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Synthesis, spectral and thermal studies of new copper (II) complexes with 1,2-di(imino-2-aminomethylpyridil)ethane

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Abstract New copper (II) complexes of Schiff bases with 1,2-di(imino-2-aminomethylpyridil)ethane with the general composition $CuLX_m(H_2O)_x$, [L = Schiff base, X = Cl^-, Br^-, NO_3^-, ClO_4^-, CH_3COO^-, $m = 2$; X = SO_4^{2-}, $m = 1$] were prepared by template synthesis. The complexes were characterized by elemental analysis, conductivity measurements, magnetic moments, IR, UV–VIS and EPR spectra. The thermal behavior of complexes was studied using thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Infrared spectra of all complexes are in good agreement with the coordination of a neutral tetradentate N_4 ligand to the cooper (II) through azomethinic and pyridinic nitrogen. Magnetic, EPR and electronic spectral studies show a monomeric distorted octahedral geometry for all Cu(II) complexes. Conductance measurements suggest the non-electrolytic nature of the compounds, except for copper (II) nitrate and perchlorate complexes which are 1:2 electrolytes. Heats of decomposition, ΔH, associated with the exothermal effects were also determined.

Keywords 2-aminomethylpyridine · Cu(II) complexes · Glyoxal · Template synthesis · Thermal analysis

Introduction

A large number of Schiff bases and their polydentate complexes have been intensively studied [1–4] for their interesting and important properties such as biological and catalytic activity, photochromic properties [5–8].

The tetradentate Schiff bases which contain N=C–C=N structural unit have, also, biological activity due to their ability to form strong chelate rings with essential heavy metal ions [9]. Particularly, complexes of first row transition metals with such ligands have a wide range of biological properties [10–13].

Numerous complexes of copper are used for the treatment of a variety of diseases, including cancer, ulcers, nervous system and heart diseases [14].

In this paper, as a continuation of our interest in the coordination behavior of Schiff bases with glyoxal [15], we report the synthesis and characterization of a series of copper (II) complexes with 1,2-di(imino-2-aminomethylpyridil) ethane (Fig. 1).

The Cu(II) complexes were characterized by different analytical and spectral methods. The thermal behaviors of the obtained complexes were also investigated. The thermal analysis techniques, such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), were widely applied in studying the thermal behavior and the structure of metal complexes [16–26]. The results allowed us to acquire information concerning the structure of these compounds, including their thermal behavior and decomposition. Thermal analysis let us also to evaluate the presence of crystallization water molecules in the complexes and to determine the endothermic and/or exothermic effects connected with such processes as: dehydration, melting, crystallization and decomposition.

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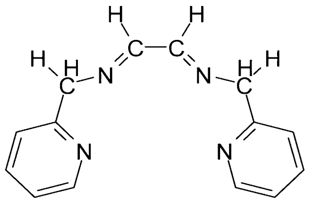

Fig. 1 1,2-di(imino-2-aminomethylpyridil)ethane (L)

Experimental

Materials

All chemicals were of pure analytical grade and were purchased from Sigma-Aldrich and Fluka.

Method and apparatus

The contents of copper (II) were determined by gravimetric method with salicylaldoxime. Carbon, hydrogen and nitrogen contents were determined using CHNS-O elemental combustion analysis with a Costech elemental analyzer model ECS 4010. The melting temperatures of complexes were directly measured with SMPI Melting Point Apparatus (Stuart Scientific). Molar conductances of the complexes were measured in 10^{-3}M DMF at room temperature using a Consort type C-533 conductivity instrument. The IR spectra were recorded between 4000 and 400 cm^{-1} in KBr pellets with a BIO-RAD FTS-135 instrument. Electronic spectra were obtained by diffuse reflectance technique with a VSU-2P Zeiss Jena instrument. EPR spectra for copper (II) complex were recorded using a JEOL JES–FA 100 X-band frequency spectrometer. Measurements of the magnetic susceptibility were carried out at room temperature using the Faraday method.

The thermal experiments were performed on a Mettler Toledo TGA/SDTA 851e thermal analyzer, within the temperature range 25–1000 °C, and a Mettler Toledo DSC 853e differential scanning calorimeter, within the temperature range 25–600 °C. The TG curves were recorded in air flow atmosphere with a flow rate of 50 mL min^{-1} and at a heating rate of 10 K min^{-1}. The DSC curves were obtained under nitrogen atmosphere, with the same heating rate. The samples were held in aluminium crucibles for DSC experiments and platinum crucibles for TG/SDTA experiments, with a pinhole in the lid, for both methods, to prevent pressure build up due to gaseous products. Sample mass was between 0.8 and 3 mg for both methods. At the end of the heating process for the DSC experiments, the mass of the remaining sample represents approximately 25% from initial values for all studied complexes. The TG/DTA and DSC curves were used to characterize the accompanying mass and heat changes during the linear heating.

Synthesis of complexes

An ethanolic solution of 2-aminomethylpyridine (2 mmol in 5 mL ethanol) and an ethanolic solution of glyoxal (1 mmol in 5 mL ethanol) were mixed with constant stirring at 50 °C for 30 min. An ethanolic solution of the corresponding copper (II) salts (1 mmol in 20 mL ethanol) was mixed with ethanolic solution of respective ligand. The acetate Cu(II) complex was prepared by addition of ethanolic solution of copper (II) acetate (1 mmol in 20 mL ethanol) and ethanolic solution of sodium (I) acetate (1 mmol in 10 mL ethanol) to the ethanolic solution of ligand. The reaction mixture was stirred for 3 h at 50 °C, after which it was concentrated to less than half of its initial volume. The complexes were obtained by adding diethyl ether to the reaction mixture. It was filtered, washed with diethyl ether, and dried under vacuum on anhydrous $CaCl_2$.

Results and discussion

All the synthesized complexes are colored powders. The complexes are soluble in acetone, DMF and DMSO, partly soluble in methanol and insoluble in $CHCl_3$, CH_2Cl_2, and CCl_4.

Elemental analyses are shown in Table 1. The analytical data show that the complexes may be formulated as $CuL(H_2O)_yX_m$, where L = 1,2-di(imino-2-aminomethylpyridil) ethane, $X = Cl^-$, Br^-, NO_3^-, ClO_4^-, CH_3COO^-, $m = 2$; $X = SO_4^{2-}$, $m = 1$.

Some physical characteristics (color, melting point and molar conductivity at 22.5 °C in DMF (10^{-3} M)) of the complexes are given in Table 1. The molar conductivity values [27] show that the complexes $[CuL(H_2O)_2](NO_3)_2$ and $[CuL(H_2O)_2](ClO_4)_2$ are 1:2 electrolytes and the others are non-electrolytes.

Infrared spectra

The assignments of the significant IR spectral bands of ligand and its cooper (II) complexes are presented in Table 2.

The ligand spectrum exhibits a ν(C=N) band at 1653 cm^{-1} assigned to the pyridinic ring and a band at 1585 cm^{-1} assigned to the vibration of the azomethine group. In the IR spectra of the complexes a considerable shift towards lower frequencies is observed, indicating that both nitrogen atoms of azomethine and pyridinic group are coordinated to the metal ion. The vibrations of the pyridinic ring of the complexes are observed in the 1603–1639 cm^{-1} range and for the azomethine groups [28] in the 1562–1573 cm^{-1} range. Moreover, the fact that the ligand is coordinated to the metal ion through the pyridinic nitrogen is

Table 1 Analytical and physical data of the complexes

No.	Compounds	Color	Content/% calc. (found)				m.p./°C	$\Lambda_M^a/\Omega^{-1}cm^2\ mol^{-1}$	μ_{eff}/BM
			C	H	N	Cu			
(I)	$[CuLCl_2]\cdot H_2O$	Green	43.03 (43.48)	4.10 (3.84)	14.34 (14.11)	16.26 (16.84)	150	34.3	2.01
(II)	$[CuLBr_2]\cdot 1.5H_2O$	Dark green	34.41 (34.86)	3.51 (3.67)	11.46 (12.03)	13.01 (13.55)	>340	19.6	1.85
(III)	$[CuL(H_2O)_2](NO_3)_2$	Green khaki	36.41 (36.92)	3.93 (4.22)	18.19 (18.86)	13.76 (13.23)	245[b]	127.3	2.09
(IV)	$[CuL(H_2O)_2](ClO_4)_2$	Dark green	31.33 (31.72)	3.38 (3.15)	10.44 (10.78)	11.84 (12.33)	200[b]	135.6	1.99
(V)	$[CuL(CH_3COO)_2]\cdot 2H_2O$	Dark khaki	47.41 (48.02)	5.31 (5.12)	12.29 (11.87)	13.94 (14.28)	190	29.6	1.78
(VI)	$[CuLSO_4]\cdot 2.5H_2O$	Dark khaki	37.96 (38.45)	4.32 (4.49)	12.65 (12.92)	14.35 (14.01)	>340	52.5	1.89

[a] At 22.5 °C

[b] With decomposition

Table 2 IR spectral bands (cm^{-1}) and their assignments

Compounds	Assignments						
	$\nu_{(O-H)}$	$\nu_{(C=N)}$ azomethine	$\nu_{(C=N)}$ Py	γ-H_2O	γ-ring Py	ν_{X^-}	$\nu_{(M-N)}$
Ligand (L)	–	1653	1585	–	771	–	–
$[CuLCl_2]\cdot H_2O$ (I)	3444	1603	1567	–	763	–	420
$[CuLBr_2]\cdot 1.5H_2O$ (II)	3416	1633	1567	–	761	–	430
$[CuL(H_2O)_2](NO_3)_2$ (III)	3423	1609	1573	824	775	1384 ν_3	430
$[CuL(H_2O)_2](ClO_4)_2$ (IV)	3534	1610	1570	828	766	1091 ν_3 625 ν_4	420
$[CuL(CH_3COO)_2]\cdot 2H_2O$ (V)	3416	1639	1562	–	763	1598 ν_{asim} 1393 ν_{sim}	415
$[CuLSO_4]\cdot 2.5H_2O$ (VI)	3414	1626	1568	–	763	1119[a] ν_3 961 ν_1 632[a] ν_4 491 ν_2	416

[a] Splitting

confirmed by variation of the vibration γ-ring Py with 5–8 cm^{-1}.

The IR spectra of all complexes show broad bands in the 3400–3550 cm^{-1} range that may be assigned to a stretch of OH group from water molecules. Complexes III and IV show weak bands at 824 cm^{-1} and 828 cm^{-1}, respectively, that may correspond to vibration γ-H_2O rocking [29]. This indicates the presence of coordinated water in these complexes.

In the infrared spectra of the complexes under study new bands with medium to weak intensities appear in the 410–430 cm^{-1} region, which are assigned to the ν (M–N) vibrations [30].

In IR spectra of III–VI complexes the occurrences of the characteristic absorption bands corresponding to anions suggest their presence in coordination or ionization sphere.

The IR spectrum of the complex III shows a strong sharp band at 1384 cm^{-1} which is attributed to the ν_3 vibration of uncoordinated nitrate ion [30].

In the perchlorato complex, the presence of ν_3 at 1091 and ν_4 at 625 cm^{-1} bands indicates that the Td symmetry of ClO_4^- is maintained in the complex. Therefore, it suggests the presence of ClO_4^- outside the coordination sphere of the complex IV [31].

The infrared spectrum of acetate complex V displays two bands, at 1598 and 1393 cm^{-1}, assigned to ν_{asim} (COO^-) and ν_{sim} (COO^-), respectively. The separation of these peaks by 205 cm^{-1} indicates the monodentate coordination of acetate group [32].

A characteristic band appears in the spectrum of the complex VI, which corresponds to the bidentate coordination of SO_4^{2-} ion. The ν_1 and ν_2 frequencies, characteristic to a Td arrangement appear as weak intensity bands, at 961 and 491 cm^{-1}. The ν_3 and ν_4 frequencies are each split into three bands, at 1044, 1119, 1192 cm^{-1}, respectively, 619, 632, 651 cm^{-1}, which suggest a low symmetry, probably reduced towards C_{2v} [30].

Electronic and EPR spectra

The electronic spectra and the magnetic moments support the stereochemistry of the complexes. The electronic spectra of all complexes display a broad band with maximum at 12820 cm^{-1} (780 nm), 15873 cm^{-1} (630 nm), 15151 cm^{-1} (660 nm), 14493 cm^{-1} (690 nm), 15385 cm^{-1} (650 nm), and 16393 cm^{-1} (610 nm) which suggested an octahedral coordination of the metal ion. The magnetic moments at room temperature lying in the range of 1.78–2.09 BM (Table 1) correspond to one unpaired electron. This indicates the monomeric nature of the complexes and the absence of any metal–metal interaction [33].

Room temperature EPR spectra of Cu(II) complexes were recorded. The analysis of spectra (Fig. 2) gives $g_{\parallel} = 2.204$, $g_{\perp} = 2.077$; $g_{\parallel} = 2.427$, $g_{\perp} = 2.093$; $g_{\parallel} = 2.271$, $g_{\perp} = 2.090$, for the III, IV, and VI complexes. The trend $g_{\parallel} > g_{\perp} > 2.0023$ observed for these complexes indicates a distorted tetragonal geometry. The unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the copper (II) ion, giving $^2B_{1g}$ as the ground state [33]. For the complex II the '*g*' parameter has three values ($g_1 = 1.91$, $g_2 = 2.088$, $g_3 = 2.427$). This characteristic, according with literature data, is in favor of a rhombic copper (II) ion environment [34]. From the EPR spectra of the complexes I and V, it cannot propose the exact geometry of the metal ions. The '*g*' parameter has only one value ($g_{\text{isotropic}} = 2.121$ and 2.101, respectively). The electronic spectra, the magnetic moment values, and the relative isotropy of 'g' parameter indicate the octahedral stereochemistry of the Cu(II) complexes [35].

Thermal analysis

Due to the explosive nature of perchlorato and nitrato complexes [36–39], we have investigated only the thermal properties of chloro, bromo, acetate, and sulphato complexes. The TG/DTA and DSC curves, at a 10 K min^{-1} heating rate, of Cu(II) complexes are represented in Figs. 3, 4, 5, and 6. The decomposition stages, temperature ranges, heat of decomposition, as well as found and

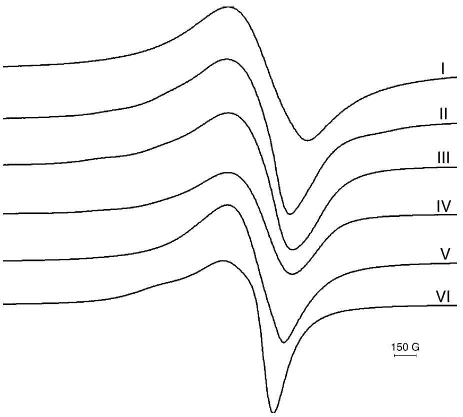

Fig. 2 The EPR spectra of the copper (II) complexes at room temperature

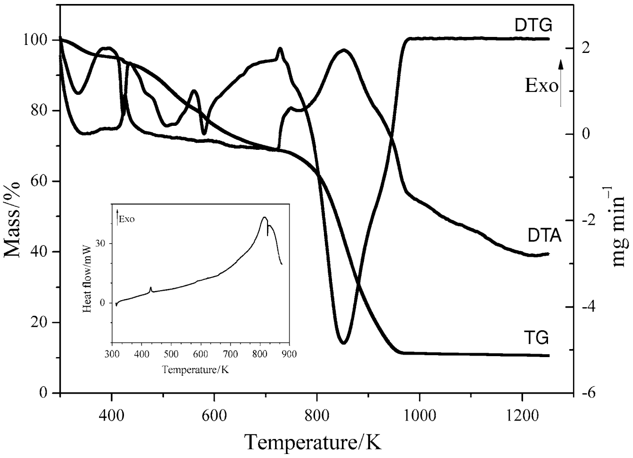

Fig. 3 TG/DTA and DSC curves of the $[CuLCl_2]\cdot H_2O$

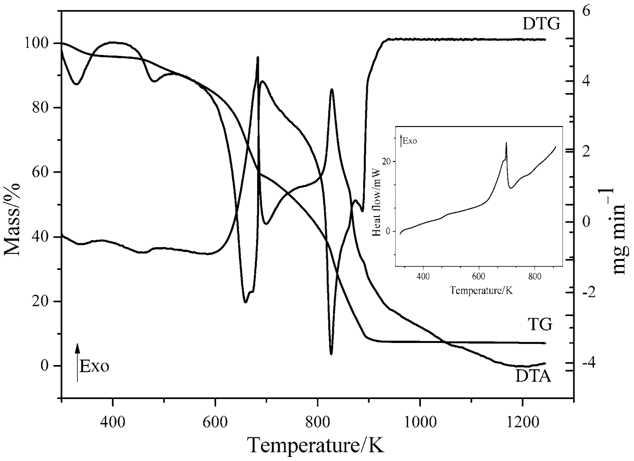

Fig. 4 TG/DTA and DSC curves of the $[CuLBr_2]\cdot 1.5H_2O$

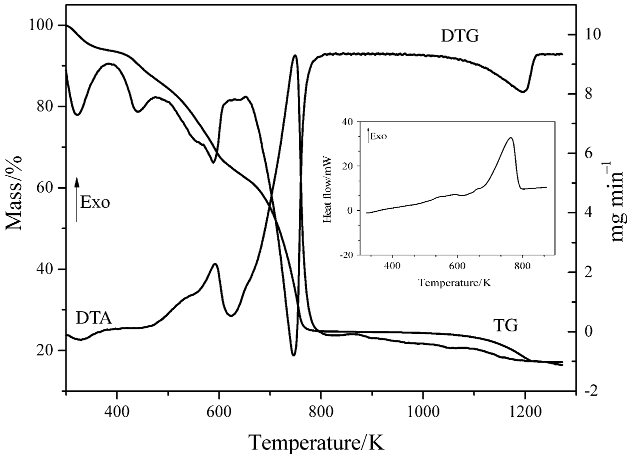

Fig. 5 TG/DTA and DSC curves of the $[CuL(CH_3COO)_2]\cdot 2H_2O$

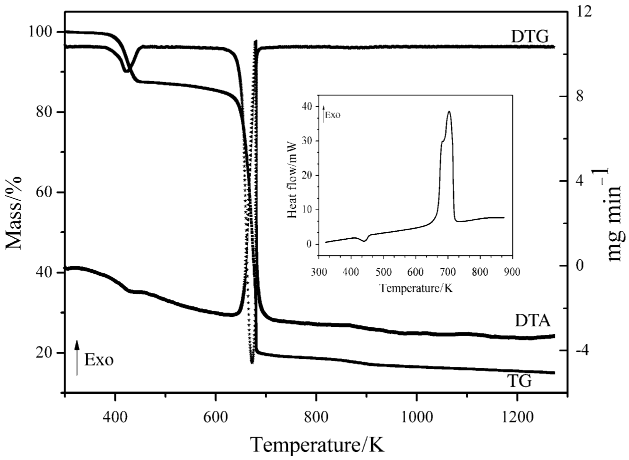

Fig. 6 TG/DTA and DSC curves of the $[CuL(SO_4)]\cdot 2.5H_2O$

calculated weight loss percentages of the complexes are given in Table 3.

The complexes $[CuLCl_2]\cdot H_2O$, $[CuLBr_2]\cdot 1.5H_2O$, and $[CuL(CH_3COO)_2]\cdot 2H_2O$ undergo decomposition mainly in four stages. The complex $[CuL(SO_4)]\cdot 2.5H_2O$ undergoes decomposition in three stages. The first stage, for the first three complexes, takes place in the 50–130, 50–190 and 50–155 °C ranges corresponding to dehydration process and release of one or two crystallization water molecules. Dehydration of the complex $[CuL(SO_4)]\cdot 2.5H_2O$ takes place in the 50–160 °C temperature range and releases of two and half crystallization water molecules. The DSC curve of this complex shows an endothermic peak at 187 °C representing dehydration process.

The second decomposition stage of the complexes corresponds to the partial decomposition. The DTA curve of the complex $[CuL(CH_3COO)_2]\cdot 2H_2O$ has a wide range of thermal change with two exothermic peaks at 260 and 319 °C. Partial decomposition of the complex is also confirmed by two exothermic peaks on the DSC curve with two maxima at 268 and 320 °C. The second stage of the complex $[CuL(SO_4)]\cdot 2.5H_2O$ takes place in the 160–600 °C temperature range with a strong exothermic peak on DTA curves with maximum at 407 °C. This is correlated with the decomposition of the ligand molecule and expulsion of SO_3 molecule. Decomposition of the complex is also confirmed by strong exothermic effect on DSC curve with maximum at 431 °C. The evaluation of the exothermal peak area gives a value of $-7461.8\ Jg^{-1}$.

The third decomposition stage of the complexes $[CuLCl_2]\cdot H_2O$ and $[CuLBr_2]\cdot 1.5H_2O$ is in continuation of the second stage, in the 220–315 and 210–408 °C temperature ranges. This step is due to the expulsion of the remaining part of the Cl_2 and Br_2 molecules. The third decomposition step of the complex $[CuL(CH_3COO)_2]\cdot 2H_2O$ is in the 342–960 °C range with maximum DTA exothermic peak at 476 °C and maximum on DSC curve at 492 °C. The

Table 3 Thermal analysis data of the Cu(II) complexes

Compounds	Temperature range/°C	Mass loss %		DTA peak T/°C	DSC peak T/°C	Process	Products
		Exp.	Calcd.				
$[CuLCl_2]\cdot(H_2O)$	50–130	4.88	4.61	–	–	Dehydration	$1H_2O$
	130–220	6.38	6.46	152 exo	158 exo	Partial decomposition	$0.36Cl_2$
	220–315	11.53	11.68	313 exo	315 exo	Partial decomposition	$0.64Cl_2$
	315–1000	65.91	66.04	476 exo	545 exo	Final decomposition	L and partial CuO
				580 exo	560 exo		
$[CuLBr_2]\cdot 1.5(H_2O)$	50–190	5.25	5.53	183 endo	180 endo	Dehydration	$1.5H_2O$
	190–310	8.64	8.18	212 exo	214 exo	Partial decomposition	$0.25Br_2$
	310–408	24.78	24.53	–	–	Partial decomposition	$0.75Br_2$
	408–1000	53.07	53.63	410 exo	425 exo	Final decomposition	L and partial CuO
				466 exo	478 exo		
				553 exo			
$[CuL(CH_3COO)_2]\cdot 2(H_2O)$	50–155	8.22	7.90	–	–	Dehydration	$2H_2O$
	155–342	25.91	26.34	260 exo	268 exo	Partial decomposition	$2CH_3COOH$
				319 exo	320 exo		
	342–960	48.64	48.31	476 exo	492 exo	Partial decomposition	L
	960–1000	17.23	17.45	–	–	Final decomposition	CuO
$[CuL(SO_4)]\cdot 2.5(H_2O)$	50–160	10.25	10.17	158 endo	167 endo	Dehydration	$2.5H_2O$
	160–600	72.06	71.87	407 exo	410 exo	Partial decomposition	$L + SO_3$
					431 exo		
	600–1000	17.69	17.96	–	–	Final decomposition	CuO

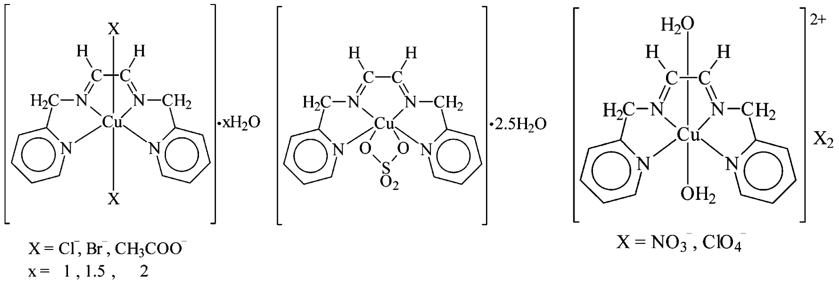

Fig. 7 Proposed structural formula of Cu(II) complexes

evaluation of heat of decomposition gives a value of $-5430.1\ \mathrm{Jg}^{-1}$. It brings a weight loss of 48.64% (calcd. 48.31%), which is due to the expulsion of the ligand molecule.

The final decomposition process for all complexes corresponds with the formation of copper oxide as the final product. Final process of the complexes $[\mathrm{CuLCl_2}]$ $(\mathrm{H_2O})$ and $[\mathrm{CuLBr_2}]\cdot1.5(\mathrm{H_2O})$ is in the 315–1000 and 408–1000 °C range, respectively, with two DTA maxima at 476 and 580 °C for the first complex and 466 and 553 °C for the second one. These intensive exothermic peaks are correlated with a violent decomposition together with expulsion of a part of the residue. The DSC curves of the complexes show also intensive exothermic peaks with two maxima 545 and 560 °C for the complex $[\mathrm{CuLCl_2}]\cdot\mathrm{H_2O}$, with $\Delta H = -12020\ \mathrm{Jg}^{-1}$ (evaluated as peak area, neglecting the partial superposition of exothermal process) and 425 and 478 °C for the complex $[\mathrm{CuLBr_2}]\cdot1.5\mathrm{H_2O}$, with $\Delta H = -1360.93\ \mathrm{Jg}^{-1}$ confirming the runaway behavior. The final decomposition of the complexes $[\mathrm{CuL(CH_3COO)_2}]\cdot2\mathrm{H_2O}$ and $[\mathrm{CuL(SO_4)}]\cdot2.5\mathrm{H_2O}$, with copper oxide formation, occurs in the 960–1000 °C for the first complex and 600–1000 °C for the second one.

On the basis of the above analytical and spectral data and the thermal analysis, the structure and the stoichiometry indicated in Fig. 7 were proposed for the Cu(II) complexes.

Conclusions

New six copper (II) complexes with Schiff bases derived by glyoxal and 2-aminomethylpyridine were obtained by template synthesis. The structures of the complexes were proposed based on elemental analysis, molar conductance, magnetic moment values, IR, UV–VIS and EPR spectra and thermal analysis. From the IR spectra, it was concluded that the ligand is a neutral tetradentate N_4 and is coordinated to the metal ion through the azomethinic and pyridinic nitrogen. On the basis of the magnetic moments and EPR data a deformed octahedral geometry is suggested for all Cu(II) complexes investigated. The thermal results allowed acquiring the information concerning the stoichiometry of these compounds.

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