	700
M - N vibration	-	480

Table 8 : IR Absorption frequency (cm^{-1}) of [Bis (Ethyl- α -(4-bromo phenylazo acetoacetato) diiodo) dioxouranium (VI)]

Assignment	Ligand	Complex
Aromatic CH stretching	3200	3400
C=O stretching in ester	1750	1600
C=C stretching	1520	1520
C=O stretching in ester	1350	1390
Disubstituted Benzene	1100	1080
C - H deformation for disubstituted benzene	800	800
C - Br stretching	550	600
M - N vibration	-	480

Table 9 : IR Absorption frequency (cm^{-1}) of [Bis (Ethyl- α -(4-bromo phenylazo acetoacetato) diacetato) dioxouranium (VI)]

Assignment	Ligand	Complex
Aromatic CH stretching	3200	3250
C=O stretching in ester	1750	1600
C=C stretching	1520	1510
C=O stretching in ester	1350	1310
Disubstituted Benzene	1100	1100
C - H deformation for disubstituted benzene	800	810
C - Br stretching	550	520
M - N vibrational	-	480

Table 10 : IR Absorption frequency (cm^{-1}) of [Bis (Ethyl- α -(4-bromo phenylazo acetoacetato) dinitro) dioxouranium (VI) Solvent $\text{C}_2\text{H}_5\text{OH}$]

Assignment	Ligand	Complex
Aromatic C - H stretching	3200	3450
C=O stretching in ester	1750	1600
C=C stretching	1520	1550
C=O stretching in ester	1350	1390
Disubstituted Benzene	1100	1100
C - H deformation for disubstituted benzene	800	850
C - Br stretching	550	550
M - N vibration	-	480

Table 11: IR Absorption frequency (cm^{-1}) of [Bis (Ethyl- α -(4-bromo phenylazo acetoacetato) dinitro) dioxouranium (VI) Solvent $\text{C}_2\text{H}_5\text{OH} + \text{KOH}$]

Assignment	Ligand	Complexes
Aromatic C - M stretching	3200	3450
C=O stretching in ester	1750	1760
C=C stretching	1520	1520
C=O stretching in ester	1350	1400
Disubstituted Benzene	1100	1100
C - H deformation for disubstituted benzene	800	900
C - Br stretching	550	760
M - N vibration	-	490

Infrared (IR) spectroscopy has also been proved to be a tool to establish anions present in the complexes. In this present paper nitrate (NO_3^-); acetate (CH_3COO^-); and halo ($\text{X} = \text{Cl}^-$ and I^-) are chiefly used as anionic counter part to metal ions in the complexes under investigation. The IR studies of nitrate ions in these complexes under studies are reported in table 12 below.

Table 12: Infrared Absorption frequencies (cm^{-1}) of Nitrate Groups of dioxouranium (VI) metal Complexes of Azoester Ligands

Complexes	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5	Ref.
$\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{MeP})$	1510 sh	1310 s	1040 m	805 sh	742 m	705 m	8, 9
$\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{MPP})$	1500 s	1280 w	1025 s	820 m	755 s	-	8, 9
$\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{MNP})$	1500 sh	1310 m	1040 m	805 m	742 w	705 w	8, 9
Bis (Ethyl- α -(3-chloro phenylazo acetoacetato) dinitro) Dioxouranium (VI)	1500 sh	1310 sh	1040 m	820 m	750 w	710 w	This work
Bis (Ethyl- α -(4-bromo phenylazo acetoacetato) dinitro) Dioxouranium (VI)	1510 s	1300 sh	1050 w	825 w	760 m	710 w	This work

Lever separation rule may be applied to distinguish between mono-dentate or bi-dentate nitrate ions. Lever et. al¹⁸ showed that this to be true that the separation for mono-dentate nitrate in ($\nu_1 - \nu_4$) is appeared to be $5 - 26 \text{ cm}^{-1}$ and that for bi-dentate nitrate group this may lies in $20-60 \text{ cm}^{-1}$. This method has been tried in present complexes and a separation of $\text{Ca } 250 - 200 \text{ cm}^{-1}$ in the combination bands in the region $1550 - 1290 \text{ cm}^{-1}$ has been investigated which suggest that nitrate ion may be bi-dentate in nature in these complexes¹⁹⁻²¹. Similar to nitrate, acetate ion in the present study of complexes also appears to be bi-dentate ligand. In the case of halo complexes (M-X) IR spectral vibrations could not be assigned because they are out of the range of studied region used in the present investigations.

Oxocation (O=U=O) Vibrations:

Uranyl (VI or dioxouranium (VI) ion is quite peculiar both in its own structure and in its coordination behavior. This ions retains its identity over a wide range of vibrations in experimental conditions and can be considered as a single particle from geometric point of view. It has four fundamental vibrations viz.

- (i) Non-degenerate symmetric stretching vibration ν_2 (normally IR forbidden $\sim 900-800 \text{ cm}^{-1}$)
- (ii) Non-degenerate symmetric stretching vibration ν_3 (usually IR active $\sim 1000-900 \text{ cm}^{-1}$) and
- (iii) Doubly degenerate O-U-O bending vibration ν_2 (IR active $\sim 750-700 \text{ cm}^{-1}$)

In the present investigation the U=O in all the cases has been assigned ν_3 and ν_1 approximately in the region $920-890 \text{ cm}^{-1}$ and $850-800 \text{ cm}^{-1}$ respectively as recorded and shown in table 13.

Table 13: Oxocation (O=U=O) Related Vibrations ν_1 and ν_3 (cm^{-1}) for Dioxouranium (VI) Complexes of Azoester Ligands

Complexes	ν_1	ν_3
[Bis (Ethyl- α -(4-bromo phenylazo) acetoacetato) diacetato] dioxouranium (VI)	810 w	920 s
[Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) diacetato] dioxouranium (VI)	820 sh	910 s
[Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) dinitro] dioxouranium (VI)	825 w	890 s
[Bis (Ethyl- α -(4-bromo phenylazo) acetoacetato) dinitro] dioxouranium (VI) Solvent $\text{C}_2\text{H}_5\text{OH} + \text{KOH}$	825 w	900 s
[Bis (Ethyl- α -(4-bromo phenylazo) acetoacetato) dinitro] dioxouranium (VI) Solvent $\text{C}_2\text{H}_5\text{OH}$	850 m	900 sh
[Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) dichloro] dioxouranium (VI)	850 m	900 sh
[Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) diiodo] dioxouranium (VI)	810 w	890 s
[Bis (Ethyl- α -(4-bromo phenylazo) acetoacetato) diiodo] dioxouranium (VI)	800 s	920 s

UV- Visible spectral studies

UV- Visible spectral analysis of some of the representative complexes have also been done and these are reported in tables 14,15 below

Table 14 : UV-Visible Spectra of Ethyl- α -(3-Chlorophenyl azo aceto acetato) and Various Complexes with Dioxouranium (VI) Transition (nm)

S. No.	Ligands/Complex	$\pi - \pi^*$	$\pi - \pi^*$
1.	Ethyl - α -(3-Chloro phenylazo) acetoacetate	402	487
2.	[Bis (Ethyl - α -(3-Chloro phenylazo) acetoacetato) diiodo] dioxouranium (VI)	340	360
3.	[Bis (Ethyl - α -(3-Chloro phenylazo) acetoacetato) dinitro] dioxouranium (VI)	340	360
4.	[Bis (Ethyl- α -(3-Chloro phenylazo) acetoacetato) diacetato] dioxouranium (VI)	450	460
5.	[Bis (Ethyl - α - (3-Chloro phenyl azo) acetoacetato) dichloro] dioxouranium (VI)	450	460

Table 15 : UV-Visible Spectra of Ethyl- α -(4-bromo phenylazo) aceto acetato) and Various Complexes with Dioxouranium (VI) Transition (nm)

S. No.	Ligands/Complex	$n \rightarrow \pi^*$	$\pi - \pi^*$
1.	Ethyl - α -(4-bromo phenylazo) acetoacetate	374	437
2.	[Bis (Ethyl - α -(4-bromo phenylazo) acetoacetato) diiodo] dioxouranium (VI)	360	440

3.	[Bis (Ethyl – α -(4-bromo phenylazo) acetoacetato) diacetato] dioxouranium (VI)	360	420
4.	[Bis (Ethyl – α -(4-bromo phenylazo) acetoacetato) dinitro] dioxouranium (VI) solvent C ₂ H ₅ OH	320	360
5.	[Bis (Ethyl – α -(4-bromo phenylazo) acetoacetato) dinitro] dioxouranium (VI) solvent C ₂ H ₅ OH + KOH	400	410

Magnetic Behaviour of Complexes:

Complexes of uranyl (VI) metal salts are diamagnetic in nature depending upon the other ions present and the corresponding ligand field. The magnetic susceptibilities are independent of field strength and temperature. In the present studies complexes are weakly diamagnetic as observed²²⁻²⁴.

DTA studies of the Complexes

The results of these Differential Thermal Analysis (DTA) studies which are carried out on representative complexes under studies are reported in Table 13 -14. The observed DTA graphs clearly show the stability of complexes up to considerably higher temperature range. The peaks located as EXO and ENDO peaks are mentioned in tables below. In all of these cases oxides are formed as final products viz. stable ThO₂ and U₃O₈ over a comparatively high range of temperatures. These studies confirm the high stability of these complexes under studies up to high temperature. In intermediate steps of DTA analysis it has been suggested that ligand moiety may left the complex molecules. Results of DTA are presented in tables 16 and 17.

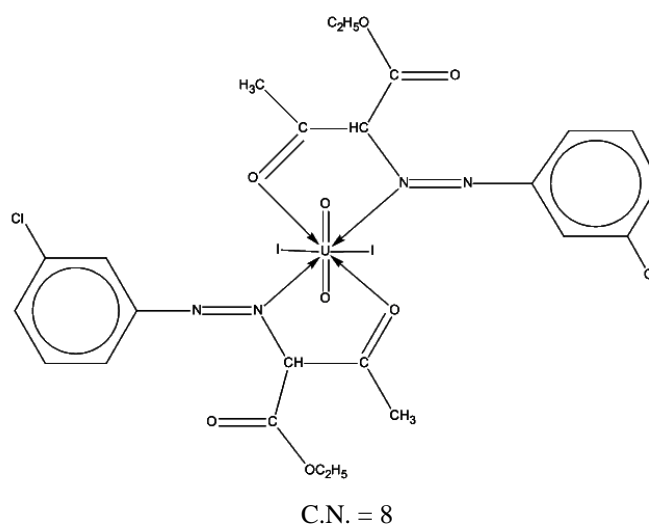
Table 16 : DTA Study of [Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) diacetato] Dioxouranium (VI) (C₂₈H₃₂Cl₂N₄O₁₂U), Mol. Wt. – 924.19

S. No.	Temperature Range (°C)	Peaks	Final Product
1.	110° - 120°	Endo	–
2.	200° - 210°	Exo	–
3.	340° - Above	Exo	U ₃ O ₈

Table 17: DTA Study of [Bis (Ethyl- α -(4-bromo phenylazo) acetoacetato) dinitro] Dioxouranium (VI) (C₂₄H₂₆Br₂N₆O₁₄U), Mol. Wt. – 1020.33

S. No.	Temperature Range (°C)	Peaks	Final Product
1.	40° - 50°	Endo	–
2.	150° - 180°	Exo	–
3.	300° - 325°	Exo	U ₃ O ₈

Based on the studies done on newly synthesized complexes of uranyl(VI) metal salts, their tentative structures were proposed along with their coordination numbers which are given in figure 3 below.



Chemical Formula: C₂₄H₂₆Cl₂I₂N₄O₈U

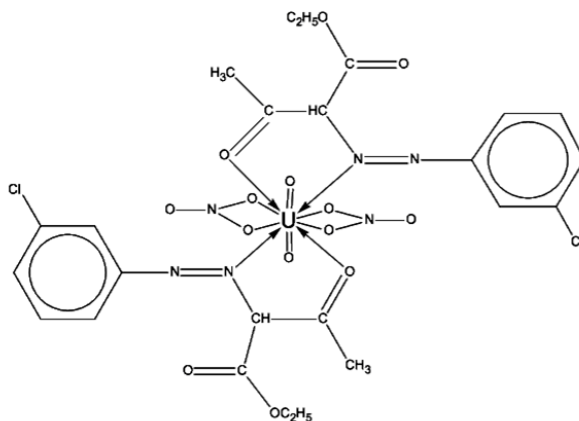
Exact Mass: 1059.97

Molecular Weight: 1061.23

m/z: 1059.97 (100.0%), 1061.97 (64.2%), 1060.98 (26.5%), 1062.97 (17.7%), 1063.97 (11.5%), 1061.98 (5.0%), 1064.97 (2.8%), 1063.98 (2.2%), 1060.97 (1.5%)

Elemental Analysis: C, 27.16; H, 2.47; Cl, 6.68; I, 23.92; N, 5.28; O, 12.06; U, 22.43

Bis (Ethyl- α -(3-chlorophenylazo) acetoacetato) diiodo dioxouranium(VI)



C.N. = 10

Chemical Formula: $C_{24}H_{26}Cl_2N_6O_{14}U$

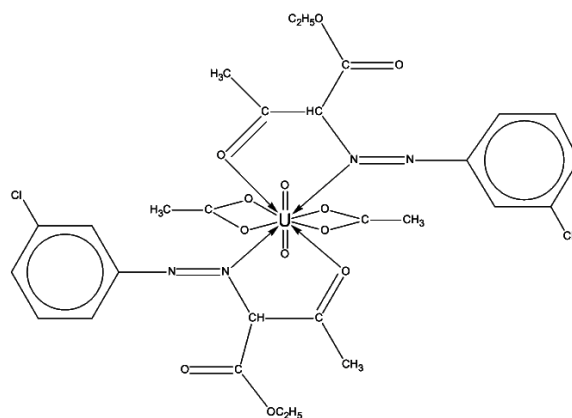
Exact Mass: 930.14

Molecular Weight: 931.43

m/z: 930.14 (100.0%), 932.14 (67.4%), 931.14 (28.7%), 933.14 (17.3%), 934.13 (10.2%), 934.14 (4.4%),
932.15 (3.4%), 935.14 (3.3%), 933.13 (1.4%), 933.15 (1.1%)

Elemental Analysis: C, 30.95; H, 2.81; Cl, 7.61; N, 9.02; O

Bis (Ethyl- α (3-chlorophenylazo acetoacetato) dinitro dioxouranium(VI)



C.N. = 10

Chemical Formula: $C_{28}H_{32}Cl_2N_4O_{12}U$

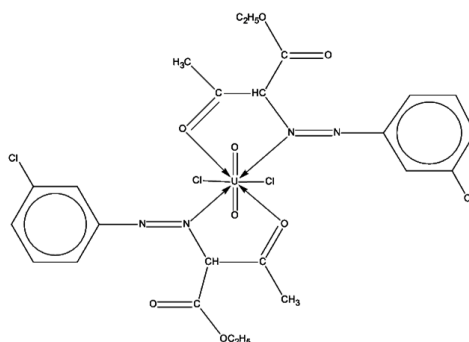
Exact Mass: 924.19

Molecular Weight: 925.51

m/z: 924.19 (100.0%), 926.19 (66.8%), 925.19 (32.2%), 927.19 (20.0%), 928.18 (10.2%), 928.19 (4.8%),
926.20 (4.7%), 929.19 (3.7%), 927.20 (1.2%)

Elemental Analysis: C, 36.34; H, 3.49; Cl, 7.66; N, 6.05; O, 20.74; U, 25.72

Bis (Ethyl- α (3-chlorophenylazo acetoacetato) diacetato dioxouranium(VI)



C.N. = 8

Chemical Formula: $C_{24}H_{26}Cl_4N_4O_8U$

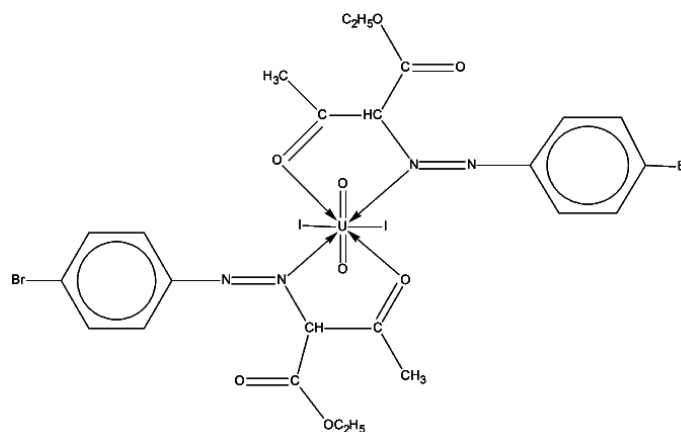
Exact Mass: 876.10

Molecular Weight: 878.33

m/z: 878.10 (100.0%), 876.10 (78.0%), 880.10 (49.8%), 879.10 (28.0%), 877.10 (21.4%), 881.10 (12.8%), 882.09 (10.2%), 878.11 (3.9%), 880.11 (3.4%), 883.10 (2.9%), 882.10 (2.6%)

Elemental Analysis: C, 32.82; H, 2.98; Cl, 16.15; N, 6.38; O, 14.57; U, 27.10

[Bis(Ethyl- α (3-chlorophenylazo acetoacetato) dichloro) dioxouranium (VI)



C.N. = 8

Chemical Formula: $C_{24}H_{26}Br_2I_2N_4O_8U$

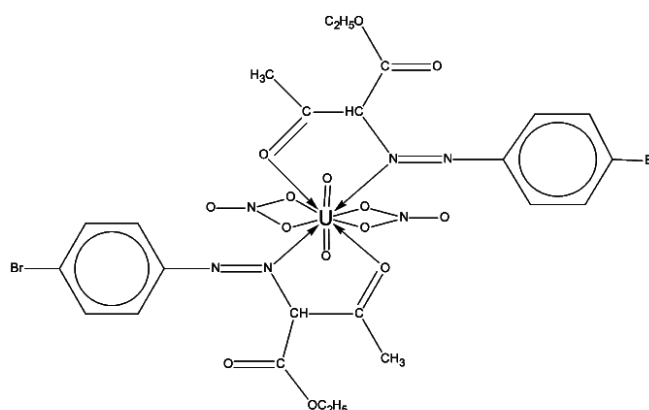
Exact Mass: 1147.87

Molecular Weight: 1150.13

m/z: 1149.87 (100.0%), 1147.87 (51.5%), 1151.87 (50.6%), 1150.87 (27.7%), 1148.87 (14.1%), 1152.87 (13.0%), 1151.88 (3.4%), 1153.87 (2.6%), 1149.88 (2.6%)

Elemental Analysis: C, 25.06; H, 2.28; Br, 13.89; I, 22.07; N, 4.87; O, 11.13; U, 20.70

[Bis(Ethyl- α (4-bromophenylazo acetoacetato) diiodo) dioxouranium (VI)



Chemical Formula: $C_{24}H_{26}Br_2N_6O_{14}U$

Exact Mass: 1018.04

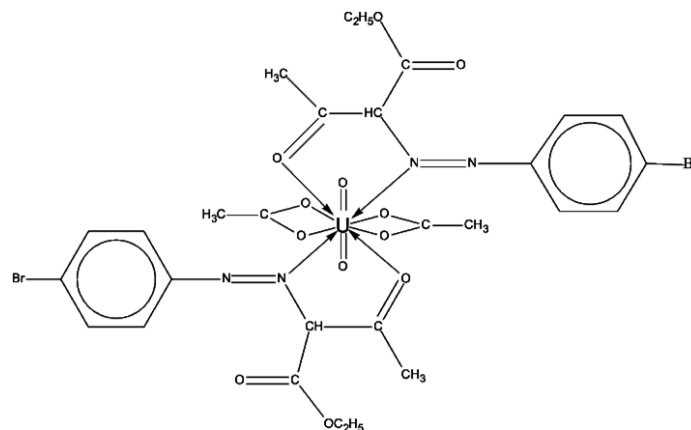
Molecular Weight: 1020.33

m/z: 1020.04 (100.0%), 1018.04 (49.7%), 1022.03 (47.0%), 1021.04 (26.0%), 1019.04 (14.4%), 1023.04 (13.5%), 1022.04 (6.6%), 1024.04 (3.0%), 1021.03 (2.2%), 1023.03 (1.0%)

Elemental Analysis: C, 28.25; H, 2.57; Br, 15.66; N, 8.24; O, 21.95; U, 23.33

C.N. = 10

[Bis (Ethyl- α (4-bromo phenylazo aceto acetato) dinitro) dioxouranium (VI)



C.N. = 10

Chemical Formula: $C_{29}H_{35}Br_2N_4O_{12}U$

Exact Mass: 1027.11

Molecular Weight: 1029.44

m/z: 1029.11 (100.0%), 1027.11 (51.4%), 1031.11 (51.4%), 1030.11 (16.4%), 1031.12 (5.1%), 1029.12 (3.8%), 1033.12 (2.6%), 1033.11 (1.4%), 1032.12 (1.3%), 1030.12 (1.1%)

Elemental Analysis: C, 33.83; H, 3.43; Br, 15.52; N, 5.44; O, 18.65; U, 23.12

[Bis(Ethyl- α -(4-bromophenylazo) acetoacetato) diacetato] dioxouranium (VI)

Figure 3

Antimicrobial studies of Complexes:

The antimicrobial activities of different representative complex compound samples under studies were tested against different microbial species using Methods reported earlier²⁵⁻²⁷ on nutrient agar NA medium using paper disc method. Results obtained are presented in the table 18,19 given below. None of the complex compound products showed any significant antimicrobial activity

Table 18: Biological Activity Zone of Inhibition for Fungal Growth for Various Complexes of Dioxouranium(VI)

Complexes (20 mg/ml)	Zone of Inhibition (mm)				
	Fungal M.F.	SP M.G.	A.N.	P.S.	S.C.
Control Cyclohexamide (10 mg/ml)	10	12	16	16	20
[Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) diiodo] Dioxouranium (VI)	-	-	-	-	-
[Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) dinitro] Dioxouranium (VI)	-	-	-	-	-

MF= Microsporium fulvum

MG= Microsporium gypseum

AN= Aspergillus niger

PS= Penicillium species

SC= Saccharomyces cerevisiae

Table 19: Biological Activity Zone of Inhibition for Bacterial Growth for Various Complexes of Dioxouranium (VI)

Complexes (20 mg/ml)	Zone of Inhibition (mm)				
	Bacterial E.A.	SP P.V.	E.C.	S.A.	B.S.
Tetracycline (10 mg/ml)	20	25	10	32	30
[Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) diiodo] Dioxouranium (VI)	-	9	-	8	-
[Bis (Ethyl- α -(3-chloro phenylazo) acetoacetato) dinitro] Dioxouranium (VI)	-	8	-	8	9

EA= Enterobacter aerogens

PV= Proteus vulgaris

EC= Escherichia coil

SA= Staphylococcus aureus

BS= Bacillus subtilis

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