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Study of the products obtained by treating Glutamic Acid with Tertiary Butyl Chromate in water

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Abstract : *Di-tert-butyl chromate (TBC) was prepared by dissolving calculated quantity of pure and dry chromium trioxide (CrO_3) in tert-butyl alcohol (TBA). Glutamic acid was treated with TBC in different substrate : oxidant (TBC) molar ratio in water as solvent. The solid products obtained were isolated, washed, dried, purified and collected as GU11, GU21, GU23. The formulae of these products have been worked out on the basis of elemental analysis, thermogravimetric studies and FTIR peaks.*

Keywords : FTIR, Glutamic acid, Peaks, TBA, TBC, Water

Introduction:

TBC has been used as oxidant by several workers. They have used this oxidant for the oxidation of various types of organic compounds. In most of these studies, solid complexes of chromium have been obtained. G.D Mishra *et.al.* [1-11] have used TBC for oxidizing various organic compounds. In the present work, we have used glutamic acid with TBC in various substrate: oxidant ratios in water.

Chemical used :

Chromium trioxide (CrO_3), TBA, water, Glutamic acid, potassium persulphate ($K_2S_2O_8$), acetone etc. (Chemical used were all A.R.Grade.)

Experimental Procedure :

(a) **GU 11** (substrate : oxidant :: 1:1 molar ratio) TBC was prepared by dissolving 1 gm of pure and dry CrO_3 in 10 ml of TBA. 1.47 gm of glutamic acid was dissolved in water to get substrate solution (SS-1). Exothermic reaction took place when TBC was added to SS-1 leading to the formation of brown precipitate which turn to brown product when washed several times with acetone and dried. This was labeled as GU 11.

(b) **GU21** (substrate : oxidant :: 1:0.5 molar ratio) : TBC was prepared by dissolving 0.5 gm of pure and dry CrO_3 in 10ml of TBA 1.47 gm of glutamic acid was dissolved in water to get substrate solution (SS-2). Exothermic reaction took place when TBC was added to SS-2 leading to the formation of black precipitate. The product turned into greenish brown product when washed several times with acetone and dried. This was labeled as GU21.

(c) **GU23** (substrate : oxidant :: 1:2 molar ratio) : TBC was prepared by dissolving 0.015 gm of pure and dry CrO_3 in 10 ml of TBC. 1.47 gm of glutamic acid was dissolved in water to get substrate solution (SS-3). TBC solution was now added to SS-3 solution. After 5 minutes it started boiling which showed the highly exothermic nature of the reaction. The reaction mixture was now left overnight. The solid products obtained thus was washed successively with acetone and water. The black colour solid was labeled as sample GU 23

Results and Discussion:

The quantitative analysis of carbon, hydrogen & nitrogen were performed instrumentally. The chromium content was estimated volumetrically. The proposed formula, percentage composition of the complex was experimentally found as well as calculated theoretically.

(a) GU 11 : Table 1 shows the comparison of observed and calculated elemental percentage.
Colour - Greyish black

Table I
(COMPOSITION OF GU11)

Element	Observed %	Calculated %
Nitrogen	5.427	4.635
Carbon	23.78	23.84
Hydrogen	14.371	4.304
Chromium	17.33	17.218
Oxygen	49.09	47.68

Empirical Formula : $CrNC_6H_{13}O_9$

Proposed Formulation : $CrO[COOH.CH_2CH_2NH_2.CH_2CH_2COOH] .4H_2O$

The FTIR peaks also support the presence of the bonds and groups presents in proposed formula (Table II).

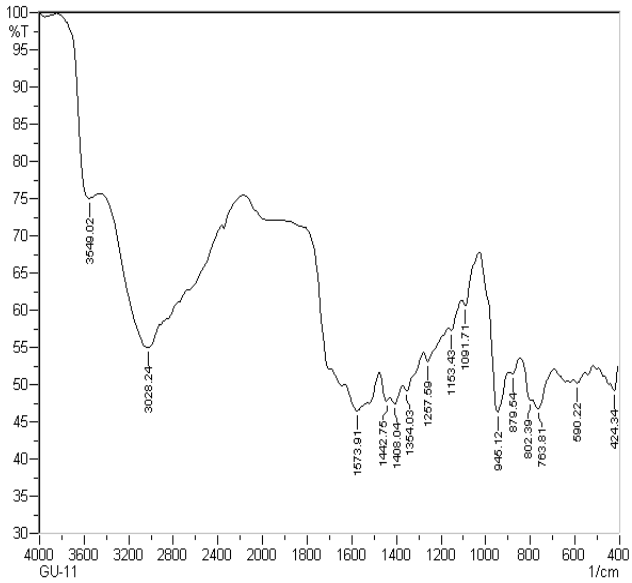


Table II
FTIR peak of complex GU11

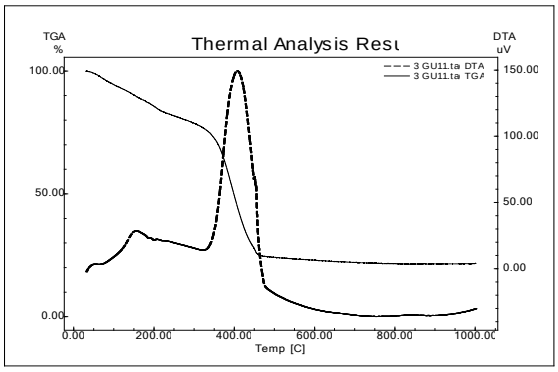
Peak at	Nature of Peaks	Group Assignment
3549.02	Broad	Ar-NO_2, C-H stretching
3028.24	Broad	Ar-NO_2, C-H stretching
1573.91	Sharp	-COO group, Coordinated COOH group
1442.75	Medium	C-H stretching, C=C stretching
1408.04	Weak	C=O stretching
1354.03	Sharp	COO^- group
1257.59	Sharp	O-NO2,V_s(C-O) + S (O-C=O) V_8
1153.43	Sharp	C-O of alcohol, COOH, aldehyde
1091.71	Weak	C-C stretching
945.12	Weak	CO coordinated water
879.54	Weak	O-H Rocking (due to water)
802.39	Weak	O-H Rocking (due to water)
763.81	sharp	HCOOH
590.22	Weak	Cr-O bonding
424.34	Weak	Cr-O bonding

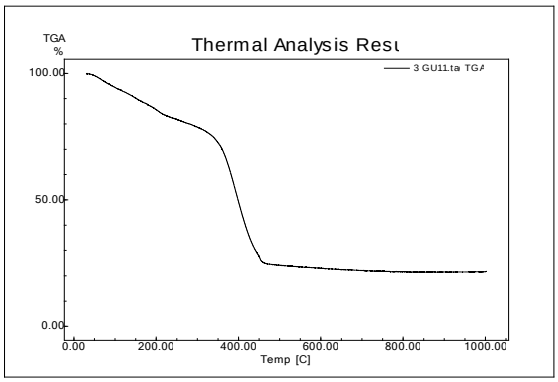
The DTA-TGA curves of the complex GU 11 show the expected loss pattern for the proposed formulation. The two stages of the loss as supported by DTA curves occur in between 33 ^{0}C and 485^{0}C. The 1st loss of 22.548 % (theoretical 24.406 %) corresponds to the escape four water molecule in the temperature range of 33- 317^{0}C. The second experimental loss of 52.99 % (theoretical 50.16%) is attributed two molecules of propanoic acid and amino group leaving behind the oxide of Cr (Table III,weight loss pattern).

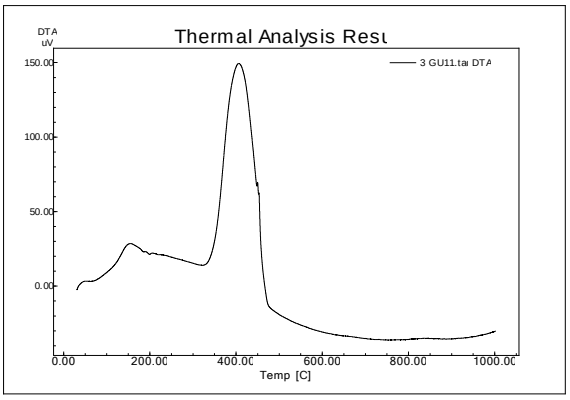
Table III
WEIGHT LOSS PATTERN

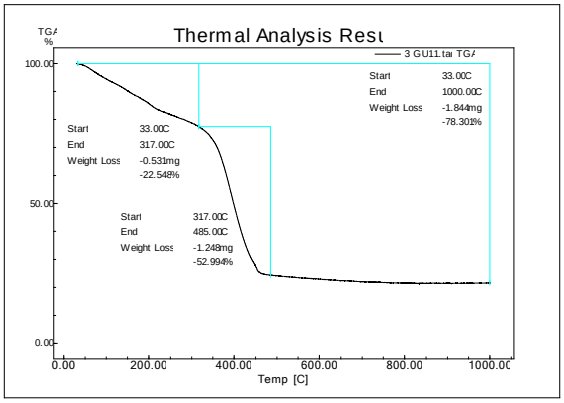
Temperture	Weight loss pattern	Percentage loss	
		Experimental	Theortical
33^0C-317^0C	$CrO[COOH\ CH_2\ CH_2\ NH_2\ CH_2\ CH_2\ COOH].\ 4H_2O$	22.548	24.406
	$\downarrow -4H_2O$		
317^0C-485^0C	$CrO[COOH\ CH_2\ CH_2\ NH_2\ CH_2\ CH_2\ COOH]$	52.99	50.16
	$\downarrow -[COOH\ CH_2\ CH_2\ NH_2\ CH_2\ CH_2\ COOH]$		
	CrO		

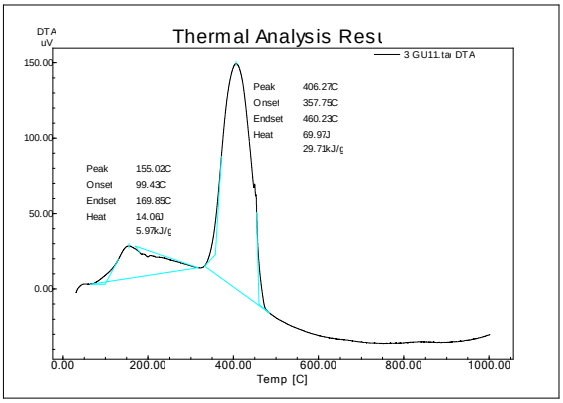
DTA-TGA curves of complex GU11











Results and Discussion :

(b) GU 21 Table 4 shows the comparison of observed and calculated elemental percentage.
Colour - Greyish black

Table IV
(COMPOSITION OF GU21)

Element	Observed %	Calculated %
Nitrogen	7.039	6.36
Carbon	30.57	27.27
Hydrogen	5.362	7.27
Chromium	12.133	11.81
Oxygen	44.896	47.27

Empirical Formula : $CrNC_{10}H_{23}O_{13}$

Proposed Formula : CrO_2 [COOH.CH_2 CH_2CH_2HCHO.HCHO $CH_2CH_2CH_2$ NH_2COOH] $5H_2O$

The FTIR peaks support the presence of the bonds and groups presents in proposed formula (Table V).

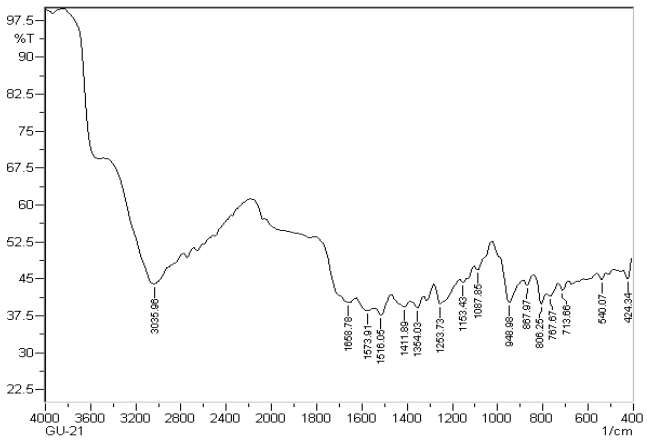


Table V
FTIR peak of complex GU21

Peak at	Nature of Peaks	Group Assignment
3035.96	Broad	Ar-NO_2, C-H stretching
1658.78	Middle	C=O stretching (aldehyde), (-C=C-) Alkene
1573.91	Weak	C=O stretching
1516.05	Sharp	-COO group, Coordinated COOH group
1411.89	Weak	C=O stretching
1354.03	Sharp	COO^- group
1253.73	Sharp	O-NO2,V_s(C-O) + S (O-C=O) V_8
1153.43	Sharp	C-O of alcohol, COOH, aldehyde
1087.85	Weak	C-C stretching
948.98	Weak	CO coordinated water
867.97	Weak	O-H Rocking (due to water)
806.25	Weak	O-H Rocking (due to water)
767.67	sharp	HCOOH
713.66	sharp	HCOOH
540.07	Weak	Cr-O bonding
424.34	Weak	Cr-O bonding

The DTA-TGA curves of the complex GU 21 show the expected loss pattern for the proposed formulation. The two stages of the loss as supported by DTA curves occur in between 150^0C ^0C and 485^0C.The 1st loss of 23.99 % (theoretical 21.06 %) corresponds to the escape of five water molecules in the temperature range of 150- 275^0C. The second experimental loss of

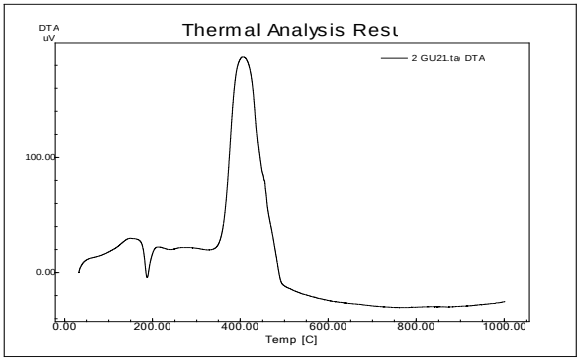
52.99 %(theoretical 50.16%) is attributed to two molecules of butanoic acid, two molecules of formaldehyde and amino group leaving behind the oxide of Cr (Table VI,weight loss pattern).

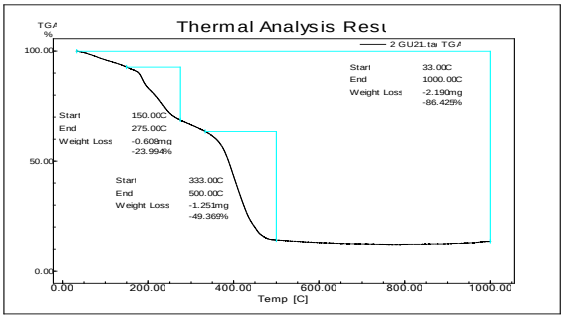
Table VI

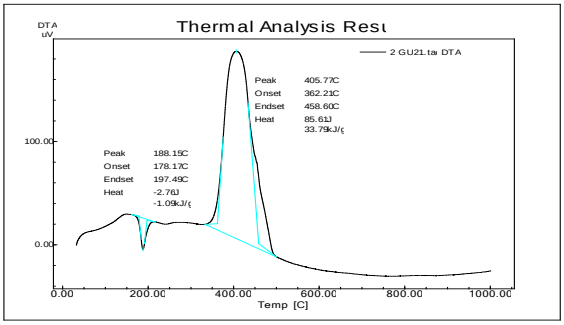
WEIGHT LOSS PATTERN

Temperture	Weight loss pattern	Percentage loss	
		Experimental	Theortical
150^0C-275^0C	CrO_2[COOH $CH_2CH_2CH_2HCHO.HCHO$ $CH_2CH_2CH_2NH_2COOH$] $5H_2O$	23.99	21.26
	-5 H_2O		
333^0C-500^0C	CrO_2[COOH $CH_2CH_2CH_2HCHO.HCHO$ $CH_2CH_2CH_2NH_2COOH$]	49.369	57.27
	[COOH $CH_2CH_2CH_2HCHO.HCHO$ $CH_2CH_2CH_2NH_2COOH$]		
	CrO_2		

DTA-TGA curves of complex GU21







Results and Discussion:

(c) GU23 : Table 7 shows the comparison of observed and calculated elemental percentage.
Colour - Black

Table – VII
COMPOSITION OF GU23

Element	Observed %	Calculated %
Nitrogen	4.247	3.286
Carbon	20.84	22.53
Hydrogen	3.823	5.63
Chromium	12.133	12.20

Empirical Formula :$CrN_1C_8H_{17}O_{15}$

Proposed Formula :CrO_3[COOH CH_2

CH_2 COOH COOH CH_2 CH_2NH_2COOH] $4H_2O$

The FTIR peaks support the presence of the bonds and groups presents in proposed formula (Table VIII).

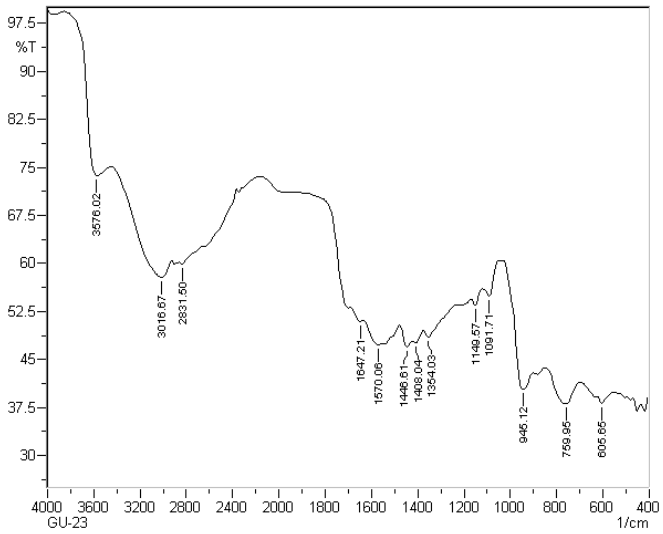


Table VIII
FTIR peak of complex GU23

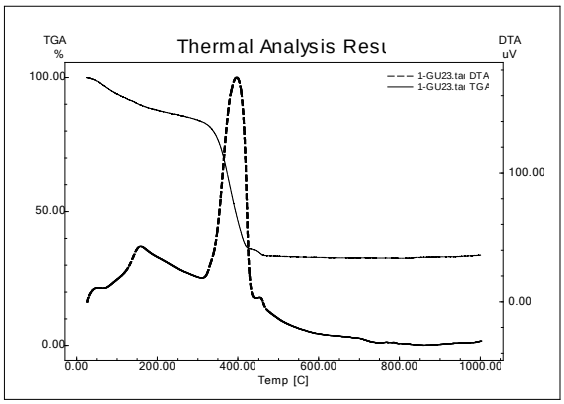
Peak at	Nature of Peaks	Group Assignment
3576.02	Broad	Ar-NO_2, C-H stretching
3016.67	Broad	Ar-NO_2, C-H stretching
2831.50	Broad	Ar-NO_2, C-H stretching
1647.21	Middle	C=O stretching (aldehyde), (-C=C-) Alkene
1570.06	Sharp	-COO group, Coordinated COOH group
1446.61	Medium	C-H stretching, C=C stretching
1408.04	Weak	C=O stretching
1354.03	Sharp	COO^- group
1149.57	Sharp	C-O of alcohol, COOH, aldehyde
1091.71	Weak	C-C stretching
945.12	Weak	CO coordinated water
759.95	sharp	HCOOH
605.65	Weak	Cr-O bonding

The DTA-TGA curves of the complex GU 23 show the expected loss pattern for the proposed formulation. The two stages of the loss as supported by DTA curves occur in between 25^0C ^{0}C and 470^0C.The 1st loss of 16.77 % (theoretical 17.118 %) corresponds to the escape of four water molecules in the temperature range of 25- 313^0C. The second experimental loss of 49.678 % (theoretical 46.062%) is attributed to two molecules of propanoic acid,two molecules of formic acid and an amino group leaving behind the oxide of Cr (Table IX,weight loss pattern).

Table IX
WEIGHT LOSS PATTERN

Temperture	Weight loss pattern	Percentage loss	
		Experimental	Theortical
25^0C-313^0C	$CrO_3[COOH\ CH_2\ CH_2\ COOH\ COOH\ CH_2\ CH_2\ NH_2\ COOH]\ 4H_2O$ ↓ -4 H_2O	16.77	17.118
313^0C-470^0C	$CrO_3[COOH\ CH_2\ CH_2\ COOH\ COOH\ CH_2\ CH_2\ NH_2\ COOH]$ ↓ $[COOH\ CH_2\ CH_2\ COOH\ COOH\ CH_2\ CH_2\ NH_2\ COOH]$ CrO_3	49.678	46.062

DTA-TGA curves of complex GU23


Thermal Analysis Resu
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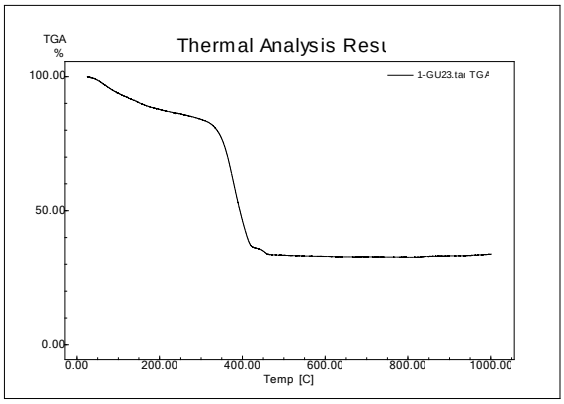
Thermal Analysis Resu
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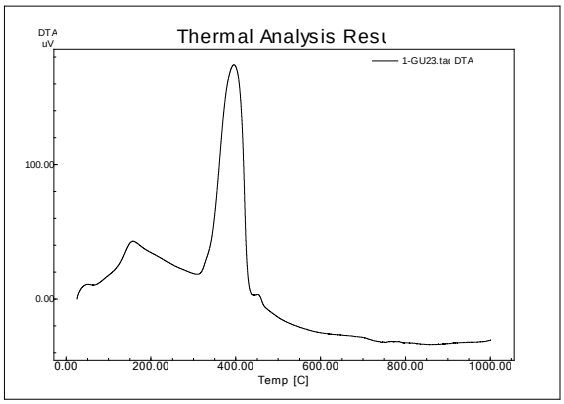
Thermal Analysis Resu
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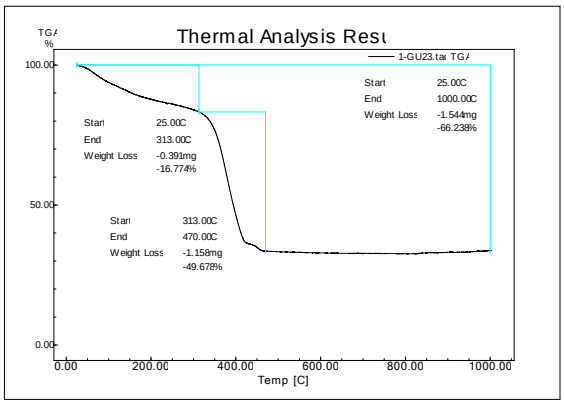

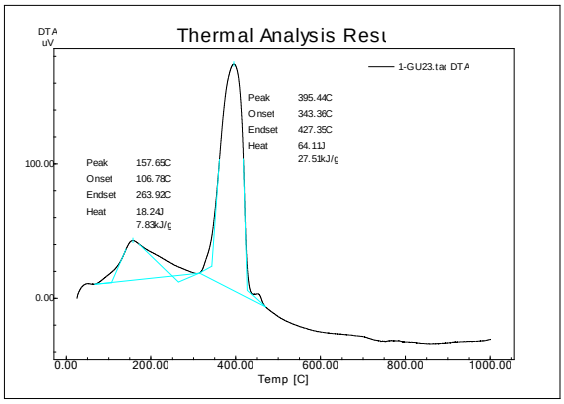

Conclusion

The reaction conditions in table show that the formation of compounds/ complexes of chromium with glutamic acid is difficult. The chemical oxidation of glutamic acid under mechanical stirring and microwave condition leads to different product including nitro derivatives. The degradative oxidation of the substrate takes place when the ratio of oxidant is more as substantiated by the presence of smaller fragments in case of GU-23. The formation of amino compound in higher ratio of oxidant is supported by its presence in GU -23 as ligand. This is not observed in other cases where the extent of oxidation is less. Extent of degradative oxidation increases as the proportion of oxidant is raised, as the lower fragment HCOOH is observed in GU-23. It is also supported by the fact that some of the complexes like GU-21 & GU-23 is formed with the unoxidised ligand along with other side products (where the oxidant ratio is less compared to GU-23). Again the solubility of the products in water is more in those cases when glutamic acid itself is present as ligand. The number of water molecule in the products GU-23 is more whereas it is less in products GU-11 and GU-21. This may be due to the fact that greater extent of oxidation leads to the formation of smaller organic moiety and greater number of water molecules.

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