

Synthesis and Characterization of Some N-Protected Amino Acid Complexes

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Abstract: Metal complexes of N-phthaloyl glycine with Cu(II), Ag(I), Cd(II), Hg(II), and Pb(II) have been prepared in aqueous methanolic solution. The complexes have been characterized by elemental analysis, thermo gravimetric analysis (TG, DTG), and mass, infrared and ¹H-NMR spectra. Infrared spectra were detected concerning, the final residual of the thermal decomposition of all the N-phthaloyl glycine complexes. N-phthaloyl glycine (Gly) molecule coordinated to the metal ions through its carboxylic group.

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Key words: complexes, Infrared spectra, ¹HNMR, Mass Spectra, Thermogravimetric analysis.

1. Introduction

Amino acids have been repeatedly shown to produce wide complexes with transition metals repeatedly in the literature [1-11]. All of naturally occurring α -amino acids bind in what is known as the glycinato way. This means that a five-membered ring is formed with the metal, amine nitrogen and the carboxylic oxygen. This arrangement is always present for the natural human amino acids even when the side chain has a ligating group. If there is a ligating group on the side chain, it will typically bind apically in place of a solvent molecule. The N-protected amino acids are used for the synthesis of peptide bonds in solid phase syntheses [12,13]. The phthalimide group acts as a protecting group for amines and amino acids [14-17]. Several phthalimide derivatives have importance in medicinal chemistry and are used as antimicrobial reagents [18,19]. Amino acid complexes are important in biology [20-26]. The metal complexes of N-protected α -amino acids are of great interest because they may be used as a basis for understanding metal-protein interactions [27]. Coordination chemistry of these amino acids with metals can give a basis for understanding the coordination chemistry for the protein at large.

Much kind of proteins within the body need metal ions to work, that can also be activated or deactivated by metal ions. These reversible effects are caused by ligation of the metal ions and the protein. If one has an understanding of the basic metal ion N-protected α -amino acid complexation, then one could better identify the coordination site within the protein much more easily. Then one could simply use the N-protected α -amino acids as models of the binding sites of various proteins [28,29].

2. Experimental

All chemicals used in this work were analytical Analar grade. The N-phthaloyl glycine, C₁₀H₇NO₄(Gly) was synthesized according to procedure described before [11], its structure was given in formula 1. Carbon, nitrogen and hydrogen contents were determined using a Perkin-Elmer CHN 2400. The metal content was gravimetrically determined by converting the compounds into their corresponding oxides.

Infrared spectra were recorded for the free N-phthaloyl glycine and all the prepared complexes on Bruker FT-IR spectrophotometer (4000-400 cm⁻¹) in KBr discs. ¹H-NMR spectra of the free N-phthaloyl glycine and its silver(I) complex were recorded on Varian Gemini 200 MHz spectrometer using DMSO- d₆ as a solvent. Mass spectra for the free N-phthaloyl glycine ligand, and their copper(II) and silver complexes were measured by using AEI MS 30 mass spectrometer.

Thermogravimetric data with the temperature range from 25 to 600 °C were recorded for the investigated complexes in a flowing nitrogen atmosphere with a heating rate of 10° C/min on a Shimadzu TGA-50H Thermal Analyzer.

2.1 Synthesis of metal complexes:

All of the Cu(II), Ag(I), Cd(II), Hg(II), and Pb(II) complexes were prepared in an aqueous methanolic solution. Copper(II) complex was prepared with metal to ligand with a molar ratio of 1: 2. Silver(I) and lead(II) complexes were precipitated with a 1:1 metal to ligand molar ratio. Cadmium(II) and mercury(II) complexes were obtained with 1:6

molar ratio. The precipitates were formed at once with stirring and gently heating. The resulted precipitates were filtered off, washed with a hot methanol and then dried under vacuum over anhydrous CaCl_2 . The copper complex is blue crystalline precipitate while the other metal complexes are white powder.

3. Results and Discussion:

The elemental analysis data and some physical characteristics of the obtained metal complexes are given in Table 1. In the literatures [30-37] the N-protected amino-acids coordinated to metal ions as a bidentate through its carboxylate group.

Table 1: Elemental analyses data of the N-phthaloyl glycine complexes

Complexes	Mwt.	Content found (calculated)			Color	m.p. °C
		% C	% H	% N		
[Cu(Gly) ₂ (H ₂ O)]	507	47.35 (47.34)	3.34 (3.16)	5.16 (5.52)	blue	300
[Cd(Gly) ₆]	1336	57.97 (53.89)	3.94 (2.69)	5.85 (6.29)	white	180
[Ag(Gly)]	311.87	38.36 (38.47)	1.15 (1.92)	4.54 (4.49)	white	310
[Hg(Gly) ₆]	1424	56.85 (50.56)	3.69 (2.53)	5.66 (5.90)	white	180
[Pb(Gly)(NO ₃)(H ₂ O) ₄]	545.19	21.51 (22.01)	2.86 (2.57)	2.33 (2.57)	white	320

3.1. Infrared spectra:

Table 2 shows the infrared spectra and its band assignments for the free N-phthaloyl

glycine and its complexes, [Cu(Gly)₂·2H₂O], [Cd(Gly)₆], [Ag(Gly)], [Hg(Gly)₆] and [Pb(Gly)NO₃(H₂O)₄].

Table 2: Infrared frequencies^(a) (cm⁻¹) and band assignments for free N-phthaloyl glycine and their metal complexes

Free Gly	Metal complexes					Assignments ^(b)
	Cu complex	Cd complex	Ag complex	Hg complex	Pb complex	
3563 m,br						$\nu_{(\text{O-H})}$ acid
	3317 m,br				3403 m,br	$\nu_{(\text{O-H})}$; H ₂ O coordinated
3102 w	3102 w	3140 sh	3095 w	3078 vw	3093 sh	$\nu_{\text{s}(\text{C-H})} + \nu_{\text{as}(\text{C-H})}$
3052 w	3037 w	3101 vw	3027 m	3068 w	3078 sh	
2995 w	2984 sh	3068 w,br	2977 w	2987 w	2991 w	
2936 vw	2969 vw	2988 w	2935 w	2968 vw	2950 vw	
2898 vw,br	2941 w	2960 vw		2936 w		
2718 w,br	2882 sh	2937 m		2890 sh		
2620 w,br		2906 sh		2773 sh		
2532 w,br		2782 vw		2750 sh		
		2750 sh		2701 vw		
		2658 w		2658 w		
		2573 m		2573 w		
1775 vs	1773 s	1775 vs	1765 ms	1775 s	1771 ms	$\nu(\text{C=O})$, carbonyl
1734 vs	1702 vs	1731vs,br	1707 vs	1730 vs	1722 vs	$\nu(\text{C=O})$, carboxylic
1713 vs						
1609 ms	1653 w	1613 m	1620 sh	1613 w		$\nu(\text{C=C})$
--	1585 sh	1521 vw	1575 vs	1521 vw	1594 m	$\nu_{\text{as}}(\text{COO}^-)$
	1563 s,br				1565 s	
1489 sh	1468 m	1468 s	1468 w	1468 ms	1464 m	$\nu_{\text{s}}(\text{COO}^-) + \delta\text{CH}_2 + \nu$ ring
1467 ms	1422 s	1415 vs	1424 vs	1415 s	1420 vs	
1425 vs	1382 s	1390 w	1377 s	1390 w	1382 ms	
1392 vs	1319 s	1319 s	1331 ms	1343 sh	1302 s	
1320 s		1248 vs	1301 s	1319 ms	1250 vw	
1248 vs				1247 s		
1215 vs	--	--	--	--	--	$\nu(\text{C-OH})$

Continue table (2)

Free Gly	Metal complexes					Assignments ^(b)
	Cu complex	Cd complex	Ag complex	Hg complex	Pb complex	
1122 s	1193 m	1195 m	1203 sh	1195 w	1188 w	$\nu_{(C-C)} + \nu_{(C-N)}$
1089 m	1171 vw	1148 sh	1193 m	1156 sh	1156 vw	δ (CH) , in-plane bend
	1116 s	1118 s	1177 m	1118 s	1113 m	
	1088 w	1085 ms	1123 ms	1085 ms	1085 w	
	1062 sh	1000 sh	1091 vw	1015 sh	1000 sh	
	1042 w		1054 sh	1000 vw		
			1000 sh			
996 m,br						δ (C-OH)
957 vs	961 s	976 vw	960 s	955 s	962 s	δ (CH) out of plane bend ,
894 m	911 w	955 vs	858 w	907 m,br	929 w	skeletal vibration
853 w	856 w	908 ms	804 m	851 vw	890 sh	
801 s	781 sh	851 w	743 s	800 m	853 w	
739 vs	752 s	800m	718 ms	739 s	799 w	
718 vs	716 s	739 vs	690 vw	712 s	765 w	
624 vs	640 s	713 vs	640 ms	622 s	745 ms	
561 m	570 vw	622 vs	585 m	561 ms	714 s	
531 ms	558 w	561 ms	560 m	530 ms	695 sh	
	532 m	531 s	531 ms		634 ms	
	468 w,br		412 sh		590 vw	

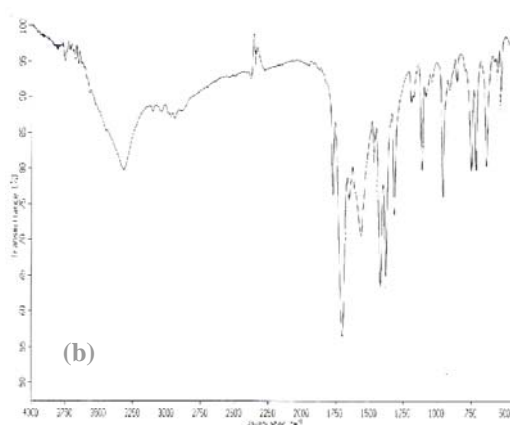
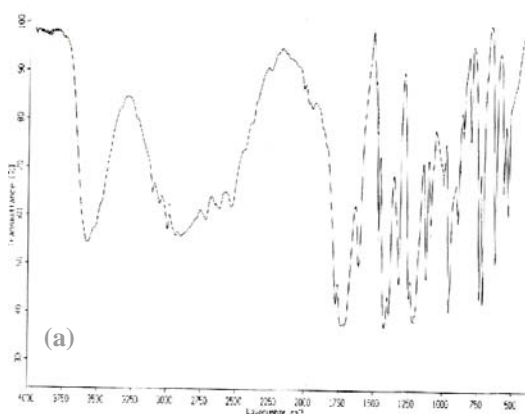
(a): s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad. (b): ν , stretching; δ , bending.

The spectra of all the prepared complexes exhibited shift in band frequencies and change in band intensities indicated that these complexes were formed, Figure 1. The stretching frequency ν (OH) of acid form which appeared at 3563 cm^{-1} in the spectrum of free N- phthaloyl glycine was disappeared in the spectra of all metal complexes confirmed that, the hydrogen ion of carboxylate group of free N-phthaloyl glycine was substituted by the metal ions in all complexes. The presence of broad bands at 3317 and 3403 cm^{-1} for Cu(II) and Pb(II) complexes, respectively, prove the presence of coordinated water molecules in these complexes [38].

The stretching frequency ν (CO) of carboxylic group in free N- phthaloyl glycine

shows two very strong bands at 1734 and 1713 cm^{-1} . In case of the respective metal complexes one of these two bands was disappeared and the other shifted to 1702 , 1731 , 1707 , 1730 and 1722 cm^{-1} in Cu(II) , Cd(II) , Ag(II) , Hg(II) and Pb(II) complexes, respectively.

The infrared spectra of metal complexes exhibited new bands characteristic to ν (COO⁻). These bands appeared at 1585 and 1563 cm^{-1} for copper(II); 1521 cm^{-1} for cadmium(II); 1575 cm^{-1} for silver(II); 1521 cm^{-1} for mercury(II) and at 1594 and 1565 cm^{-1} for lead(II) complexes. The absence of stretching frequency ν (C-OH) at 1215 cm^{-1} and its bending frequency δ (C-OH) at 996 cm^{-1} in the spectra of all metal complexes proved the carboxylate coordination [30-37, 39].



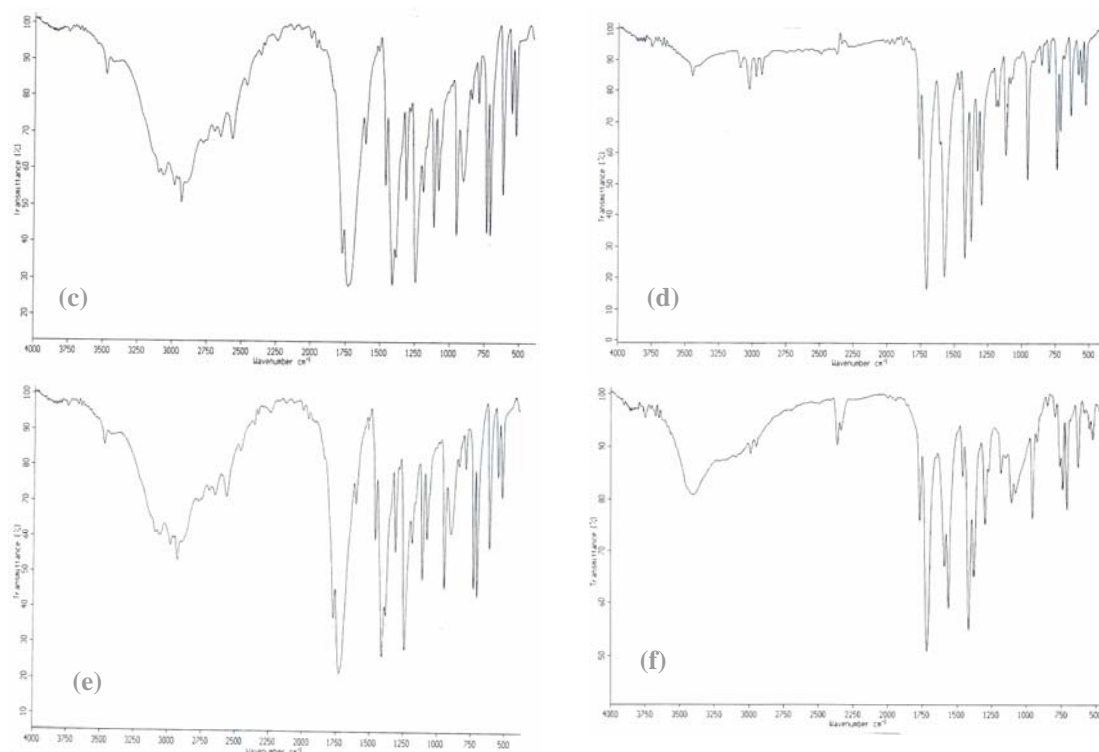


Figure 1: Infrared spectra of (a) : free N-phthaloyl glycine(Gly) ,(b) : $[Cu(Gly)_2 \cdot 2H_2O]$,
(c) : $[Cd(Gly)_6]$, (d): $[Ag(Gly)]$, (e): $[Hg(Gly)_6]$, (f): $[Pb(Gly)NO_3 \cdot 4H_2O]$ complexes

3.2. 1H NMR spectra:

The proton magnetic resonance spectrum of the Ag(I) complex was analyzed in

comparison with the spectrum of the free ligand , Figure 2 .

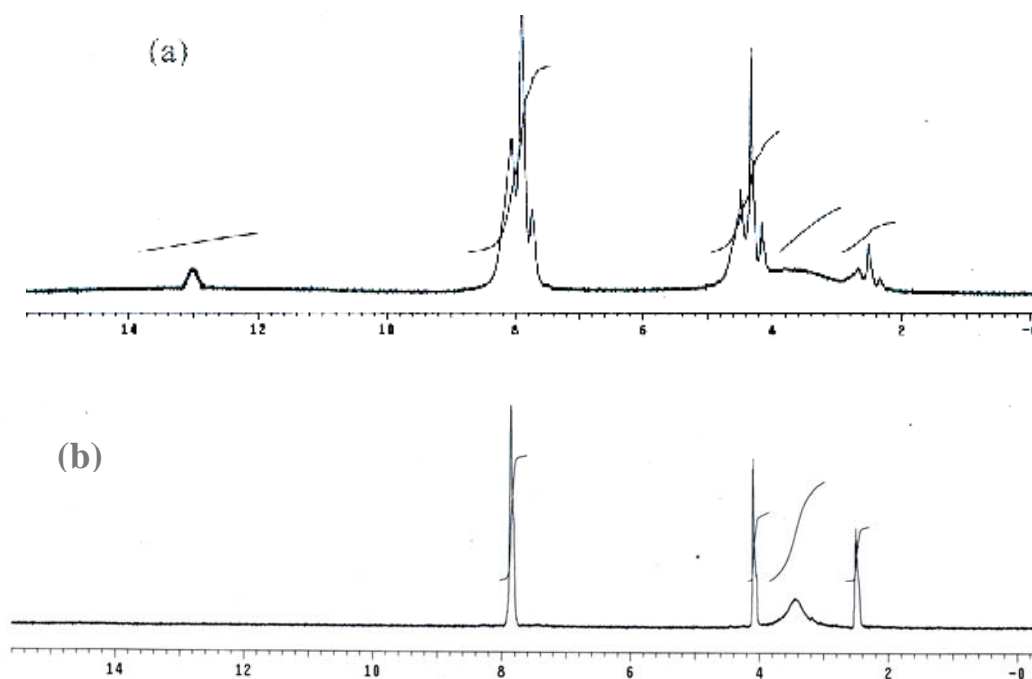


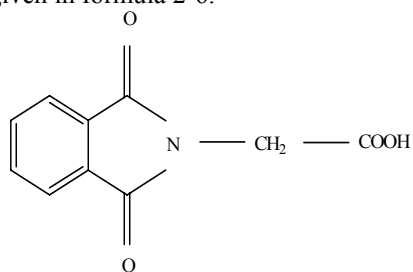
Figure 2 : 1H NMR spectra of (a): free Gly and (b) $[Ag(Gly)]$ complex

The free N- phthaloyl glycine and its Ag(I) complex, [Ag(Gly)], structures were shown in Formula 1 and 4, respectively. The shift recorded for the different signals of the protons in Table 3.

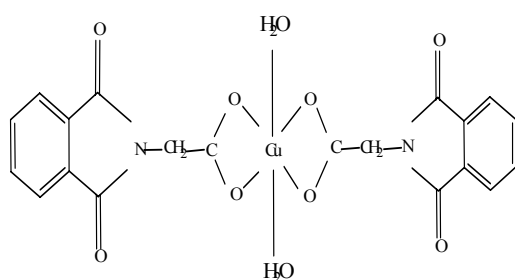
Table 3: The ^1H NMR spectral data (δ , ppm) for free N-phthaloyl glycine and its Ag(I) complex

Compound	H(1), COOH	H(2), arom atic	H(3), CH ₂
$\text{C}_{10}\text{H}_7\text{NO}_4$	13.02 (br)	8.06 (m)	
		7.91	4.48 (s)
		7.89	4.15
[Ag(Gly)]	-	7.73	
		7.87 (s)	4.11 (m)
		7.86	4.09

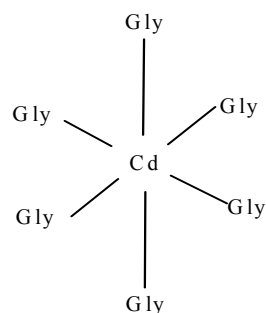
The free ligand show a broad and strong signal at 13.02 ppm due to the hydrogen atom of carboxylate group. This signal was disappeared in the Ag(I) complex, indicated the occurrence of coordination of the carboxylate group to the metal ion [11,40]. Two signals of the aromatic ring were disappeared, also the two signals of aliphatic $-\text{CH}_2-$ group were shifted to lower values indicating that the magnetic environment of the aromatic ring and CH_2 aliphatic had changed with coordination. The suggested structures of the obtained complexes are given in formula 2-6.



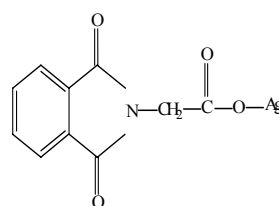
Formula 1: Structure of the free Gly, $\text{C}_{10}\text{H}_7\text{NO}_4$



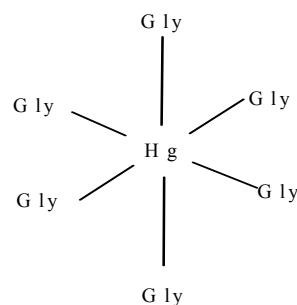
Formula 2: Structure of the [Cu(Gly)₂(H₂O)₂] complex



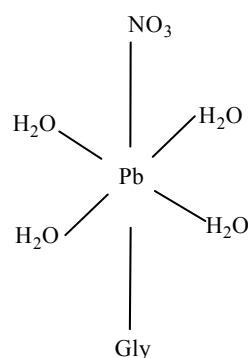
Formula 3: Structure of the [Cd(Gly)₆] complex



Formula 4 Structure of the [Ag(Gly)] complex



Formula 5: Structure of the [Hg(Gly)₆] complex



Formula 6: Structure of the [Pb(Gly)(NO₃)(H₂O)₄] complex

3.3. Mass spectra:

The mass spectra of the free N-phthaloyl glycine, [Cu(Gly)₂(H₂O)₂] and [Ag(Gly)] complexes were measured, Figure 3.

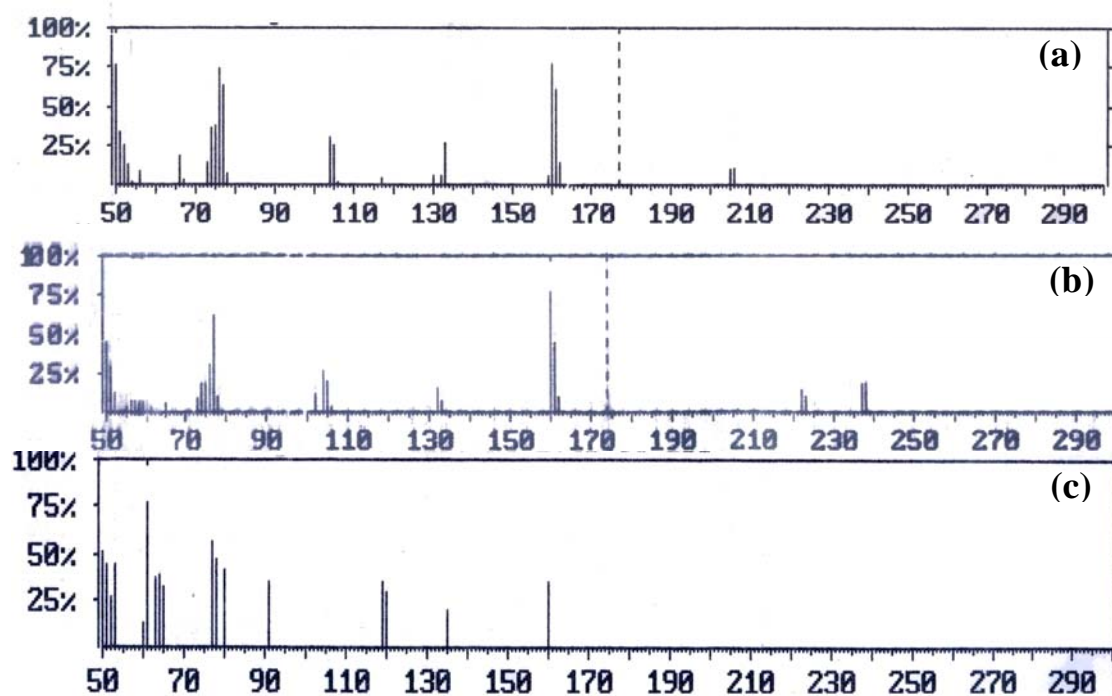
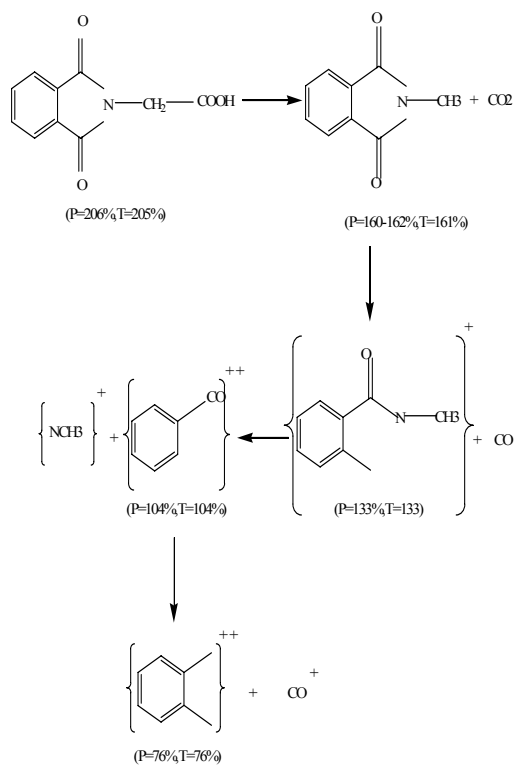


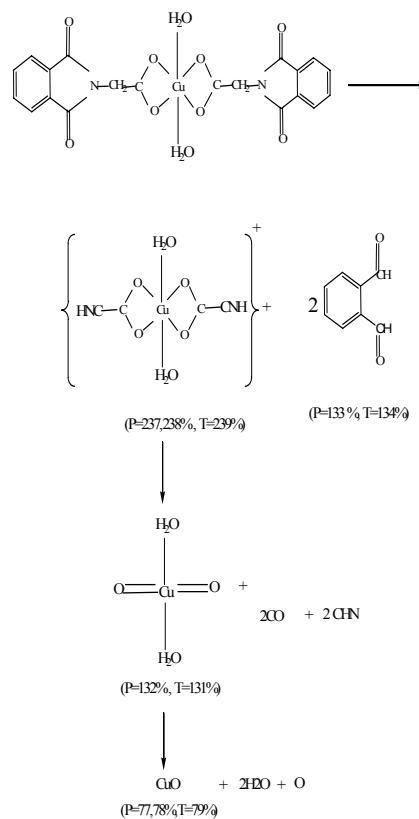
Figure 3: Mass spectra of (a):free N-phthaloylglycine(Gly), (b) [Cu (Gly)₂ · 2H₂O] and (c) [Ag (Gly)] complexes

The corresponding mass fragmentation of the free ligand and the above mentioned two complexes were suggested in schemes 1, 2, and 3. There are difference in fragmentation that was caused according to the nature of the

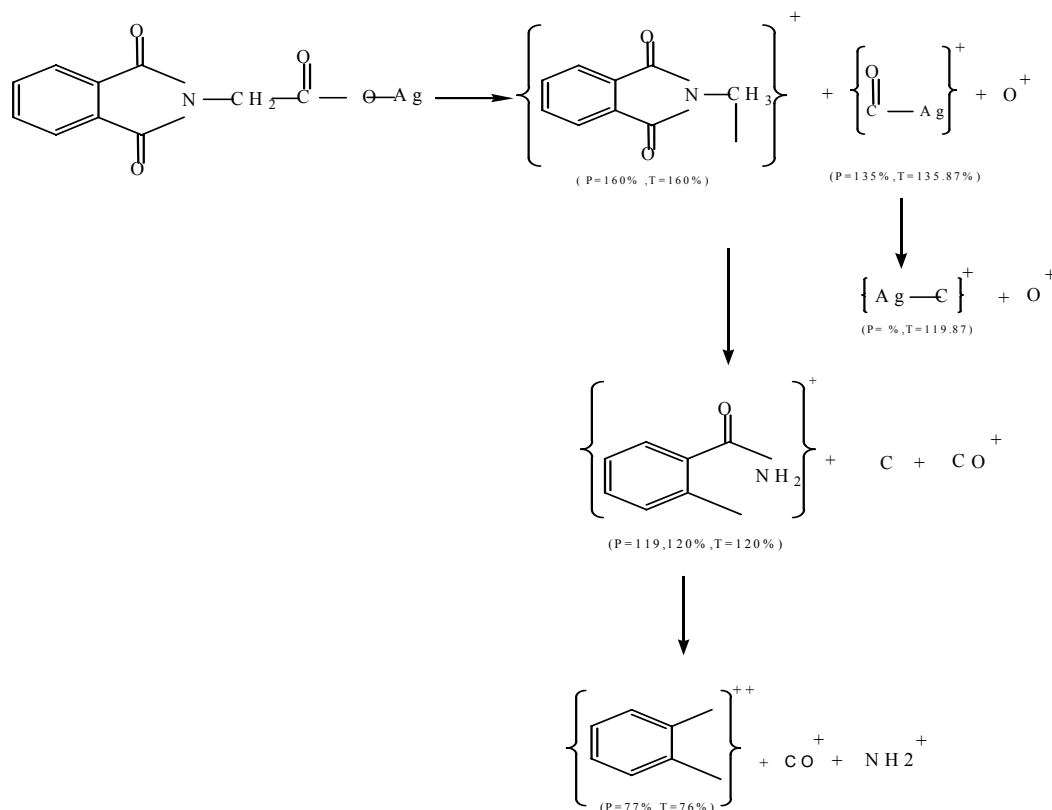
attached metal ions. Mass spectral data of the free N- phthaloyl glycine and its Cu(II) as well as Ag(I) complexes were obtained in Table 4. Their signals give an idea about the construction of them.



Scheme 1



Scheme 2

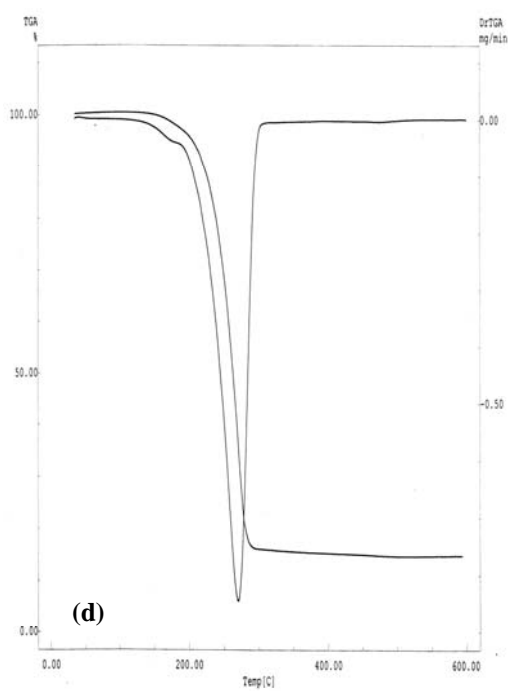
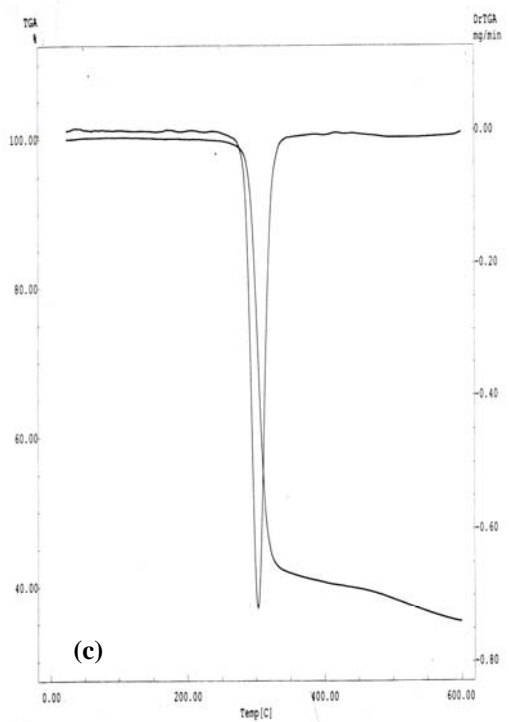
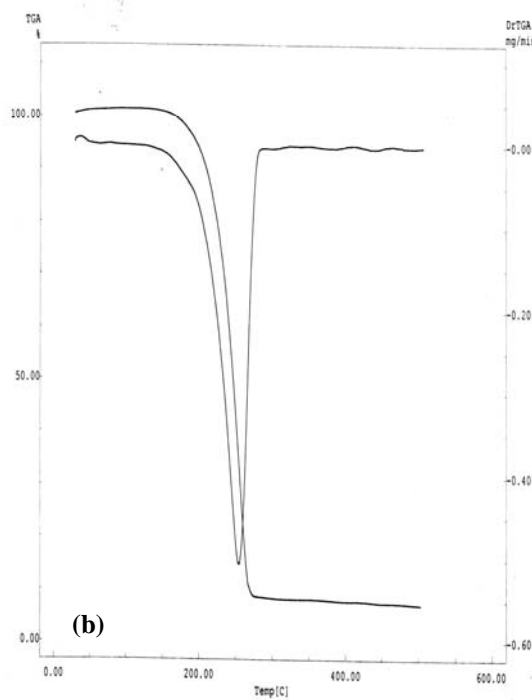
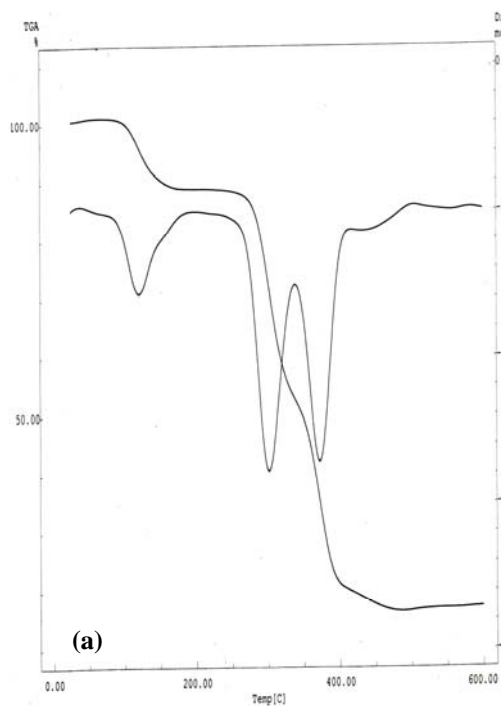
**Table 4:** Mass spectral data of free N-phthaloyl glycine , [Cu(Gly)₂.2H₂O] and [Ag(Gly)] complexes

Compound	m/z (%)
$C_{10}H_7NO_4$	206(2.7%); 205(2%); 162(14%); 161(60%); 160(91%); 159(5%); 133(26%); 132(6%); 131(0.8%); 130(5%); 118(0.8%); 117(4.7%); 106(1.6%); 105(25%); 104(32%); 78(7%); 77(63%); 76(74.8%) 75(37.6%); 74(35.3%); 73(14%); 67(2.3%); 66(17.8%); 56(8.9%); 54(1.6%); 53(12%); 52(24.8%); 51(33.3%); 50(100%) .
[Cu(Gly) ₂ .2H ₂ O]	238(4.7%); 237(4.7%); 223(2.3%); 222(3.5%); 162(10.5%); 161(44.2%); 160(100%); 133(7%); 132(15%); 106(3.5%); 105(19.8%); 104(26.7%); 102(11.6%); 78(10.5%); 77(61.6%); 76(30); 74(17.4%); 73(8.1%); 65(5.8); 61(3.5%); 60(10.4%); 59(5.8); 58(5.8%); 57(7%); 56(7); 55(3.5%); 54(1.2%); 52(12.8%); 51(29.1%); 50(44.2%).
[Ag(Gly)]	160(34.1%); 135(19.5%); 120(29.3%); 119(34.1%); 91(34.1%); 80(41.5%); 78(46.3%); 77(56.1%); 65(31.7%); 64(39%); 63(36.6%); 61(100%); 60(12.2%); 53(43.9%); 52(26.8%); 51(43.9%); 50(51.2%).

3.4. Thermogravimetric analysis:

Thermal analysis curves (TG and DTA) of all studied complexes were shown in

Figure 4. The thermoanalytical data were summarized in Table 5.



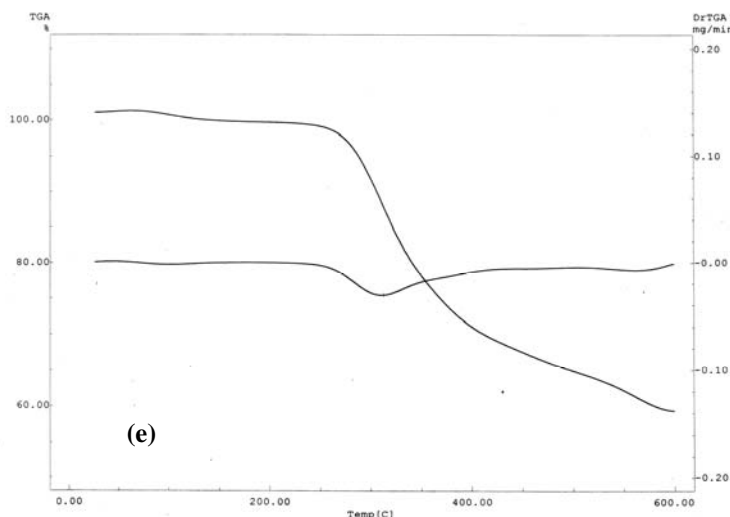


Figure 4 : Thermograms (TG and DTG) of (a): $[\text{Cu}(\text{Gly})_2 \cdot 2\text{H}_2\text{O}]$,(b): $[\text{Cd}(\text{Gly})_6]$, (c): $[\text{Ag}(\text{Gly})]$,(d): $[\text{Hg}(\text{Gly})_6]$ and (e): $[\text{Pb}(\text{Gly})\text{NO}_3 \cdot 4\text{H}_2\text{O}]$ complexes

Table 5: Thermal data of N-phthaloyl glycine metal complexes

Compound	Number of stages	Temp. range (°C)	T_{max} (°C)	TG Weight loss (%)		Decomposition species
				Found	Calc.	
$[\text{Cu}(\text{Gly})_2 \cdot 2\text{H}_2\text{O}]$	4	88-173	120.15			
		255-335	300.84	7.9	7.1	$2\text{H}_2\text{O}$
		335-414	371.88	76.15	77.32	2 Gly
		414-495				
$[\text{Cd}(\text{Gly})_6]$	1	162-280	256.07	7.12	8.38	6 Gly
		250-350	303.13			Gly
$[\text{Ag}(\text{Gly})]$	1			64.65	65.41	
$[\text{Hg}(\text{Gly})_6]$	1	180-300	271.18	15.73	14.04	6 Gly
$[\text{Pb}(\text{Gly})\text{NO}_3 \cdot 4\text{H}_2\text{O}]$	3	100-200	312.59			$4\text{H}_2\text{O}$
		235-450		14.63	13.18	Gly + NO_3
		450-600		44.43	48.81	

The thermogram curves of the complex $[\text{Cu}(\text{Gly})_2(\text{H}_2\text{O})_2]$ show that the decomposition takes place in four stages in the range of 25-600 °C, Figure 4a. The first stage occurred with endothermic peak at a maximum temperature of 120 °C. This stage is due to the loss of two water molecules with a weight loss of 7.90 % while the theoretical weight loss 7.10 %. The second, third and fourth stages in the range of 250-500 °C showing the decomposition of N-phthaloyl glycine. These three stages were associated with a weight loss of 76.15 % and the calculated weight loss value in these three stages was 77.32 %. The found total weight loss value was 84.05 % with a residue equal 15.95 % which is corresponding to copper oxide CuO . These

results are in a good agreement with the theoretical values, total loss equal 84.42% and residual 15.58 %.

The thermal degradation of the complex $[\text{Cd}(\text{Gly})_6]$ occurred in one stage at maximum temperature of 256.07 °C in the range from 162-350 °C giving cadmium metal as a final residue, Figure 4(b). The total weight loss value was 92.88 % with a final residue 7.12 % which is equivalent to the theoretical values 91.62 % and 8.38 %, respectively.

The complex $[\text{Ag}(\text{Gly})]$ shows one stage for the decomposition in its thermogram curves in the range from 250-350 °C with a maximum value of 303.13 °C giving metallic silver as a final residue equal 35.35 % . The

practical total weight loss value is 64.65 % and the calculated one was 65.41%, Table 5, Figure 4 (c).

The mercury (II) N-phthaloyl glycine complex, $[\text{Hg}(\text{Gly})_6]$ gives one stage of decomposition in their thermogram curves in the range from 180-300 °C and at 271.18 °C maximum temperature. The found total weight loss value was 84.27 % giving a final residue of 15.73 % associated with metallic mercury, Table 5, Figure 4 (d). The theoretical total loss was 85.96 % and a final residue was 14.04 %.

The thermograms of the complex $[\text{Pb}(\text{Gly})(\text{NO}_3)(\text{H}_2\text{O})_4]$, Figure 4 (e), show three stages of decomposition. The first stage occurred in the range from 100-200 °C corresponding to the loss of 4H₂O molecules with a weight loss of 14.63 % while the calculated value was 13.18 %. The second and third decomposition stages occurred in two steps in the range from 235-450 °C and 450-600 °C. These two steps associated with a weight loss value of 44.43 % related to the loss of N-phthaloyl glycine and nitrate molecules parallel to the calculated value 48.81 %. The found total weight loss value was 59.06 % which is equivalent to the theoretical value of 61.99 %. The resultant practical weight residue was 40.94 % while the considered value was 38.00 % giving a metallic lead as a final residue.

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