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Study of the ternary complexes of copper with salicylidene-2-aminothiophenol and some amino acids in the solid state

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Abstract

The ternary complexes of copper (II) with salicylidene-2-aminothiophenol (L) and glycine, alanine, valine and histidene amino acids have been studied in solution and in solid state. The mixed ligand complexes have been isolated and characterized based on elemental analyses, IR, UV-Vis, mass spectra, magnetic moment and thermal analysis (TGA). The isolated complexes were found to have the formula [M (L)(AA)] and the copper has the five coordinated square bipyramidal distorted trigonal bipyramidal (SBPTBP) geometry. The thermal stability of the complexes was studied and the weight losses were correlated with the mass fragmentation pattern. In all cases the amino acid moiety is removed first followed by the Schiff base moiety leaving CuO as the metallic residue. The metallic residue was also confirmed by powder XRD powder diffraction. The kinetics of the thermal decompositions of the complexes was studied and the thermodynamic parameters were reported.

Keywords: Copper; Schiff base; Amino acids; Thermal study

1. Introduction

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g. their ability to reversibly bind oxygen [1], catalytic activity in the hydrogenation of olefins [2], transfer of an amino group [3], photochromic properties [4], complexing ability towards some toxic metals [5] On the other hand, the interaction between metal ions and amino acids is of considerable interest as models for metal–protein reactions and models in a variety of biological systems [6]. The ternary complexes of the Schiff bases and amino acids with metal ions bear the importance of both Schiff bases and amino acids. In addition, these species may be considered as relatively simple models for ternary enzyme/metal ion/inhibitor [7]. On the other hand Cu(II) complexes have extensively been studied in recent years. Their flexibility, facility of preparation and capacity of stabilizing unusual oxidation states can explain their successful performance in mimicking peculiar geometries around the metal, leading to very interesting spectroscopic properties and varied reactivities [8–10]. The complexity of the stereochemistry of Cu(II) complexes is well known [11–13]. Owing to the plasticity of the coordination sphere, which is well-known as a feature of copper, Cu(II) ion forms a variety of complexes with coordination number 4–6 [14]. The geometries around the central Cu(II) atom are controlled primarily by the combinations of various ligands and the steric constrains in the ligand itself. For example, five-coordinate Cu(II) complexes, in most cases take on many different geometries ranging between square pyramidal (SP) and trigonal bipyramidal (TBP) [15]. The stereochemistry of five-coordinated Cu(II) complexes has been reviewed and discussed comprehensively by Hathaway [16,17]. Cu(II) complexes with tridentate [17–23] and tetradentate [24] Schiff base ligands were reported. In the five coordinate systems, the copper atom achieves distorted square pyramidal or distorted trigonal bipyramidal geometries.

The binary complexes of copper with salicylidene-2-aminothiophenol was studied by the first author and others [20]. Herein, we report the synthesis, characterization

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and thermal study of the ternary system including Cu(II), salicylidene-2-aminothiophenol (H_2L) and amino acid (AA). The amino acids used were glycine, alanine, valine, and histidine. The complexes were characterized based on elemental analyses, IR, UV-Vis, mass spectra, magnetic moment and molar conductance measurements. The thermal behavior of these complexes was studied using thermogravimetric analysis techniques. The kinetics of the thermal decomposition was also studied and the thermodynamic parameters were reported. The metal oxide residue was identified using XRD technique.

2. Experimental

2.1. Materials and reagents

The chemicals used were of the highest purity available. Glycine (Gly), alanine (Ala), valine (Val), and histidine hydrochloride (His) were received from Merck and used without further purification. Cu(II) was used as copper acetate monoydrate salt (Aldrich). The organic solvents used were obtained as pure grade materials from BDH. All solutions were prepared in bidistilled water.

2.2. Measurement techniques

Elemental analyses (C, H, N, S) were performed in the Microanalytical Center at Cairo University. UV-Vis measurements for the binary and ternary complexes were performed using a Perkin-Elmer λ_4 spectrophotometer in the wavelength range 200–900 nm.

The IR spectra were carried out using a 1430 Perkin-Elmer spectrometer and the spectra recorded as KBr pellets. The IR spectra of the calcinated products were prepared as KBr discs and recorded. This was achieved by heating the solid complexes up to the DTG peak temperature, holding for 30 min, cooling in a vacuum desiccator and preparing the KBr discs from a dried pure KBr salt. The conductometric measurements of the complexes were carried out as DMF solutions at 25 °C using Metrohm 660 conductivity meter. The mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS–MS Hewlett-Packard instrument in the Microanalytical Center at Cairo University.

The molar magnetic susceptibilities were measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant. $Hg[Co(SCN)_4]$ was used as calibration standard.

The thermal analysis of the complexes were carried out using a Shimadzu thermogravimetric analyzer TGA-50 H in a dynamic nitrogen atmosphere (flow rate 20 ml min^{-1}) with a heating rate of 10 °C min^{-1}. The % weight loss was measured from the ambient temperature up to 800 °C. Metal contents of the ternary complexes were determined by titrating their solutions with EDTA after complete decomposition of their complexes with concentrated aqua regia.

X-ray powder diffraction (XRD) was carried out at ambient temperature using Philips Analytical X-Ray B.V. with PC-APD, Diffraction Software. The instrument is equipped with a copper anode generating Ni-filtered Cu Kα radaiation ($l = 1.54056$ Å, 40 kV, 55 mA). Diffractograms were recorded in the 2θ range between 2.010 and 59.530 with a step size (2θ) of 0.080. An on-line data acquisition and handling system facilitated an automated JCPDS-ICCD library search (Fig. 1).

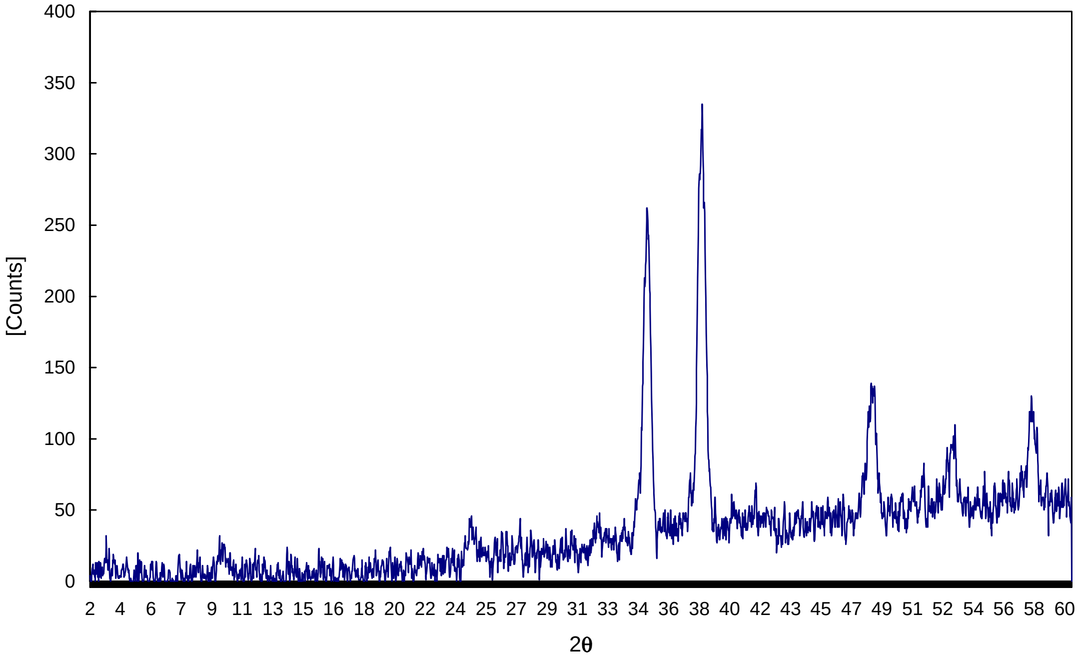
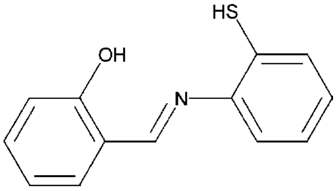


Fig. 1. XRD powder diffractogram of the metallic residue of the complexes.

2.3. *Preparation of salicylidene 2-aminothiophenol (L)*

The Schiff base ligand, H_2L, was prepared as previously reported [20,22]. Equimolecular amounts of salicylaldehyde and 2-aminothiophenol were mixed in ethanol and refluxed for 2 h, then left to cool and the separated Schiff base was recrystallized from ethanol and washed thoroughly by diethyl ether.



H_2L

2.4. *Preparation of the solid complexes*

The 1:1:1 [M:H_2L:AA] complexes were prepared from hot ethanolic solutions (60 °C) by the addition of 50 mL of the copper acetate monohydrate (10 mmol, 0.20 g) dropwisely to 50 mL of H_2L (10 mmol, 0.229) and AA (amino acid) (0.075 g Gly, 0.089 g Ala, 0.117 g Val, 0.131 g Leu and 0.155 g His). The mixture was stirred for 1 h and left in the refrigerator overnight whereby the complexes were precipitated. The isolated complexes were filtered, washed thoroughly by ethanol and then by diethyl ether. The solid complexes were dried in vacuum desiccator and subjected to elemental microanalysis (the analyses in each case (C, H, N and S) were repeated twice).

3. Results and discussion

The results of elemental analyses and mass spectra (Table 1) show that only one molecule of the Schiff base is attached per molecule of the Cu(II) ion along with one molecule of the amino acids. The sites of coordination of the Schiff base and amino acids have been obtained from the IR studies.

3.1. *IR spectra and mode of bonding*

The results of the IR measurements were tabulated in Table 2, where the band assignments of the guide bands (those affected by coordination) have been given. The free Schiff base; H_2L, show the characteristic azomethine, OH and SH frequencies at 1650, 3500 and 2600–2500 cm^{-1}, respectively. The band due to νOH is broadened in all the complexes indicating that the coordination through the phenolic OH group is difficult to be interpreted as the result of the presence of OH stretching vibration of the carboxylic group of the amino acid moiety. The participation of OH group in bonding was confirmed from the shift in the position of the δ_{OH} in plane of the free ligand (1406 cm^{-1}) by 11–14 cm^{-1} in the spectra of the complexes. Also, it was evidenced from the phenolic C−O stretch band [25] which was found to be shifted into the range 1210–1211 cm^{-1} in the ternary complexes (1236 cm^{-1} for the free H_2L). However, the band due to C=N stretch (1619 cm^{-1} in H_2L spectrum) underwent a negative shift (16–17 cm^{-1}) on complexation, suggesting that azomethine group is involved in coordination [20,22]. The negative shift of the band indicates the weakness of C–N bond upon coordination [22,26]. The SH stretching vibrations; ν_{SH}, are not of good help since they display very weak bands in the spectra of both the free ligand and complexes. However, the participation of the SH group in chelate formation was ascertained from the shift of the ν_{C-S} to lower frequencies from 759 cm^{-1} in the free ligand to 740–736 cm^{-1} in the spectra of the complexes [22]. The appearance of a very weak band at 424–420 cm^{-1} due to ν_{M-S}, also provides an additional evidence for the participation of the SH group in complex formation [22,27].

Table 1
Analytical and physical data of Cu–L–AA complexes

Compound	Colour; (% yield)	Melting point (°C)	Found (calcd. %)					Molecular weight found (calcd.)	Λ_m ($cm^2\ \Omega^{-1}$ mol^{-1})	UV absorption spectra, λ_{max}	μ_{eff} (B.M.)
			C	H	N	S	M				
[Cu(L)(Gly)] $C_{15}H_{13}N_2O_3SCu$	Reddish brown	290	49.60	4.05	8.00	8.40	17.70	368.25	16.12	490, 340, 245	2.41
	(70)	(charring)	(49.25)	(3.83)	(7.66)	(8.76)	(17.37)	(365.5)			
[Cu(L)(Ala)] $C_{16}H_{15}N_2O_3SCu$	Brown	>300	50.40	4.20	7.60	8.55	17.00	382.92	17.34	495, 400, 259	1.94
	(75)		(50.59)	(4.22)	(7.38)	(8.43)	(16.73)	(379.5)			
[Cu(L)(Val)] $C_{18}H_{19}N_2O_3SCu$	Brown	290	53.20	5.30	6.65	7.72	15.90	409.25	19.87	494, 350, 255.5	2.21
	(65)	(charring)	(53.01)	(4.91)	(6.87)	(7.85)	(15.58)	(407.5)			
[Cu(L)(His)] $C_{19}H_{17}N_4O_3SCu$	Yellowish brown	>300	51.40	4.60	12.89	7.40	14.60	445.25	12.56	495, 360, 248	2.17
	(73)		(51.18)	4.04	(12.57)	(7.18)	(14.25)	(445.25)			

Table 2
IR spectra (4000–400 cm^{-1}) of Cu–L–AA complexes

Compound	νNH$_2$; Coord, AA	ν(C=N)	ν_{asym} (COO)	ν_{sym} (COO)	δNH$_3^+$ (free AA)	δ(NH$_2$) Coord AA	ν(C–O) (Phenolic)	δ(OH)	ν(C–S)	ν(M–O)	ν(M–N)	ν(M–S)
H_2L		1619sh					1236sh	1406m	759sh			
Gly			1610sh	1413sh	1585							
Ala			1597sh	1412sh	1623							
Val			1594sh	1410sh	1622							
His			1574sh	1413sh	1623							
[Cu(L)(Gly)]	3429, 3266	1603sh	1543sh	1306m		1524sh	1211sh	1420sh	738sh	547s	460w	420m
[Cu(L)(Ala)]	3438, 3200	1602sh	1549sh	1312s		1502sh	1211sh	1417sh	736sh	547s	460w	424w
[Cu(L)(Val)]	3429, 3200	1603sh	1547sh	1308m		1504sh	1210sh	1417sh	737sh	548m	455m	423m
[Cu(L)(His)]	3436, 3250	1603sh	1552sh	1316s		1510sh	1211sh	1420sh	737sh	548s	455s	422s

sh, sharp; s, small; m, medium; w, weak.

The amino acid was found to be bidentate ligands and bound to the central copper ion through the carboxylic OH and the amino group; NH$_2$. The δNH$_3^+$ band, which is characteristic of the zwitter ion, disappears in the spectra of the complexes. This fact indicates that the NH$_2$ group must be involved in coordination. This is supported by the appearance of broad and split bands in the spectra of the complexes, in the regions 3438–3429 and 3266–3200 cm^{-1} (stretching vibration; νNH$_2$) and sharp bands in the region 1524–1502 cm^{-1} (in plane deformation; δNH$_2$), assigned for the coordinated amino group [28–30]. The bands in the regions 1594–1586 and 1412–1408 cm^{-1}, due to ν_{asym} (COO$^-$) and ν_{sym} (COO$^-$) of the amino acids, appear in the complexes at 1552–1543 and 1316–1306 cm^{-1}. The shift of these two bands suggests the involvement of the carboxylic groups of the amino acids in complex formation [31,32]. Hence, the amino acid moiety is chelated to the metal ion through five-member ring. However, the lower values of the two carboxylic vibrations compared with those of the free ligand suggests that the carboxylic group interacts weakly with the metal ions. This accounts for the disappearance of the bands due the νNH$_2$ and νCOO from the spectra of the calcinated solids as the amino acid moieties were removed in the first stages of thermal decomposition (Table 4).

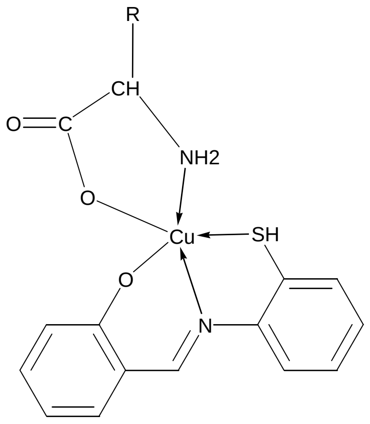
The presence of ν(C–N) band (pyridine like nitrogen) at 1300 cm^{-1} in Cu–L–His complex, indicates that the pyridine like nitrogen of the imidazole ring does not participate in bond formation with the Cu(II) ion. Also, the presence of ν(NH) band of the imidazole ring at 3063 cm^{-1} confirms the unbounded nature of the NH group.

In the far IR spectra of all the complexes, in addition to the nonligand bands observed at 424–420 cm^{-1} assigned for M–S bonds, the bands at 547–510 and 380–340 cm^{-1} may be assigned for the M–N and M–O, respectively [27,29].

3.2. Magnetic and UV-Vis measurements

The values of the magnetic measurements (μ_{eff}) are found to be in the range 1.94–2.55 B.M. (Table 1), which suggests that the copper–L–AA complexes have square bipyramid distorted trigonal bipyramidal (SBPDTBP) geometry as previously reported [17–19,24], (Fig. 2). This is in accordance with the nonplanar nature of the Schiff base molecule. The UV-Vis spectral data (Table 1) show a small shoulder band at 494–495 nm, which may be attributed to the ligand-to-metal charge transfer (LMCT) for penta-coordinated copper complexes [22,33]. The electronic spectra in ethanolic solution showed, also, absorption bands in the region of 248–259 and 350–400 nm which may be assigned to interligand transitions.

As a general conclusion, the Schiff base participated in bonding to copper as monobasic tridentate (NSO) ligand and the amino acids as monobasic bidentate ligand with a total of five coordination sites around the metal ion whose charges are neutralized by the de-protonation of the Schiff base phenolic OH and the amino acid COOH (Fig. 2). The nonelectrolytic nature of the complexes was evidenced from the low values of the molar conductance of the complexes measured in DMF (Table 1).



R=H(Gly), CH_3(Ala), C_3H_7(Val) and $C_4H_5N_2$(His)

Fig. 2. The general proposed structure for the Cu–L–AA complexes.

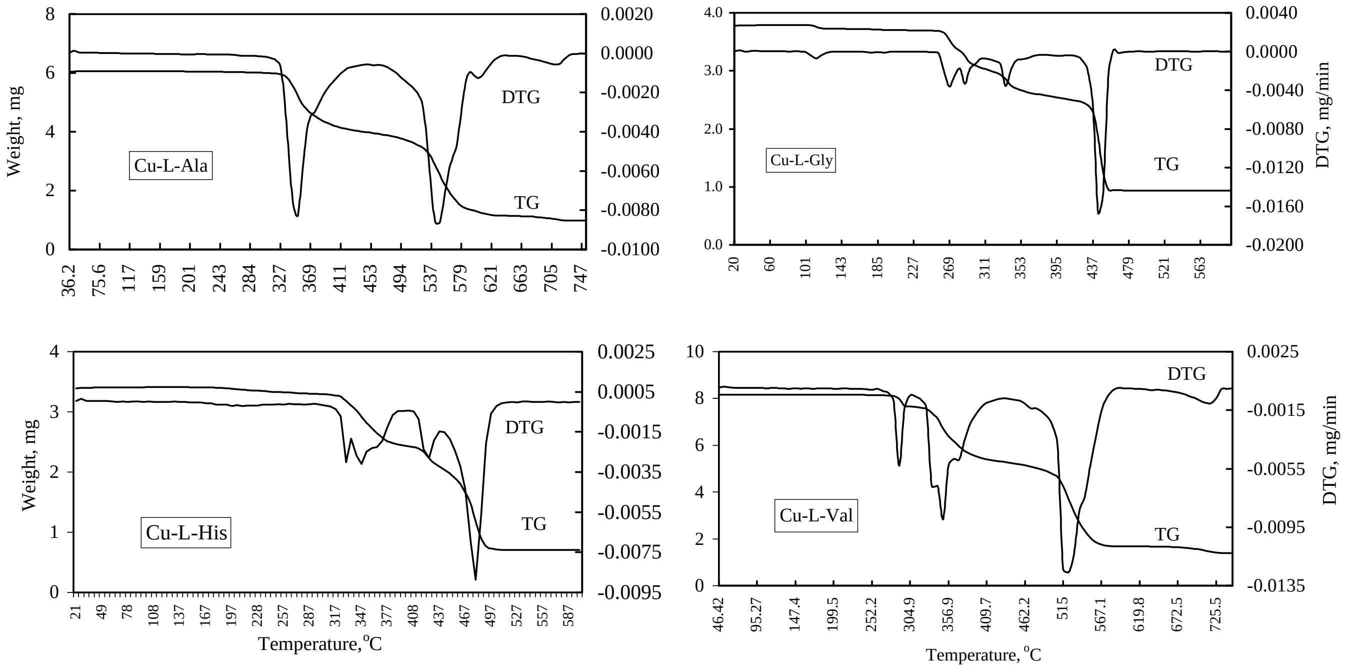


Fig. 3. TG and DTG plots of the complexes.

3.3. Thermal analysis

The thermogravimetric (TG) and the derivative thermogravimetric (DTG) plots of the complexes were given in Fig. 3 The assignment of the different decomposition steps were given in Table 3 and the assignment of the IR at the peak temperatures of the decomposition steps were given in Table 4. The decomposition schemes of the complexes can be approached as follows:

3.3.1. Cu–HL–Gly

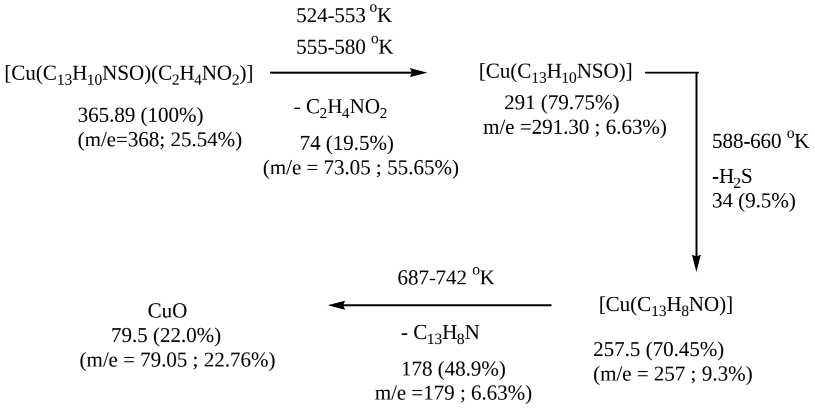
Cu–L–Gly complex decomposed in four steps (Scheme 1). The first two close steps found in the temperature ranges 524–553 K and 555–580 K with a total mass loss of 19.5% were assigned to the removal of the glycine molecule. This is followed by an estimated mass loss of 9.5% at 588–660 K with a molar mass of 34.7 which may be due to the partial decomposition of the Schiff base moiety (L) releasing H_2S species. The last step found in the range 687–742 K with a

Table 3
Thermoanalytical results (TGA) of Cu–L–AA complexes

Complex	Molar mass	TG range (°C)	DTG_{max} (K)	Mass loss found (calcd. %)	Assignment of the removed sepecies	Metallic residue found (calcd. %)
[Cu(L)(Gly)]	365.5	524–553	540	19.50 (20.25)	$C_2H_4NO_2$	CuO
$[Cu(C_{13}H_{10}NSO)(C_2H_4NO_2)]$		555–580	560	9.50 (9.30)	H_2S	22.10
		588–660	611	48.9 (48.70)	$C_{13}H_{10}N$	(21.75)
		687–742	717			
Total mass loss				77.90 (78.25)		
[Cu(L)(Ala)]	379.5	586–727	630	23.19 (23.19), 8.90 (8.96)	$C_3H_6NO_2$, H_2S	CuO
$[Cu(C_{13}H_{10}NSO)(C_3H_6NO_2]$		737–918	820	46.62 (46.90)	$C_{13}H_{10}N$	21.29
						(20.95)
Total mass loss				78.71 (79.05)		
[Cu(L)(Val)]	407.5	541–583	560	6.20 (6.87)	CO	CuO
$[Cu(C_{13}H_{10}NSO)(C_5H_{10}NO_2]$		583–713	630	21.60 (21.59), 8.18(8.34)	$C_4H_{10}NO$	20.34
		714–874	980	43.68 (43.68)	H_2S	19.50
Total mass loss				79.66 (80.49)		
[Cu(L)(His)]	445.5	608–670	630	25.76 (24.69)	$C_5H_8N_3$	CuO
$[Cu(C_{13}H_{10}NSO)(C_6H_8N_3O_2]$		680–714	700	10.57 (9.88)	CO_2	17.39
		715–791	750	46.28 (47.58)	$C_{13}H_{10}N$	(17.85)
Total mass loss				82.61 (82.15)		

Table 4
IR spectra data at the peak temperatures of the decomposition steps of copper–L–AA complexes

Compound	$T_{\text{calcinations}}$	νNH_2	ν(C=N)	ν_{asym} (COO)	ν_{asym} (COO)	$\delta(NH_2)$	ν (C–O) (Phenolic)	δ(OH)	ν(C–S)	ν(M–O)	ν(M–N)	ν(M–S)
L	–	–	1619sh	–			1236sh	1406m	759sh	–	–	–
Gly		–	–	1594sh	1325sh	1524sh			–	–	–	–
[Cu(L)(Gly)]	540	3429, 3266	1603sh	1543sh	1306m	1485sh	1211sh	1406br	736m	547s	460w	420m
[Cu(L)(Gly)]	560	–	1603sh	–	–	–	1211sh	1406br	736m	547s	460w	420m
[Cu(L)(Gly)]	717	–	1647m	–	–	–	–	1406br	–	530br	–	–
[Cu(L)(Gly)]	1073	–	–	–	–	–	–	–	–	532br	–	–
Ala		–		1568sh	1330sh	1502sh	–	–	–	–	–	–
[Cu(L)(Ala)]	630	3438, 3200	1603sh	1543sh	1306s	1485sh	1211sh	1450s	754sh	547s	460w	424w
[Cu(L)(Ala)]	680	3436	1599br	1540 m	1314m	1483sh	1211br	1454s	756sh	619sh	460w	424s
[Cu(L)(Ala)]	820	–	–	–	–	–	1200m	–	–	575s	484w	–
[Cu(L)(Ala)]	1073	–	–	–	–	–	–	–	–	580s	–	–
Val		–	–	1588sh	1336sh	1516sh	–	–	–	–	–	–
[Cu(L)(Val)]	560	3429, 3200	1602sh	1543sh	1306m	1485sh	1210sh	1417sh	737sh	548m	455m	423m
[Cu(L)(Val)]	630	–	1601br	1543w	1316m	1485w	1213br	1452s	–	550w	457m	430m
[Cu(L)(Val)]	980	–	1603w	–	–	–	1204s	1435w	–	619s	–	–
[Cu(L)(Val)]	1073	–	–	–	–	–	–	–	–	526br	–	–
His		–	–	1590sh	1330sh	1520sh	–	–	–	–	–	–
[Cu(L)(His)]	630	3436, 3250	1603sh	1543sh	1306s	1485sh	1211sh	1420sh	737sh	548s	455s	422s
[Cu(L)(His)]	700	–	1602m	1541w	–	–	–	1456s	720s	617s	–	420w
[Cu(L)(His)]	750	–	–	–	–	–	–	–	–	590s	–	–
[Cu(L)(His)]	1073	–	–	–	–	–	–	–	–	543sh	–	–



Scheme 1.

total mass loss of 47.9 may be regarded as the final decomposition of the Schiff base moiety leaving CuO as a residue. The molar masses of the removed and remaining species in every step were found to match with mass spectral fragments of the same value (Table 5), which indicates the reliability of the decomposition scheme proposed.

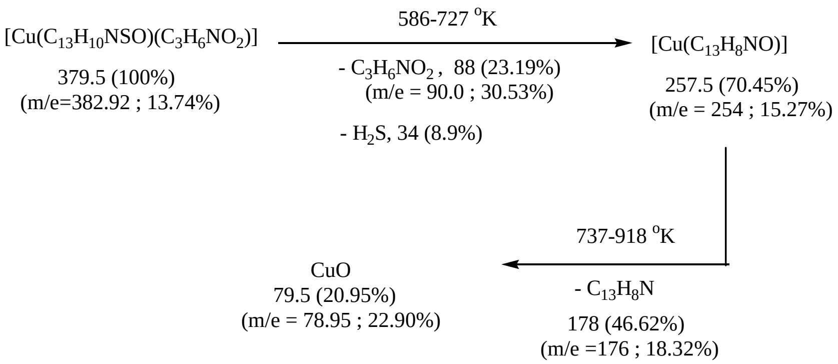
3.3.2. *Cu–L–Ala*

Cu–L–Ala ternary complex decomposed in two well separated steps (Scheme 2). The first step found in the range 586–727 K, with an estimated mass loss of 23.19%, may be due to the loss of the alanine moiety. The second step found in the temperature range 737–918 K with a mass loss

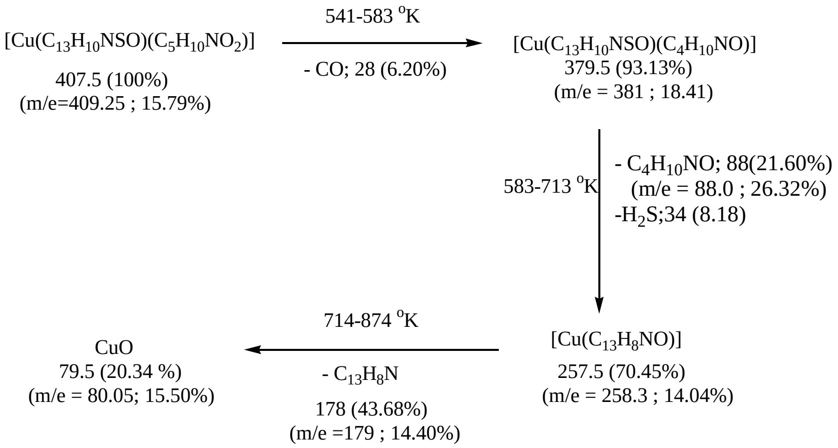
Table 5
Selected mass spectral data of the complexes

Complex	Molar mass	*m/z* values [a]
[Cu(L)(Gly)] [Cu($C_{13}H_{10}$NSO)(C2H4NO$_2$)]	365.5	368.50, 313.20, 291.30, 257.5, 236.25, 199.15, 179.15, 149.15, 125.15, 110.15, 79.05, 55.05
[Cu(L)(Ala)] [Cu($C_{13}H_{10}$NSO)($C_3H_6NO_2$)]	379.5	382.95, 254.45, 199.10, 176.00, 160.10, 145.15, 129.15, 118.50, 107.00, 90.00, 78.95
[Cu(L)(Val)] [Cu($C_{13}H_{10}$NSO)($C_5H_{10}NO_2$)]	407.5	409.25, 381.45, 258.30, 223.40, 181.15, 179.20, 146.00, 91.00, 88.00, 80.05, 79.05, 59.05
[Cu(L)(His)] [Cu($C_{13}H_{10}$NSO)($C_6H_8N_3O_2$)]	445.5	445.25, 409.30, 339.30, 290.55, 261.20, 212.20, 150.20, 126.10, 109.15, 80.00, 68.00, 56.00

[a] Most abundant peaks.



Scheme 2.



Scheme 3.

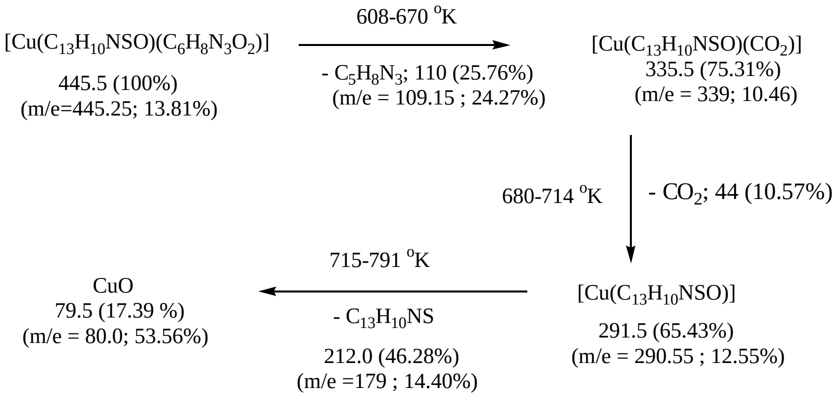
of 46.12 °C was assigned to the removal of the Schiff base moiety. The residue with a mass of 20.95% was regarded as CuO which is further evidenced by the XRD analysis.

3.3.3. *Cu–L–Val*

Cu–L–Val complex decomposed in three main steps (Scheme 3). The first step observed in the range 541–583 K with small mass loss of 6.20%, was assigned to the partial decomposition of the valine moiety as CO molecule. The second step found in the range 583–713 K, was found to be split and the sum of its mass loss was approximate to 29.78% which may be due to the decomposition of the remaining part of the valine moiety and a partial decomposition of the Schiff base moiety as H_2S molecule. The third step found in the range 714–874 K was assigned to the complete removal of the Schiff base moiety leaving CuO as residue.

3.3.4. *Cu–L–His*

Cu–L–His complex decomposed in four steps (Scheme 4). The first two steps found in the range 608–670 K were very



Scheme 4.

Table 6
Comparison of the X-ray powder diffraction data of CuO

Angle 2θ	Observed		Reference [a]		Δd (Å)[b]
	d-value (Å)	I/I_o	*d*-value (Å)	I/Io	
24.450	3.6377	8	3.6255	19	0.0122
34.940	2.5658	80	2.5444	87	0.0214
38.125	2.3585	100	2.3380	100	0.0205
48.240	1.8849	33	1.8722	42	0.0127
52.935	1.7283	15	1.7168	26	0.0115
57.625	1.5983	23	1.5877	31	0.0106

[a] JCPDS-ICDD 44-706; for convenience, peaks with intensity less than 7% are omitted.

[b] $\Delta d = d_{\mathrm{obsd}} - d_{\mathrm{ref}}$.

close and treated as one step of decomposition. This twin step with a mass loss of 25.76% together with the third step (680–714 K); with a mass loss of 10.57%, were regarded as the removal of the histidene moiety. The final step found in the range 715–791 K with a mass loss of 46.28% was assigned to the removal of the Schiff base moiety leaving CuO as residue.

3.4. HT-DRIFT and XRD analysis

The IR spectral data of the calcinated solid complexes (Table 4) indicates that the amino acid moiety is that being removed first followed by the Schiff base moiety as a final step. The removal of the amino acid part is evidenced by the disappearance of the bands due to the NH_2 and COO^- from the spectra of the calcinated complexes at the DTG peak temperatures. The IR spectra at the end of decomposition revealed nothing except the bands at 619–532 cm^{-1} assigned for the formation of the metal oxide (CuO) as the end product (Table 5).

The XRD data are listed in Table 6. As seen from the table, it is clear that the observed XRD data matched the reference data (JCPDS-44-706) very well and it was found that the final decomposition product of all complexes is to be CuO. This conclusion is consistent with the results of the TG analysis (see Table 3 and Schemes 1–4) and the IR data of the calcinated complexes (Table 4).

3.5. Kinetics of the decomposition of the complexes

3.5.1. Determination of reaction order of decomposition

The Horowitz and Metzger [34] equation $C_s = (n)^{1/1-n}$, where C_s is the weight fraction of the substance present at the DTG peak temperature; T_s, is given by.

$$C_s = (W_s - W_f)(W_o - W_f) \tag{1}$$

and was used for the determination of the values of the reaction order. Here, W_s stands for the weight remaining at a given temperature T_s, i.e. the DTG peak temperature, W_o and W_f are the initial and final weights of the substance, respectively. The values of C_s for the thermal decomposition of the complexes are in the range 0.28–0.33 which indicates that the decomposition follows first order kinetics [22,34,35] (Table 7).

3.5.2. Integral method using the Coats–Redfern equation

For a first order process the Coats–Redfern equation [36] may be written in the form:

$$\log\left[\frac{\log(W_f/W_r)}{T^2}\right] = \log\left[\frac{AR}{\theta E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \tag{2}$$

where W_f is the mass loss at the completion of the reaction, W the mass loss up to temperature T; ($W_r = W_f - W$), R the gas constant, E^* the activation energy in J mol^{-1}, θ is the heating rate. Since 1–($2RT/E^*$) ≅ 1, a plot of the left hand side of Eq. (2) against $1/T$ was drawn which gave straight lines, where E^* and A (Arrhenius constant) were calculated from the slope and the intercept, respectively.

Table 7
The kinetic and thermodynamic data of the thermal decompositions of the three complexes

Complex	Decomposition temperature (K)	E^* (kJ mol^{-1})	R^2[a]	A (s^{-1})	S^* (J K^{-1} mol^{-1})	H^* (kJ mol^{-1})	G^* (kJ mol^{-1})	C_s
[Cu(L)(Gly)]	524–553	373.26	0.99	4.59×10^{35}	52.06	369.75	340.53	0.29
[$Cu(C_{13}H_{10}NSO)(C_2H_4NO_2)$]	555–580	272.85	0.99	1.19×10^{25}	27.65	268.18	252.64	0.30
	588–660	124.16	0.98	1.06×10^{10}	−7.10	119.08	123.42	0.31
	687–742	678.30	0.99	2.46×10^{49}	83.4	672.33	612.53	0.30
[Cu(L)(Ala)]	586–727	243.92	0.99	1.06×10^{15}	4.12	237.11	233.73	0.30
[$Cu(C_{13}H_{10}NSO)(C_3H_6NO_2$]	737–918	536.296	0.96	2.11×10^{28}	34.58	528.21	494.597	0.31
[Cu(L)(Val)]	541–583	328.20	0.99	1.57×10^{30}	39.40	323.50	301.2	0.29
[$Cu(C_{13}H_{10}NSO)(C_5H_{10}NO_2$]	583–713	228.00	0.98	2.19×10^{14}	2.57	222.30	220.28	0.30
	714–874	456.3	0.97	8.89×10^{23}	24.5	448.00	424.20	0.31
[Cu(L)(His)]	608–670	234.69	0.99	1.96×10^{16}	18.03	224.45	235.6	0.32
[$Cu(C_{13}H_{10}NSO)(C_6H_8N_3O_2$]	680–714	568.00	0.98	1.88×10^{42}	67.04	562.19	515.46	0.33
	715–791	402.84	0.99	7.01×10^{27}	33.74	396.70	371.34	0.28

[a] R^2; correlation coefficient.

The activation entropy ΔS^*, the activation enthalpy ΔH^* and the free energy of activation G^* were calculated using the following equations:

$$\Delta S^* = 2.303 \left(\log \frac{Ah}{kT}\right) R \qquad (3)$$

$$\Delta H^* = E^* - RT \qquad (4)$$

$$\Delta G^* = \Delta H^* - T_\mathrm{s} \Delta S^* \qquad (5)$$

where k and h are the Boltzman and Planck constants respectively.

The calculated values of E^*, A, ΔS^*, ΔH^* and ΔG^* for the decomposition steps are given in Table 6. The most significant result is the considerable thermal stability of the complexes reflected from the high values of the activation energy of the decomposition. The second essential result from Table 6 is that the entropy change ΔS^* for the formation of the activated complexes from the starting reactants is in most cases of positive values. The positive sign of the ΔS^* suggests that the degree of structural “complexity” (arrangement, “organization”) of the activated complexes was higher than that of the starting reactants and the decomposition reactions are slow reactions [37].

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