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COORDINATION COMPOUNDS

Copper(II) and Zinc(II) Complexes of Thiophene/Furan Carboxamides: Synthesis, Structure and Properties[1]

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Abstract—Cu(II) and Zn(II) complexes were synthesized from equimolar amounts of carboxamides; 1,8-bis(2-thiophenecarboxamido)-*p*-menthane (tkdam) and 1,8-bis(2-furancarboxamido)-*p*-menthane (furdam). The structure of the carboxamides were determined by elemental analysis; ^{1}H NMR, ^{13}C NMR, FT-IR and LC-MS spectra. The relative energies and the electronic properties (LUMO, HOMO, LUMO-HOMO gap) of the ligands were investigated theoretically by performing Semi-empirical molecular orbital theory PM3 method in Hyperchem 7 (Release). Carboxamide complexes having general formula as; monomeric, $[ML]Cl_2$ and dimeric $[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$ were synthesized and characterized by using element analysis; FT-IR, LC-MS spectra; magnetic susceptibility, molar conductivity and thermal (TGA/DTA curve) studies. It was found that the coordination number of the monomeric complexes is four whereas dimeric's is six. The changes in the selected vibration bands in FT-IR indicate that, carboxamides behave as tetradentate ligands and coordinate to metal ions from acyl ring (through S/O) and amide carbonyl (C=O). Molar conductivity measurements indicate the 1 : 2 ionic nature of the carboxamide complexes.

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INTRODUCTION

The carboxamide linkages (–CO–NH–) are an essential building unit in proteins, which has attracted much attention because of its high resistance to hydrolysis. This fact is of crucial importance in biological systems, since it permits for the building of peptides from relatively simple amino acid precursors [1–4].

The continuing interest in the study of carboxamide complexes are derived from their ability to model active sites present in some metalloproteins and the search for a better understanding of physicochemical properties of such complexes, especially the stereochemistry of the metallic centers. In order to expand on the function of the metal ions in the biological systems, we are involved in a study of the impact of structure changes on the physicochemical properties of the model complex of the first row transition metal [5, 6].

There is a considerable interest in the pharmacology of heterocyclic ligands containing nitrogen, oxygen, sulfur etc. and their metal chelates [7, 8] as antitumor, antibacterial, antifungal and antiviral agents. Copper complexes have been widely used in metalmediated DNA cleavage to obtain the activated oxygen species [9].

In this paper, we report the synthesis and characterization of thiophene-2-carboxamide and furan-2-carboxamide by the reaction of the acide chlorides with 1,8-diamino-*p*-menthane. The structures of the carboxamides were determined by spectral methods (^{1}H NMR, ^{13}C NMR, LC-MS, FT-IR). The relative energies: total energy, binding energy, heat of formation and the electronic properties: the highest occupied molecular obital (HOMO) energy, lowest unoccupied molecular orbital (LUMO) energy and LUMO-HOMO gap (ΔE) of the ligands were calculated by using Semi-empirical PM3 method in Hyperchem 7 (Release). The coordination behaviour of ligands towards transition metal ions was investigated via the FT-IR, molar conductance, magnetic moment and thermal analysis.

EXPERIMENTAL

Materials and Methods

1,8-diamino-*p*-menthane, 2-thiophenecarbonyl chloride and 2-furancarbonyl chloride, metal salts as chlorides (all from Aldrih) and solvents (all from Merck) were used without further purification. All chemicals and solvents used in syntheses were of analytical grade. The elemental analyses (C, H, N, S) were performed on a LECO–CHSNO-9320 type elemental analyzer. Geometry optimization of ligands were performed by Semi-empiricai molecular orbital theory PM3 method in Hyperchem 7 (Release). The IR spectra (4000–400 cm^{-1}) were recorded on a Mattson-1000 FT-IR spectrophotometer with samples prepared as KBr pellets. NMR spectra were recorded on a Bruker–Spectrospin Avance DPX-400 Ultra–Shield (400 MHz) using DMSO-d$_6$ as a solvent. UV-

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Table 1. Elemental analysis data of ligands and their complexes; found/(calculated)

Compound	C, %	H, %	N, %	S, %	M, %	Cl, %
tkdam	61.37(61.54)	6.50(6.66)	7.10(7.18)	15.98(16.38)	–	–
$[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$	41.78(42.14)	5.23(5.44)	5.12(4.92)	10.61(11.24)	10.57(11.15)	11.74(12.47)
$[Zn(tkdam)]Cl_2$	45.34(45.61)	4.65(4.94)	4.95(5.32)	11.78(12.18)	12.34(12.42)	12.49(13.36)
furdam	66.77(67.06)	7.54(7.26)	8.23(7.82)	–	–	–
$[Cu(furdam)]Cl_2$	48.36(48.76)	5.09(5.28)	5.95(5.69)	–	12.72(12.90)	13.45(14.39)
$[Zn(furdam)]Cl_2$	48.13(48.58)	5.47(5.26)	5.91(5.67)	–	12.68(13.24)	15.23(14.37)

Table 2. Physical properties of carboxamides and their complexes

Compound	Formula	FW (g/mol)	Yield (%)	μ_{eff} (B.M.)	Λ_m (cm^{-1} mol^{-1} Ω^{-1})
tkdam	$C_{20}H_{26}N_2O_2S_2$	390.33	70	–	–
$[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$	$C_{40}H_{62}N_4O_9S_4Cu_2Cl_4$	1139.04	63	1.67	98
$[Zn(tkdam)]Cl_2$	$C_{20}H_{26}N_2O_2S_2ZnCl_2$	526.69	60	dia	87
furdam	$C_{20}H_{26}N_2O_4$	358.17	67	–	–
$[Cu(furdam)]Cl_2$	$C_{20}H_{26}N_2O_4CuCl_2$	492.62	64	1.88	96
$[Zn(furdam)]Cl_2$	$C_{20}H_{26}N_2O_4ZnCl_2$	494.47	62	dia	90

Vis spectra were recorded on UNICAM-UV 2-100 spectrophotometer. Magnetic susceptibility data for the metal complexes was recorded on a Sherwood Scientific magnetic balance. The molar conductance measurements were carried out using a Siemens WPA CM 35 conductometer. A Du Pont Instrument 951 thermal analyzer was used to record simultaneously TG and DTA curves. The experiments were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of 10°C min^{-1} in the temperature range 30–400°C using platinum crucibles.

Synthesis of the Ligands

To a solution of acide chlorides (30.00 mmol) in dichloromethane (20 cm^3), triethylamine (30.00 mmol) was added then 1,8-diamino-*p*-menthane (15.00 mmol) in dichloromethane (10 cm^3) was added dropwise by cooling the balloon in the ice bath. The reaction mixture was stirred magnetically under reflux for a day. The precipitate was filtered and dried on vacua. The crude product was dissolved in a 30 mL of MeOH by heating on a magnetic stirrer. The solvent was evaporated to half of its original volume. The solution was filtered warmly to remove impurities, then left for crystallization at room temperature. Recrystallization from methanol yielded a white solid ligands and than these crystals were dried on A4 molecular sieve [8].

Synthesis of Metal Complexes

The metal complexes of the carboxamides were prepared by the addition of hot solution (40°C) of the appropriate metal chloride (1.00 mmol) in 25 mL methanol to the hot solution (40°C) of ligand (1.00 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux whereupon the complexes precipitated. They were recrystallized from methanol and than dried in dessiccant [10].

RESULTS AND DISCUSSION

The carboxamide compounds were prepared as described in the experimental part, crystallized, dried and subjected to elemental analysis. The results of elemental analysis (C, H, N, S) and analytical data are presented in Tables 1 and 2.

The results obtained are in good agreement with those suggested formula below. In all of the synthesized carboxamides behave as tetradentate ligands. The preparation of the ligands are given in Fig. 1.

In general, 1 : 1 (M : L) solid complexes were isolated and found to have the general formula given as $MX_m \cdot nH_2O + L \longrightarrow [ML]X_2$ where M = Cu, Zn; X = Cl; $m = 2$; $n = 0.2$ whereas dimeric complex (tkdamCu) has the general formula as $[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$.

NMR Spectra

^1H NMR and ^{13}C NMR data of carboxamide ligands are collected in Table 3.

The ^1H NMR spectra of carboxamides in deutero form of DMSO displayed the expected resonances. The integration which is in accordance with 1 : 2 for-

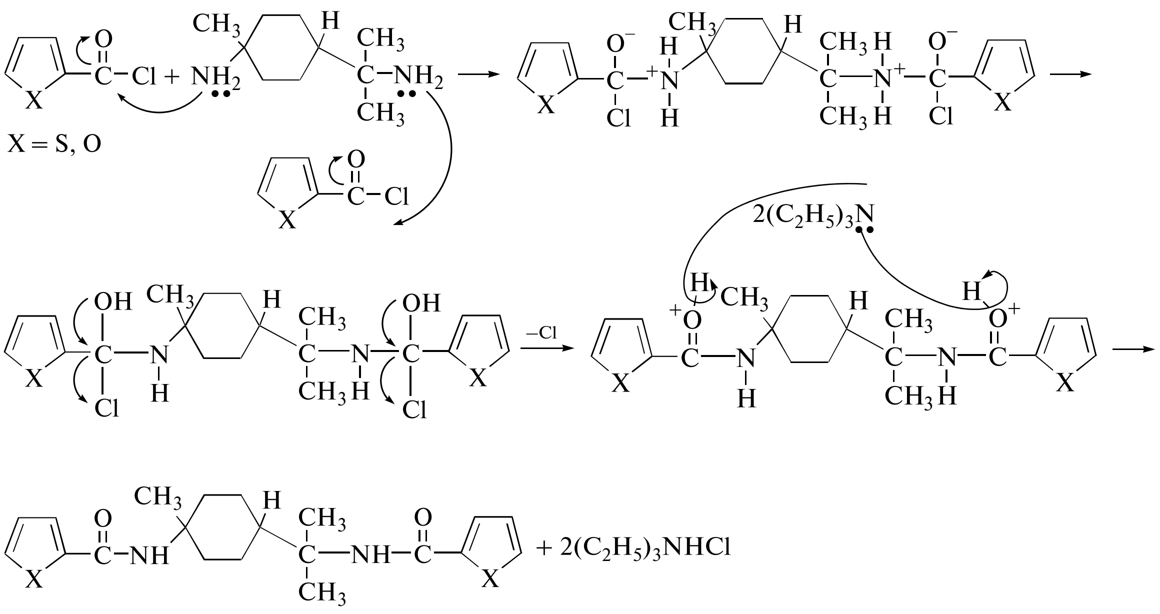


Fig. 1. Preparation of the carboxamide ligands.

mulation proposed by elemental analysis, allows the assignment of them. In general, the multiplates observed between 7.11–7.85 ppm and 7.06–7.79 ppm are asigned to thiophene and furan ring protons, respectively. N(1)H and N(2)H protons are observed between 7.43–7.66 ppm as singlet [11–14]. In the ^{13}C-NMR spectra, carbonyl C(5), C(16) groups have the highest chemical shifts and observed between 161.46 ppm, 161.11 ppm for tkdam and 158.10 ppm, 157.74 ppm for furdam [8, 15]. The functional groups at each side of the menthane ring have similar or very close chemical shifts because of asymetry.

Geometry Optimization

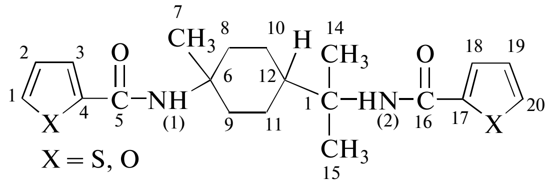
Geometry optimization calculations for the free ligands were performed by Semi-empirical PM3 method in Hyperchem 7 (Release) whereas this method is not satisfactory for the complexes. Table 4 shows the PM3 optimized total energy, binding energy, semi-empirical heats of formation and the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energies and the inter-frontier molecular orbital energy gap (LUMO-HOMO, ΔE) with the lowest and highest level energy values of the carboxamide ligands.

Thiophene carboxamide molecule has a heat of formation of about –31.86 kcal/mol, while furan-2-carboxamide has the value of about –102.46 kcal/mol by PM3 method. As shown in Table 4 the heat of formation of the molecules change with variation of donors (S, O etc.). On the other hand, the values of HOMO, LUMO and ΔE energies may be affected by the variety of the donors. Furan carboxamide leads to more increase in ΔE gap (9.52 eV), while thiophene carboxamide leads to less decrease in ΔE (9.05 eV), this means that in any excitation process of thiophene carboxamide needs less energy than furan carboxamide [6–18] LUMO, HOMO orbitals and energy spectra of tkdam molecule are shown in Figs. 2 and 3.

FT-IR Spectra and Mode of Bonding

The most chracteristic vibrations of carboxamide compounds are selected by comparing the vibrational frequencies of the ligands with those of their metal complexes and recorded in IR spectra gives enough information to elucidate the way of bonding of the ligands to the metal ions. Carboxamides have three donor sites: thiophene ring S/furan ring O; carbonyl O and amide N. As tetradentate ligands the bonding takes place through either the ring donors (S/O) and carbonyl O (Amide **I**) [19, 20]. Carboxamides have characteristic amide bands such as: Amide **A**, Amide **I**, Amide **II**, Amide **III** etc. Amide **A** occurs as a strong band between 3335–3367 cm^{-1} by the vibration of N–H bond (ν_{N-H}). Amide **I** band which results from composite N–C=O vibriation consists mainly of carbonyl C=O vibriation ($\nu_{C=O}$). Amide **II** and Amide **III** bands arise from ν_{C-N} as well as δ_{N-H}, these modes are coupled to one another [7, 8, 21]. The carbonyl frequencies (Amide **I**) of the ligands are observed between 1632–1654 cm^{-1}. In the complexes, a significant negative shift of the carbonyl frequency takes place, because of coordination through the carbonyl O [22, 23]. The other bonding mode is supported by these additional observations: (i) the shift of $\nu_{CS} + \delta_{ring}$ to lower wawenumbers and δ_{C-S-C} to higher wawenumbers by coordination through thiophene ring [14]. (ii) the shift of in plane ring deformation mode of furan

Table 3. The NMR data for carboxamides using d_6-DMSO as solvent



^{1}H NMR (ppm)			^{13}C NMR (ppm)	
Assignment	tkdam	furdam	tkdam	furdam
N(1)H	7.66 (s, 1H)	7.53 (s, 1H)	–	–
N(2)H	7.59 (s, 1H)	7.43 (s, 1H)	–	–
C(1)H	7.69 (d, 1H)	7.79 (d, 1H)	130.76	145.12
C(2)H	7.14 (m, 1H)	7.06 (m, 1H)	128.32	112.93
C(3)H	7.85 (d, 1H)	7.66 (d, 1H)	141.98	113.95
C(4)	–	–	128.67	148.69
C(5)	–	–	161.46	158.10
C(6)	–	–	56.67	56.85
C(7)H_3	1.39 (s, 3H)	1.31 (s, 3H)	27.84	24.59
C(8)H_2–C(11)H_2	2.02–1.21 (m, 8H)	2.47–1.12 (m, 8H)	36.06–22.65	43.72–22.02
C(12)H	2.17 (m, 1H)	2.09 (m, 1H)	43.13	36.81
C(13)	–	–	56.09	54.09
C(14)H_3, C(15)H_3	1.33 (s, 6H)	1.27 (s, 6H)	24.38	23.42
C(16)	–	–	161.11	157.74
C(17)	–	–	128.63	147.50
C(18)H	7.82 (d, 1H)	7.66 (d, 1H)	141.90	113.82
C(19)H	7.11 (m, 1H)	7.06 (m, 1H)	128.32	112.64
C(20)H	7.69 (d, 1H)	7.79 (d, 1H)	130.70	145.02

ring, $\nu_{C-C} + \nu_{C-O}$ to lower wawenumbers and the shift of β_{C-H}(ring) to higher wawenumbers by coordination through the furan ring [24, 25].

Molar Conductivity

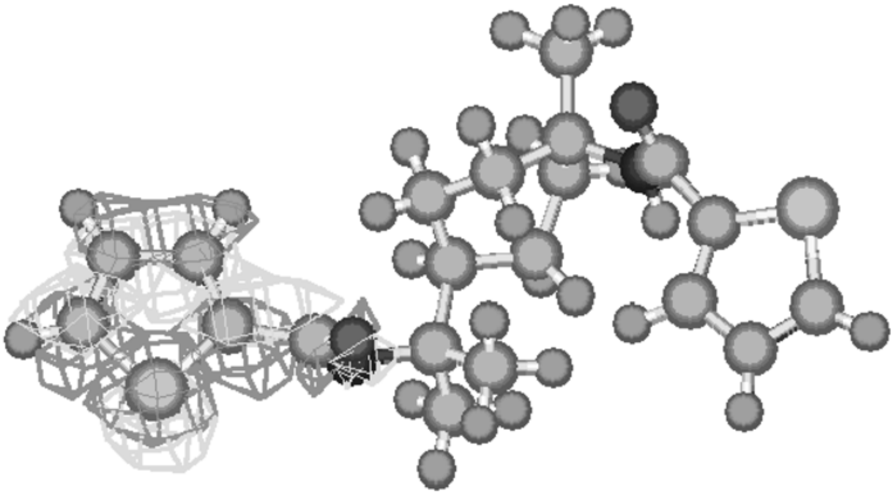
The molar conductivity (Λ_m) of 10^{-3} M solutions of the complexes were measured in MeOH at 25°C and exhibitted in Table 2. It is concluded that all the complexes have the molar conductivity of 87–98 Ω^{-1} mol^{-1} cm^2 indicating the ionic nature of these complexes. The molar conductivity of 10^{-3} M $CaCl_2$ solution in methanol was also measured as 88 Ω^{-1} mol^{-1} cm^2 which is around the molar conductivity of complexes. It means that all complexes have 1 : 2 electrolyte type by comparing $CaCl_2$ solution and two chloride anions bonds to the coordination sphere of the complexes as counter ions [26].

Mass Spectra

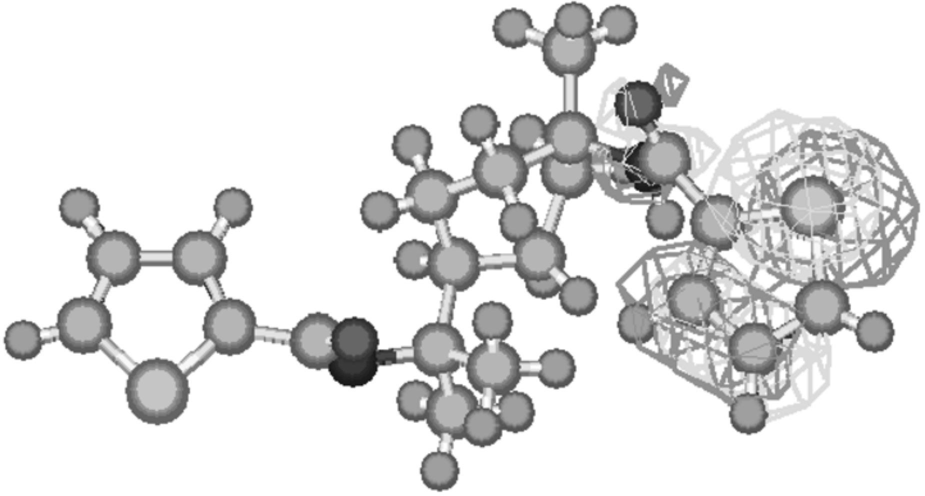
Mass spectra of tkdam gives the molecular ion peak as fragment **I** at m/z= 391.2 (4.3%). The main peak occurs by the removal of the amine (dam) as fragment **IV** is observed at m/z = 171.1 (100.0%) [27]. The mass spectra of $[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$ is scanned up to 1200 (m/z), molecular ion peak was observed at 1050.6 (3.5%), $[Cu(tkdam)Cl]_2Cl^+$ fragment is observed at 1013.0 (6.3%) by lossing of one chlorine atom, $[Cu(tkdam)Cl]_2^{2+}$ fragment was observed at 978.7 (weakly) by lossing of two chlorine atoms and

Table 4. Semi-empirical PM3 calculation results of ligands

Assignment	tkdam	furdam
Total energy (kcal/mol)	–93497.89	–98438.58
Binding energy (kcal/mol)	–5582.23	–5339.15
Heat of formation (kcal/mol)	–31.86	–102.46
HOMO energy (eV)	–9.74	–9.65
LUMO energy (eV)	–0.69	–0.13
LUMO-HOMO gap (ΔE, eV)	9.05	9.52

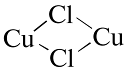


LUMO



HOMO

Fig. 2. The shape of LUMO and HOMO of tkdam. Balls and cylinders model was used for the geometry optimization by Semi-empirical PM3 method.

μ-dichloro bridging dicopper () fragment is observed at 198.1 (7.1%) [28, 29]. These fragmentations support the proposed dimeric nature of tkdamCu complex in which other fragments are as follows: 882.1 (3.7%), 803.2 (17.5%), 488.0 (18.7%), 453.0 (36.4%), 128.0 (100%). In mass spectra of [Zn(tkdam)]Cl_2 complex, molecular ion peak is observed at 544.2 (3.8%), [Zn(tkdam)]$^+$ fragment occurs by lossing of two chlorine atoms at (m/z) 455.2 with 58.5% strong peak intensity. Mass spectra of furdam gives the molecular ion peak as fragment **I** at m/z = 359.2 (12.3%) and other fragments are as follows: fragment **II** ($C_4H_3O \cdot CO$) is at m/z = 95.1 (23.8%), fragment **III** ($C_{15}H_{22}N_2O_2$) is at 265.2 (35.0%) resulting from the elimination of 2-thiophene carbonyl group. Also the removal of the amine(dam) fragment **IV** from fragment **III** can be observed at m/z = 171.2 (76.3%) [27, 30]. Mass spectra of [Cu(furdam)]Cl_2 and [Zn(furdam)]Cl_2 are scanned up to 1200 (m/z), molecular ion peaks with bonded fragment which belongs to menthane ring (m/z = 82.1), [ML + 2Cl + 82.1]$^+$ are observed around 573.0 (6.3%) and 577.0 (4.7%) which are the highest fragment (m/z) values in the spectra. This shows that furdam complexes are monomeric [14, 27]. [Cu(furdam)]$^{2+}$ and [Zn(furdam)]$^{2+}$ fragments which occur by losing of two chlorine atoms are observed at 422.5 (4.1%) and 424.5 (5.5%). The proposed fragmentation route of complexes and the main fragments (**I**, **II**, **III**, **IV**) of ligands are shown in Fig. 4.

Thermal Studies

Thermal behaviour of complexes was determined in nitrogen atmosphere (20 ml min^{-1}) with a heating rate of 10°C min^{-1} in the temperature range 30–400°C.

Fig. 3. The molecular orbital energy spectra of tkdam, Semi-empirical PM3 results.

As seen in Fig. 5, there are mainly two continuous mass loss steps in the TGA curve of $[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$. The first step with mass loss of 9.525% from 90.57 to 132.13°C may be assigned to the loss of the five crystal water molecules of hydration. There is mainly large mass loss step which starts at 260.08°C and ends at 300.14°C with loss percentage of 68.798% which is attributed to the organic decomposition. In the DTA curves, $[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$ behaves different heat effects on heating such as two intense exothermic peak at 119.77°C ($\Delta H = -598.50$ J/g) and 270.04°C ($\Delta H = -93.42$ J/g), one intense endothermic peak at 284.23°C ($\Delta H = 230.63$ J/g). In the TGA curves of other complexes, there are no mass loss up to 250°C because of non hydration. For $[Zn(tkdam)]Cl_2$ and $[Cu(furdam)]Cl_2$ complexes, there are observed mainly one intense exothermic peak with mass loss of 87.927% at 290.74°C ($\Delta H = -598.50$ J/g) and 74.753% at 288.28°C ($\Delta H = -778.72$ J/g) depending on organic decomposition. There are different mass loss rates starting at 259.33°C and finishing at 287.32°C which is predicted as the continuous organic decomposition of $[Zn(furdam)]Cl_2$ [31, 32]. Thermal results shows good agreement with the theoretical formula as suggested from the analytical data (Tables 1 and 2) and proposed structure of complexes shown in Fig. 6.

CONCLUSION

In this study, we have reported the synthesis of carboxamide ligands which contain N, S and O donors and their tetradentate complexes. The structure of ligands were determined by using elemental analysis, several spectral methods (NMR, FT-IR, LC-MS). The relative energies and the electronic properties of ligands were calculated by Semi-empirical molecular orbital theory PM3 method in Hyperchem 7 (Release).

The spectral, conductivity, thermal and magnetic studies of complexes have been discussed. Carboxamides act as a tetradentate through the two amide carbonyl (C=O) and two S/O donors of thiophene/furan ring according to vibrational shifts on IR spectra. Conductivity measurements showed that all complexes are electrolite (1 : 2 type) and contain two Cl atoms out of coordination sphere. The structures of monomeric complexes are proposed as tetragonal

Table 5. Characteristic IR bands (4000–400 cm^{-1}) of carboxamides and their complexes

Compound	Amide **A**	Amide **I**	Amide **II**	Thiophene ring	Furan ring
				ν(CS) + δ(ring), δ_{C-S-C}	$\nu_{C-C} + \nu_{C-O}$, β_{C-H}(ring)
tkdam	3338	1632	1537	717, 611	–
$[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$	3337	1623	1540	706, 643	–
$[Zn(tkdam)]Cl_2$	3335	1621	1542	706, 636	–
furdam	3363	1654	1597	–	1019, 1253
$[Cu(furdam)]Cl_2$	3358	1645	1596	–	1012, 1270
$[Zn(furdam)]Cl_2$	3367	1644	1597	–	1012, 1272

The main fragments of $[(ML)]Cl_2$ complexes, m/z (intensity %)

Comp.	$[(ML)]Cl$ + fragm.	$[M + L]Cl^+$	$[MH + L]^+$	L
tkdamZn	526.2 + 18.0[a] (3.8)	491.4 (3.2)	455.2 (58.5)	391.1 (36.2)
tkdamCu	492.6 + 82.1[b] (6.3)	–	422.5 (4.1)	359.1 (2.5)
furdamZn	494.5 + 82.1[b] (4.7)	459.0 (2.6)	424.5 (5.5)	359.0 (3.9

[a]: NH_4^+; [b]: bonded fragment product (menthane ring).

The main fragments of ligands, m/z (intensity %)

Comp.	I	II	III	IV
tkdam	391.2 (4.3)	111.1 (10.2)	284.2 (4.1)	171.1 (100.0)
tkdamCu	391.1 (7.8)	111.0 (26.5)	283.8 (5.2)	172.2 (17.8)
tkdamZn	391.1 (36.2)	111.1 (3.4)	284.2 (8.0)	171.0 (3.1)
furdam	359.2 (12.3)	95.1 (23.8)	365.2 (35.0)	171.2 (76.3)
furdamCu	359.1 (2.5)	95.0 (18.6)	265.1 (10.0)	171.1 (42.7)
furdamZn	359.0 (3.9)	95.1 (24.9)	265.2 (22.4)	171.2 (40.2)

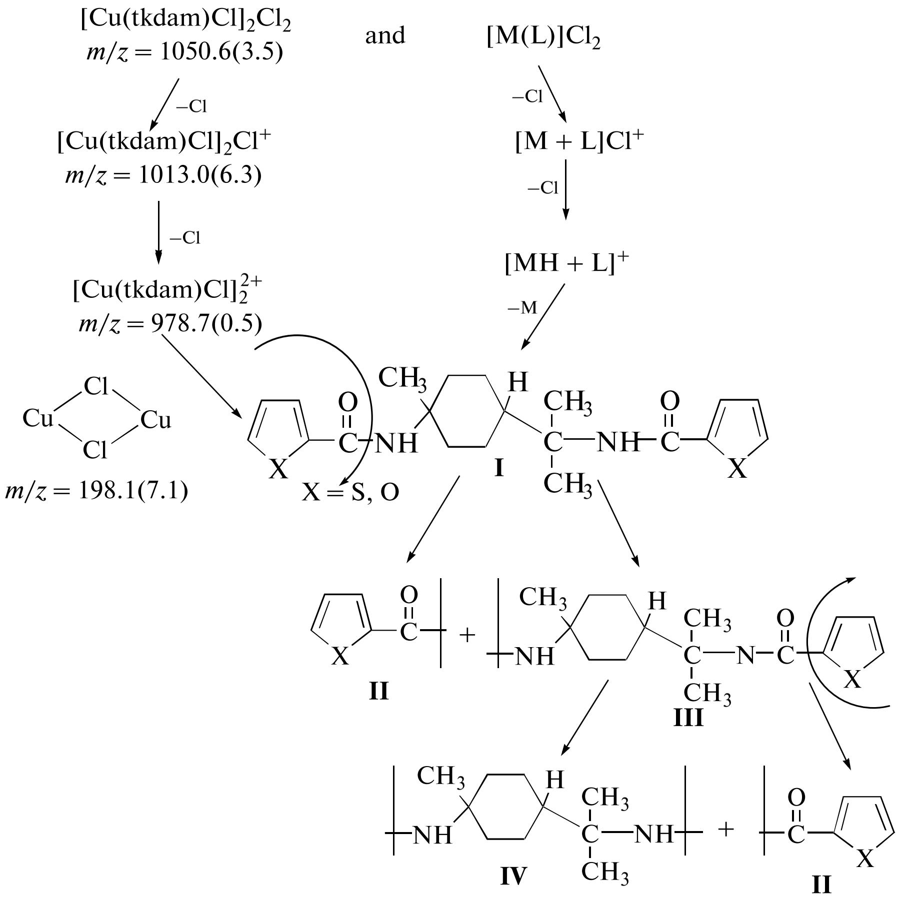


Fig. 4. Proposed fragmentation steps of carboxamides and their complexes.

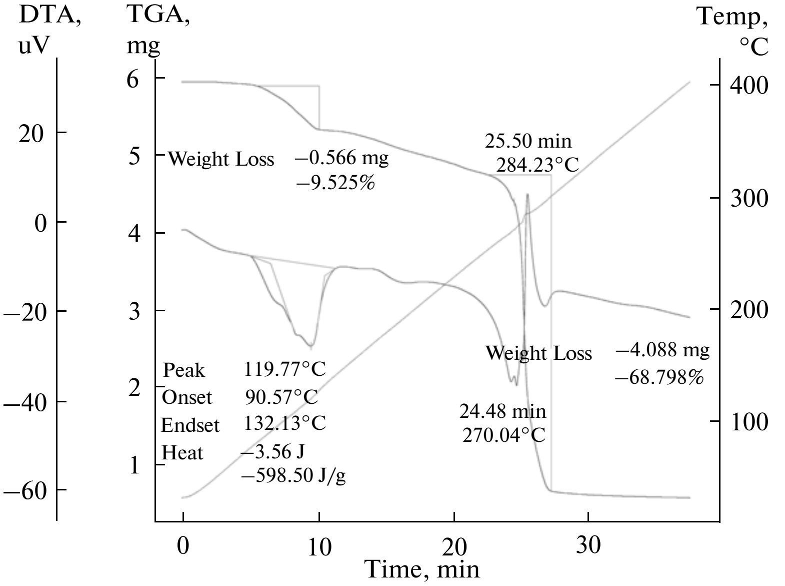
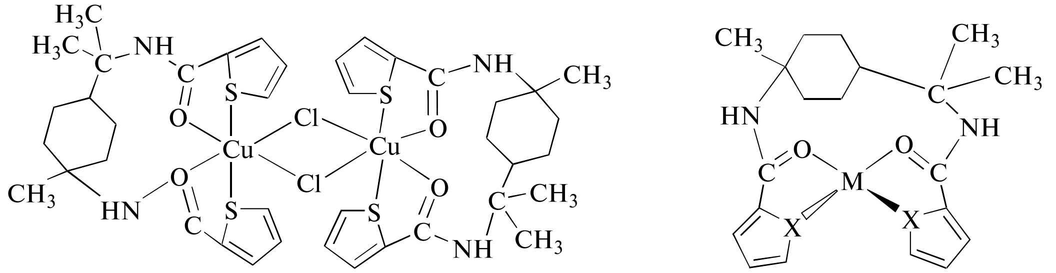


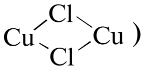
Fig. 5. TGA-DTA curve of $[Cu(tkdam)]_2Cl_2 \cdot 5H_2O$ complex.



tkdamCu

$[ML]Cl_2$ (M = Cu, Zn; X = S, O)

Fig. 6. The proposed structure of the carboxamide complexes.

geometry. Two extra bonding to tetragonal geometry are provided by the coordinated two bridging chlorine atoms in distorted octahedral dimeric complex, $[Cu(tkdam)Cl]_2Cl_2 \cdot 5H_2O$ [33, 34]. In the physicochemical aspects magnetic properties of dicopper complexes are differ from monocopper complexes with their antiferromagnetic coupling depending upon the bridging and distortion. This is in agreement with bridging tkdamCu complex and its magnetic moment ($\mu = 1.67$ B.M.) is lower than other synthesized monocopper complex, furdamCu ($\mu = 1.88$ B.M.) [35, 36]. In the mass spectra, the peak at (m/z) 198.1 corresponds to μ-dichloro bridging dicopper ( $Cu\overset{Cl}{\underset{Cl}{\diamond}}Cu$) fragment. The electronic spectra of dinuclear copper chelate showed an extra band at 422 nm between $10D_q$ band for distorted octahedral geometry corresponding to the transitions $^2E_g \longrightarrow {}^2T_{2g}$ [19]. These magnetic and spectral data support the proposed dimeric structure [28, 29].

In our previous work, 1,3-bis(2-thiophenecarboxamido)-propane, 1,3-bis(2-furan carboxamido)-propane and their Cu(II), Zn(II), Co(III) complexes were synthesized and their antimicrobial activities were screened against several bacteria and fungi (*C. albicans*) [14]. In our further applications, the antibacterial activies of the newly synthesized carboxamide compounds presented in this paper will be investigated.

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