ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 3, pp. 593–601. © Pleiades Publishing, Ltd., 2014.

Synthesis and Spectroscopic Studies of Mn(II), Co(II), and Cu(II) Complexes of Novel 2-[2,4-Dioxo-4-(thiophen-2-yl)butanamido]benzoic Acid Ligands[1]

Moamen S. Refat[a,b], Ibrahim M. El-Deen[b], and Reda F. M. El-Shaarawy[c]

[a] Department of Chemistry, Faculty of Science, Taif University, 888 Taif, Kingdom Saudi Arabia
e-mail: msrefat@yahoo.com

[b] Department of Chemistry, Faculty of Science, Port Said University, Port Said, Egypt

[c] Department of Chemistry, Faculty of Science, Suez Canal University, Egypt

Received February 10, 2014

Abstract—Mn(II), Co(II), and Cu(II) complexes with novel heterocyclic ligands derived from anthranilic acid and its 5-bromo derivative with ethyl-2-thionylpyruvate were synthesized and characterized by means of elemental analysis, molar conductivity, spectral methods (IR, ^{1}H NMR, and UV-Vis spectra) and simultaneous thermal analysis (TG and DTG) techniques. The IR spectra of the two ligands and their complexes were used to identify the type of bonding. The kinetic thermodynamic parameters such as: E^*, ΔH^*, ΔS^*, and ΔG^* were estimated from the DTG curves. New ligands and their complexes have been tested for their possible antibacterial and antifungal activity.

DOI: 10.1134/S1070363214030311

INTRODUCTION

Metal complexes of nitrogen and sulfur containing chelating ligands have attracted considerable attention [1] because of their interesting physicochemical properties, pronounced biological activities and as models of the metalloenzyme active sites. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules. Schiff-base metal complexes [2–5] have been widely studied because they found industrial, antifungal, antibacterial, anticancer and herbicidal applications. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing N and S as donor atoms [6, 7] show broad spectrum of biological activity [8–11] and are of special interest because of the variety of modes in which they are bonded to metal ions [12]. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities.

In the present paper we report the synthesis and characterization of Mn(II), Co(II), and Cu(II) complexes with novel heterocyclic ligands derived from anthranilic acid and its 5-bromo derivative with ethyl-2-thionylpyruvate. The aim of our research was to gain more information about related structural and spectral properties as well as their microbial activities known from the literature for similar compounds especially with Mn(II), Co(II), and Cu(II) complexes.

EXPERIMENTAL

All chemicals were reagent grade and were used without further purification. Anthranilic acid and its 5-bromo derivative were purchased from Fluka Chemical Co., $MnCl_2\cdot4H_2O$, $CoCl_2\cdot6H_2O$, and $CuCl_2\cdot2H_2O$ from Merck Co.

Carbon and hydrogen contents were determined using a Perkin-Elmer CHN 2400 instrument in the Micro-analytical Unit at the Faculty of Science, Cairo University, Egypt. The metal content was found gravimetrically by converting the compounds into their corresponding oxides. IR spectra were recorded on a Bruker FTIR spectrophotometer (4000–400 cm^{-1}) in KBr pellets. UV–Vis spectra were determined in 1.0×10^{-3} M solutions(DMSO as solvent) for the free ligand and its complexes using Jenway 6405 spectrophotometer with 1 cm quartz cell, in the range of 200–

---

[1] The text was submitted by the authors in English.

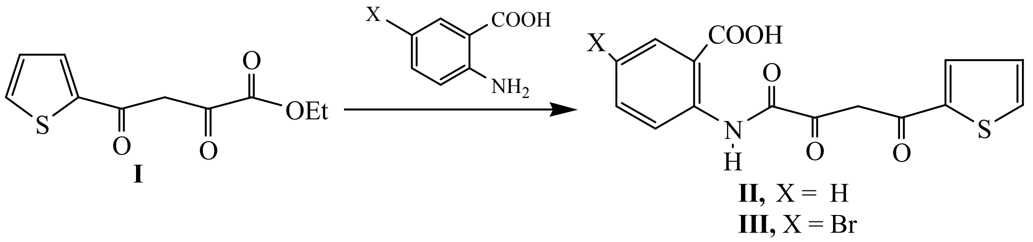


Fig. 1. Synthetic route for obtaining ligands **II** and **III**.

800 nm. Molar conductivities of freshly prepared 1.0×10^{-3} M DMSO solutions were measured using Jenway 4010 conductivity meter. ^{1}H NMR spectrum of the two ligands and CuL_1 complex were recorded on a Varian Gemini 200 MHz spectrometer using DMSO-d_6 as solvent and TMS as an internal reference. The purity of the two ligands were checked from mass spectra at 70 eV by using AEI MS 30 Mass spectrometer. Thermogravimetric analysis (TGA and DTG) were carried out in dynamic nitrogen atmosphere (30 mL/min) with a heating rate of 10 C/min using a Schimadzu TGA-50H thermal analyzer.

Ethyl-2-thionylpyruvate (I). A mixture of 2-acetylthiophene (0.01 mol) and diethyl oxalate (0.01 mol) in 50 mL of sodium methoxide solution (0.005 g Na in 25 mL of methanol) was warmed for 20 min and then cooled. The solid that separated was washed with dilute hydrochloric acid and recrystallized from ethanol to give **I** as yellow crystals, mp: 95°C, yield 82%, ν_{max}, (KBr), cm^{-1}: 1745 (CO of ester), 1643 (CO of β-diketone). δ_H ($CDCl_3$), ppm: 1.30 t (3H, CH_3), 3.31 s (2H, $COCH_2CO$), 4.23 q (2H, OCH_2), and 6.32–7.50 m (3H, thiophene ring). Calculated, %: C 53.01, H 4.42, S 14.16. $C_{10}H_{10}O_4S$. Found, %: C 52.89, H 4.24, S 14.00.

Synthesis of ligands II and III *(general procedure).* A mixture of **I** (0.01 mol) and anthranilic acid or its 5-bromo derivative (0.01 mol) in acetic acid (5 mL) was heated under reflux for 1 h. The product obtained after cooling was collected by filtration, washed with ethanol, dried and purified by recrystallization with acetic acid to give ligands **II** (**III**) (Fig. 1).

2-[2,4-Dioxo-4-(thiophen-2-yl)butanamido]benzoic acid (II). Yellow crystals, yield 67%, mp: 220°C. ν_{max} (KBr), cm^{-1}: 3230 (OH), 3164 (NH), 1690 (CO of β-

Table 1. Elemental analyses and physical data of the two ligands and their complexes

Compounds	*MW*	mp, °C	Color	Content, % (calculated/found)				Λ_m, μs
				C	H	N	M	
H_2L_1 (**II**, $C_{15}H_{11}NO_5S$)	317.00	220	Yellow	56.78/56.72	3.47/3.40	4.41/4.78	–	11.10
H_2L_2 (**III**, $C_{15}H_{10}NO_5BrS$)	395.90	240	Yellow	45.46/45.49	2.52/2.33	3.53/3.56	–	10.00
$[Mn(L_1)(H_2O)_2].2H_2O$ (**IV**, $C_{15}H_{17}NO_9SMn$)	441.94		Orange	40.72/40.70	3.84/3.74	3.16/3.39	12.43/12.59	16.70
$[Co(L_1)(H_2O)_2].2H_2O$ (**V**, $C_{15}H_{17}NO_9SCo$)	445.93		Brownish green	40.36/40.66	3.81/3.56	3.13/2.99	13.21/13.61	15.55
$[Cu(L_1)(H_2O)_2]$ (**VI**, $C_{15}H_{13}NO_7SCu$)	414.55		Green	43.42/43.44	3.13/3.00	3.37/3.47	15.32/14.84	13.10
$[Mn(L_2)(H_2O)_2]$ (**VII**, $C_{15}H_{12}BrNO_7SMn$)	484.84		Yellow	37.12/37.10	2.47/2.55	2.88/2.39	11.33/11.52	19.67
$[Co(L_2)(H_2O)_2].2H_2O$ (**VIII**, $C_{15}H_{17}BrNO_9SCo$)	524.83		Light brown	34.29/34.23	3.23/3.15	2.66/2.47	11.22/10.97	16.83
$[Cu(L_2)(H_2O)_2]$ (**IX**, $C_{15}H_{13}BrNO_7SCu$)	493.45		Green	36.47/36.38	2.63/2.43	2.83/2.39	12.87/ 12.63	16.56

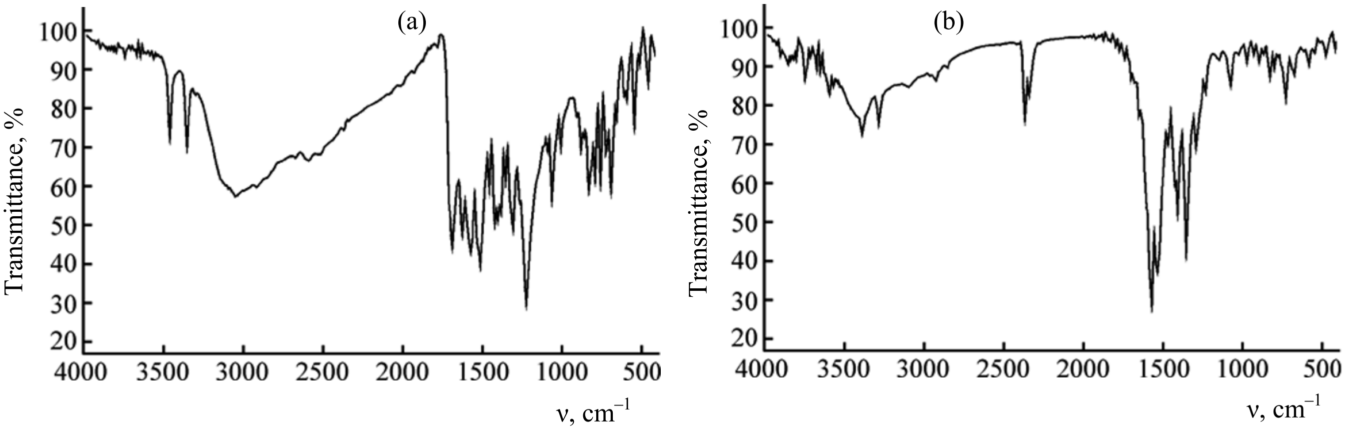


Fig. 2. The FT-IR spectra of (a) ligand **III** and (b) its Cu complex **IX**.

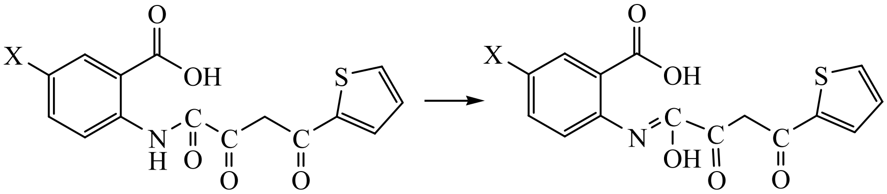


Fig. 3. Proposed proton shift, based on IR spectrum.

diketone), 1670 (amide CO), 1620 (C=N), 1603, 1582 (C=C). Calculated, %: C 56.78; H 3.49; N, 4.41; S 10.11. $C_{15}H_{11}NO_5S$. Found, %: C 57.01; H 3.48; N, 4.48; S 10.37.

5-Bromo-2-[2,4-dioxo-4-(thiophen-2-yl)butanamido]-benzoic acid (III). Faint yellow crystals, yield 72%, mp: 240°C. ν_{max} (KBr), cm^{-1}: 3230 (OH), 3164 (NH), 1690 (CO of β-diketone), 1670 (amide CO), 1620 (C=N), 1603, 1582 (C=C). Calculated, %: C 45.47; H 2.54; N, 3.54; S 8.09. $C_{15}H_{10}BrNO_5S$. Found, %: C 45.70; H 2.48; N, 3.32; S 8.11.

Synthesis of the complexes IV–IX *(general procedure).* the desired portion of the free ligand was dissolved in 30 mL of methanol and pH was adjusted to 7.0 by addition of methanolic sodium hydroxide solution. The metal salts were dissolved in 20 mL of methanol and then the prepared solutions were slowly added to the solution of the ligand under stirring. After heating for about 1 h, the pH of each solution was adjusted to 7.0 again by addition of methanolic solution of sodium hydroxide. The obtained precipitates were filtered off, washed with hot methanol and dried

Table 2. IR frequencies (ν, cm^{-1}) of the free ligands and their metal complexes

Assignments	Compound							
	II	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
ν_{as}(OH); H_2O	–	–	3418	3422	3421	3469		3389
ν(N–H)	3284	3467; 3359	–	–	–	–	–	–
ν(C–H)$_{arom}$	3109	3055	3050	3045	3098	3025		3098
ν(COOH)	1703	1690	–	–	–	–	–	–
ν(C=O)	1676; 1632	1625	–	1657	1677	1653		–
ν_{as}(COO$^-$)	–	–	1581	1573	1565	1569		1565
ν(C=N)	–	–	1650	1649	1626	1602		1649
ν_s(COO$^-$)	–	–	1406	1404	1403	1409		1404
ν(M–O)	–	–	420	419	458	422		418

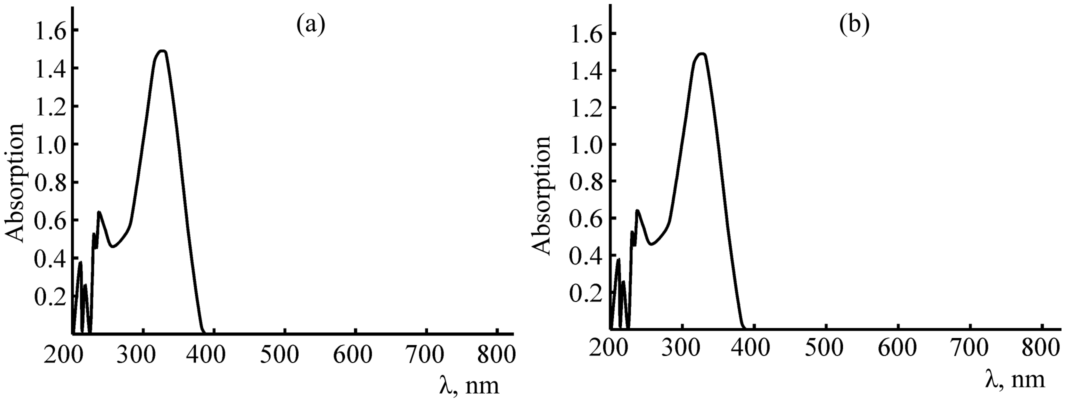


Fig. 4. UV spectra of (a) ligand **III** and (b) its Cu complex **IX**.

at 60°C. Elemental analyses and physical data for the ligands and their complexes are given in Table 1.

Microbiological screening. The hole well method was applied. The investigated isolates of bacteria were seeded in tubes with nutrient broth (NB). The seeded NB (1 cm^3) was homogenized in the tubes with 9 cm^3 of melted (45°C) nutrient agar (NA). The homogeneous suspensions were poured into Petri dishes. The holes (4 mm in diameter) were done in the cool medium. After cooling 2×10^{-3} mL of the investigated compounds (1.0×10^{-3} M DMSO solution) was applied using a micropipette. After incubation for 24 h in a thermostat at 25–27°C, the inhibition (sterile) zone diameters were measured and expressed in mm. An inhibition zone diameter over 7 mm indicates that the tested compound is active against the bacteria under investigation.

The antibacterial activities of the investigated compounds were tested against *E. Coli* and *Staphylococcus aureus* as well as some kinds of fungi, namely *Aspergillus flavus* and *Candida albicans*. In the same time with the antibacterial and antifungal investtigations of the complexes, the two ligands were also tested, as well as the pure solvent as a blank.

RESULTS AND DISCUSSION

The complexes are air-stable, hygroscopic, with high melting points, insoluble in H_2O and most of organic solvents, but partly soluble in DMSO and DMF. Condensation of ethyl 2,4-dioxo-4-(thiophen-2-yl) butanoate with anthranilic acid or its bromo derivative readily gives corresponding ligands **II** and **III**, which were easily identified by its IR, ^{1}H NMR and mass spectra. Ligands **II** and **III** on reaction with $MnCl_2·4H_2O$, $CoCl_2·6H_2O$ and $CuCl_2·2H_2O$ salts, yield complexes corresponding to the general formula $[MnL_1(H_2O)_2]·2H_2O$ (**IV**), $[CoL_1(H_2O)_2]·2H_2O$ (**V**), $[CuL_1(H_2O)_2]$ (**VI**), $[MnL_2(H_2O)_2]$ (**VII**), $[CoL_2(H_2O)_2]·2H_2O$ (**VIII**), $[CuL_2(H_2O)_2]$ (**IX**). The analytical data are in a good agreement with the proposed stoichiometry of the complexes. The metal-to-ligand ratio in the Mn(II), Co(II), and Cu(II) complexes was found to be 1 : 1.

Molar conductivities of the metal chelates. The molar conductivity values for the complexes in DMSO solutions (1.0×10^{-3} M) were in the range of $13 \times 10^{-19.67}$ μs, located in the range typical for non-electrolytes (Table 1). Conductivity measurements have frequently been used in structural elucidation (mode of coordination) of metal chelates within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the more molecular ions a complex liberates into solution (in case of anions outside the coordination sphere): the higher will be its molar conductivity and vice verso [13]. Also the molar conductance values indicate that the anions may be outside or or inside the coordination sphere. These results were strongly supported with the chemical analysis (elemental analysis data) where Cl^- ions were not detected by addition of $AgNO_3$ solution.

Infrared spectra. The main IR data of the ligands H_2L_1 and H_2L_2 and its complexes **IV–IX** are summarized in Table 2 and IR spectra for substances **III** and **IX** are shown in Fig. 2. The presence of the broad water bands in the 3469–3389 cm^{-1} zone confirms the presence of water molecules in all complexes. However, the absence of the absorption bands at 1703 and 1696 cm^{-1}, arising from the carboxylic group (COOH), indicates that the hydrogen ions in the ligands are substituted by the metal ions.

The stretching asymmetric (ν_{as}) of carboxylate group between 1581 and 1565 cm^{-1} and symmetric vibrations (ν_s) at 1409–1403 cm^{-1} confirm this hypothesis. The coordination of the metal ions via carboxylate is confirmed by the ν(M–O) bands at range of 458–418 cm^{-1}. The stretching vibration, ν(NH), which appears at 3284, 3467 and 3359 cm^{-1} in the spectra of H_2L_1 and H_2L_2, respectively, is disappeared in the spectra of their complexes, where a new band appeared at 1650–1602 cm^{-1}, which can be attributed to ν(C=N). This means transferring of the proton from NH group to CO group to be OH (Fig. 3).

Electronic absorption spectra. UV-Vis spectra of the ligands and their complexes in DMSO are shown in Fig. 4 and the spectral data are listed in Table 3. There are two detected absorption bands in the spectra of the free ligands and their complexes, the first one which appears at range of 205–260 nm was assigned to π–π* [14], and the second at 285–385 nm was assigned to *n*–π* intraligand transitions [15, 16]. These transitions also found in the spectra of the complexes, but they are shifted. There are evident that the increasing in the absorbance (hyperchromic effect) clarified in all of the spectra of the complexes attributed to the complexation behavior of two ligands towards metal ions, confirming the coordination of the ligands to the metallic ions. The absorption bands at 448 nm in the spectrum of $[Co(L_2)(H_2O)_2]\cdot 2H_2O$ (**VIII**) can be attributed to ligand to metal charge transfer.

Table 3. Electronic spectral data

Comp. no.	λ_{max}, nm	ε, mol^{-1} cm^{-1}	Assignment
II	220	234	π–π*
	235	1788	π–π*
	325	1945	*n*–π*
III	210	407	π–π*
	220	270	π–π*
	240	676	π–π*
	330	1516	*n*–π*
IV	220	3000	π–π*
	235	1431	π–π*
	345	1861	*n*–π*
V	205	3000	π–π*
	215	3000	π–π*
	240	1426	π–π*
	335	2656	*n*–π*
VI	210	3000	π–π*
	220	595	π–π*
	245	2196	π–π*
	285	2377	*n*–π*
	330	2977	*n*–π*
	350	2905	*n*–π*
VII	235	1539	π–π*
	340	2855	*n*–π*
	350	2719	*n*–π*
VIII	215	1054	π–π*
	240	1054	π–π*
	250	1054	π–π*
	260	802	π–π*
	285	541	*n*–π*
	385	1412	*n*–π*
	448	440	L→Co (C.T.)
IX	210	1854	π–π*
	235	785	π–π*
	335	1091	*n*–π*

^{1}H NMR spectra. The proton magnetic resonance spectra of the H_2L_1 (**II**), $[CuL_1(H_2O)_2]$ (**VI**) and $[CuL_2(H_2O)_2]$ (**IX**) complexes were analyzed (Fig. 5). The chemical shift (δ, ppm) of the different protons have been recorded in Table 4. The signal exhibited by the free ligand (H_2L_1) due to the carboxylate group proton at 12.62 ppm disappears in the spectra of the two complexes indicating the coordination of oxygen atom (carboxylate ion) with the metal ion [17, 18]. The signal at 12.41 ppm indicates the transfer of the proton from NH group to CO group to be OH as mention above. This signal also disappeared in the spectra of the two complexes confirming that the formation of the second bond with the metal ion. The aromatic signals

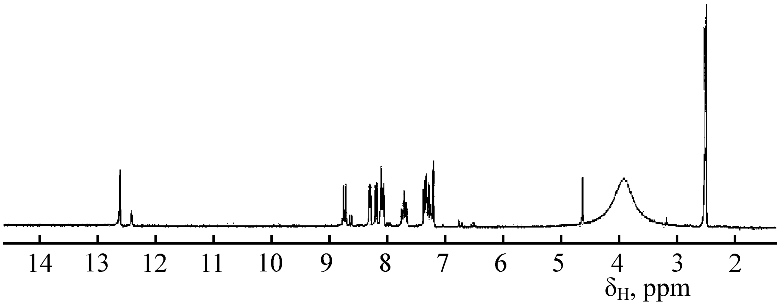


Fig. 5. ^{1}H NMR spectrum of ligand **II.**

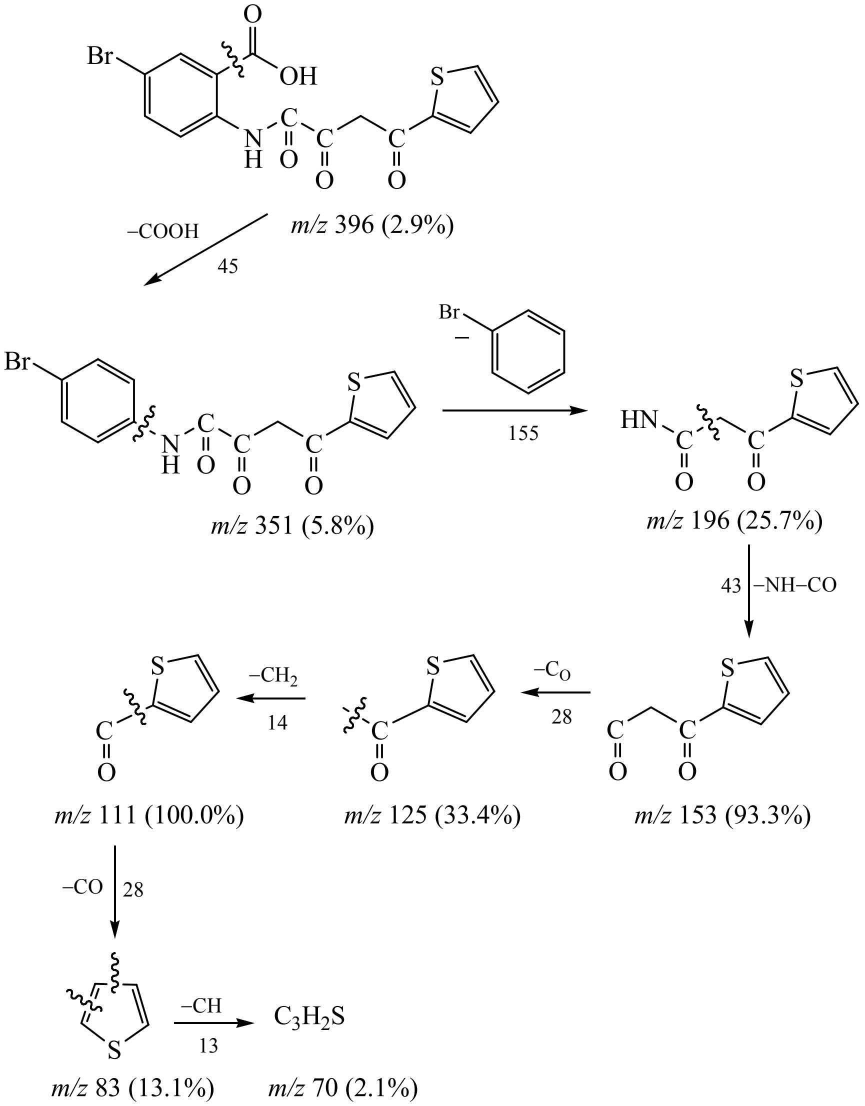


Fig. 6. Fragmentation pattern of ligand **III**.

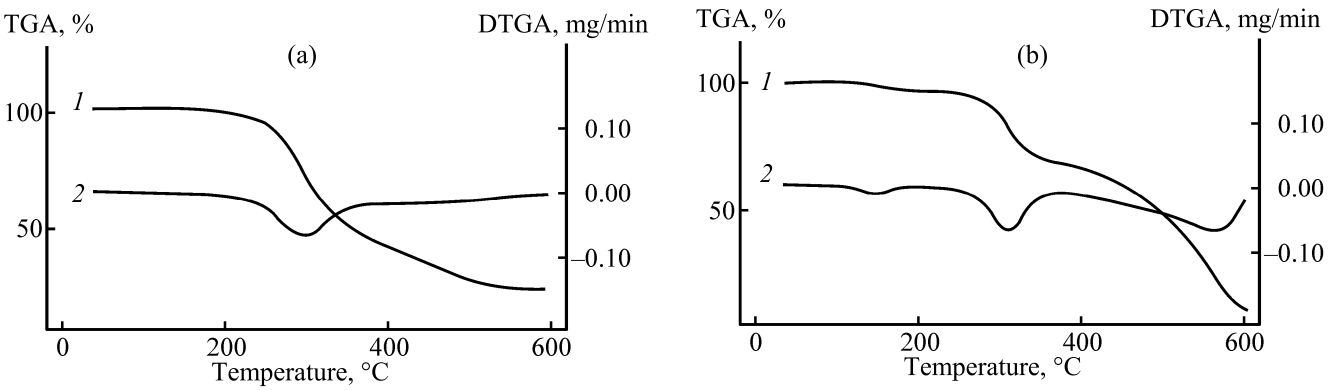
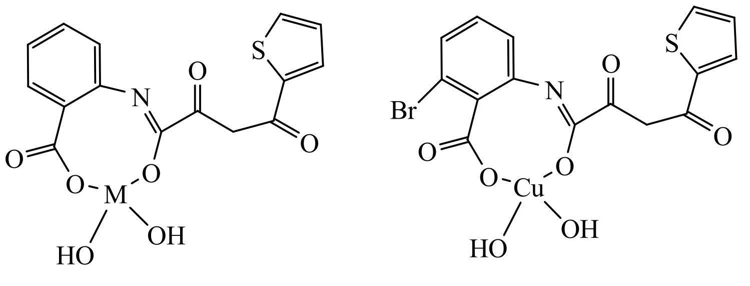


Fig. 7. (*1*) TG and (*2*) DTG curves of complexes (a) **VI** and (b) **IX**.



$M–H_2L_1$ $Cu–H_2L_2$

Fig. 8. Proposed structures of metal complexes.

do not shift significantly, thus showing that the magnetic environment of the aromatic ring has not changed significantly with coordination. Also, according to the ^1H NMR spectra for the two complexes, there is a peak appeared at range 3.43–3.39 ppm, which can be attributed to the presence of water molecules in the complexes.

Mass spectra. The purity of the ligands H_2L_1 and H_2L_2 was checked from mass spectra where the spectra showed that a clearly base peaks (*m*/*e*) molecular weights and the intensity (%) of both. The fragmentation patterns of ligand **III** is presented in Fig. 6.

Thermogravimetric analysis. The thermoanalytical results are summarized in Table 4, an example of such curves is given in Fig. 7.

Kinetic studies. In recent years there has been increasing interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves. Several equations [19–27] have been proposed as means of analyzing a TG curve and obtaining values for kinetic parameters. Many authors [19–24] have discussed the advantages of this method over the conventional isothermal method. The rate of a decomposition pro-

Table 4. Thermal data for metal complexes

Comp. no.	Steps	Temperature, °C	DTG peak, °C	TG weight loss, %		Assignments
				calculated	found	
IV	1	30–75	45	8.15	8.83	$2H_2O$
	2	75–250	173	8.15	8.00	$2H_2O$
	3	250–410	362	25.12	24.28	C_5H_3OS (organic moiety)
	4	410–600	479	20.35	19.84	C_6H_4N (organic moiety)
				38.23	39.05	$MnCO_3 + C_3H_2O$ (residue)
V	1	30–175	48	8.07	7.83	$2H_2O$
	2	175–475	403	45.97	46.28	$C_{11}H_{11}NOS$ (organic moiety)
	3	475–600	563	13.01	12.92	2CHO (organic moiety)
				32.95	32.79	$CoCO_3 + CO$ (residue)
VI	1	150–375	297	52.35	52.53	$2H_2O + C_8H_5O_3S$ (organic moiety)
	2	375–550	466	21.71	22.29	C_6H_4N (organic moiety)
				25.94	25.18	CuO + CO (residue)
VII	1	30–300	150	7.42	7.51	$2H_2O$
	2	300–550	392	60.21	60.05	$C_{12}H_6NOBrS$ (organic moiety)
	3	550–600	579	11.96	11.94	2CHO (organic moiety)
				20.41	20.50	MnO + CO (residue)
IX	1	30–185	148	3.64	3.52	H_2O
	2	185–385	311	26.14	26.84	$H_2O + C_5H_3OS$ (organic moiety)
	3	385–600	565	54.10	53.69	$C_{10}H_5NO_3Br$ (organic moiety)
				16.12	15.95	CuO (residue)

Table 5. Kinetic parameters using the Coats–Redfern (CR) and Horowitz–Metzger (HM) methods for the complexes **IV–IX**

Comp. no.	Stage	Method	Parameter					r
			E, kJ/mol	A, s^{-1}	ΔS, J mol^{-1} K^{-1}	ΔH, kJ/mol	ΔG, kJ/mol	
IV	3	CR	1.05×10^{5}	3.20×10^{6}	-1.27×10^{2}	1.00×10^{5}	1.80×10^{5}	0.9894
		HM	1.18×10^{5}	4.57×10^{7}	-1.05×10^{2}	1.12×10^{5}	1.79×10^{5}	0.9999
		average	1.11×10^{5}	2.44×10^{7}	-1.16×10^{2}	1.06×10^{4}	1.79×10^{5}	
V	2	CR	2.18×10^{5}	8.01×10^{14}	33.6	2.13×10^{5}	1.90×10^{5}	0.9900
		HM	2.21×10^{5}	1.60×10^{15}	39.3	2.16×10^{5}	1.89×10^{5}	0.9985
		average	2.19×10^{5}	1.20×10^{15}	36.4	2.14×10^{5}	1.89×10^{5}	
VI	1	CR	9.91×10^{4}	7.11×10^{6}	-1.19×10^{2}	9.44×10^{4}	1.52×10^{5}	0.9899
		HM	1.08×10^{5}	8.49×10^{7}	-9.85×10^{2}	1.04×10^{5}	1.60×10^{5}	0.9995
		average	1.03×10^{5}	4.60×10^{7}	-4.33×10^{2}	9.74×10^{4}	1.56×10^{5}	
VII	3	CR	9.38×10^{4}	9.01×10^{4}	-1.56×10^{2}	8.85×10^{4}	1.88×10^{5}	0.9883
		HM	1.05×10^{5}	3.26×10^{6}	-1.27×10^{2}	9.95×10^{4}	1.80×10^{5}	0.9998
		average	9.94×10^{4}	1.67×10^{6}	-1.41×10^{2}	9.40×10^{4}	1.84×10^{5}	
IX	2	CR	1.61×10^{5}	2.61×10^{12}	-1.28×10^{1}	1.56×10^{4}	1.64×10^{5}	0.9967
		HM	1.67×10^{5}	1.39×10^{13}	-1.39×10^{1}	1.63×10^{4}	1.62×10^{5}	0.9993
		average	1.64×10^{5}	8.25×10^{12}	-1.33×10^{2}	1.59×10^{4}	1.63×10^{5}	

cess can be described as the result of two separate functions: temperature and conversion [20], using equation:

$$d\alpha/dt = k(T)f(\alpha), \qquad (1)$$

where α is the fraction decomposed at time t, $k(T)$ is the temperature dependent function and $f(\alpha)$ is the conversion function dependent on the decomposition mechanism. It has been established that the temperature dependent function $k(T)$ is of the Arrhenius type and can be considered as the rate constant k.

$$k = A\,e^{-E^*/RT} \qquad (2)$$

where R is the gas constant in (J mol^{-1} K^{-1}). Substituting Eq. (2) into Eq. (1), we get,

$$d\alpha/dT = (A/\varphi\,e^{-E^*/RT})f(\alpha),$$

where, φ is the linear heating rate dT/dt. On integration and approximation, this equation can be obtained in the following form:

$$\ln g(\alpha) = -E^*/RT + \ln\,[AR/\varphi E^*],$$

where $g(\alpha)$ is a function of α dependent on the mechanism of the reaction. The integral on the right hand side is known as temperature integral. So, several techniques have been used for the evaluation of temperature integral. Most commonly used methods for this purpose are the differential method of Freeman and Carroll [19] integral method of Coats and Redfern [21], the approximation method of Horowitz and Metzger [24]. In the present investigation, the general thermal behavior in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in Table 5. The kinetic parameters have been evaluated using the both Coats and Redfern and Horowitz and Metzger methods and the results obtained by these methods are matching each other.

Table 6. Antibacterial and antifungal activity

Comp. no.	*E. coli*	*Staphylococcus aureus*	*Aspergillus flavus*	*Candida albicans*
II	15	10	0	20
III	15	10	0	20
IV	15	15	0	15
V	15	10	0	15
VI	20	20	0	20
VII	20	15	0	20
VIII	15	15	0	20
IX	15	20	0	20

The correlation coefficients of the Arhenius plots of the thermal decomposition steps were found to lie in the range 0.9883 to 0.9999, showing a good fit with linear function. It is clear that the thermal decomposition process of all complexes is non-spontaneous, i.e., the complexes are thermally stable.

Microbiological screening. The results of antibacterial activities in vitro of the ligands and their complexes are given in Table 6. From the results we can see that they have almost the same effect on *E. coli* and

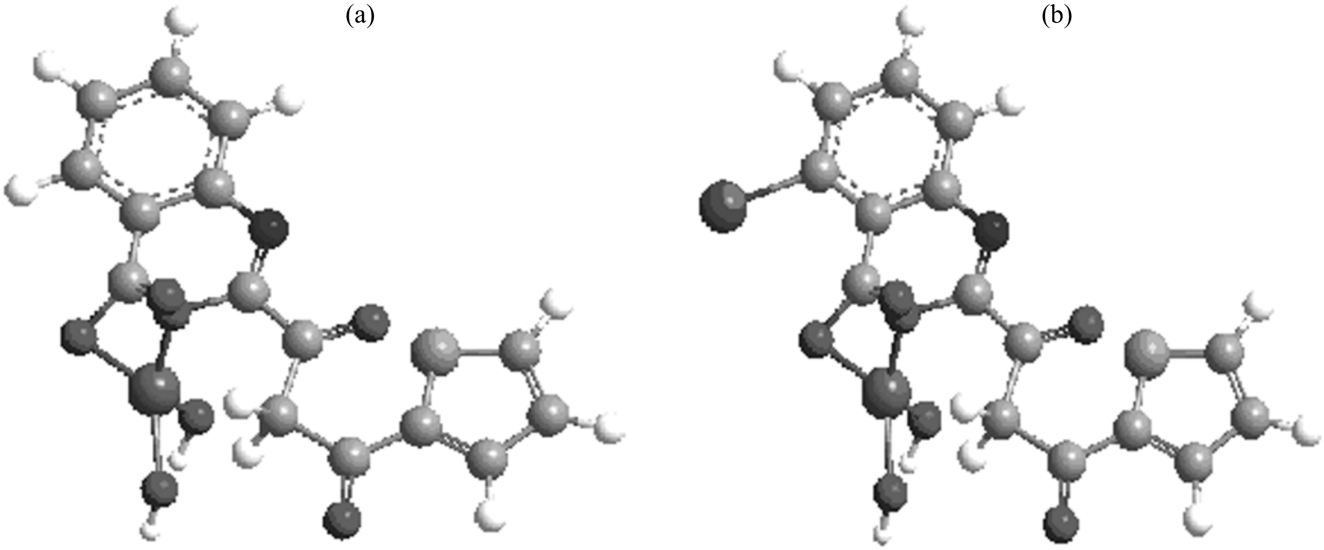


Fig. 9. 3D structures of (a) **II** and (b) **III** complexes.

Staphylococcus aureus. All new substances have also been evaluated for their antifungal activity. The minimal inhibitory concentration values listed in Table 6 show that all tested compounds have no effect on *Aspergillus flavus,* but have high effect on *Candida albicans.*

Structure of the H_2L_1 and H_2L_2 and their complexes. The fact that these compounds were isolated as powders and not as single crystals means that no complete structure determination (XRD) could be made. Accordingly, using elemental analysis, molar conductance, (infrared, ^{1}H NMR, and mass) spectra as well as thermogravimetric analysis; the suggested structures of ligands **II** and **III** and their complexes can be represented in Figs. 8–9.

REFERENCES

1. Chohan, Z.H., Farooq, M.A., Scozzafava, A., and Supuran, C.T., *J. Enzyme Inhib. Med. Chem.*, 2002, vol. 17(1), p. 1.
2. Singh, K., Barwa, M.S., and Tyagi, P., *Eur. J. Med. Chem*., 2006, vol. 41(1), p. 147.
3. Singh, K., Singh, D.P., Barwa, M.S., Tyagi, P., and Mirza, Y., *J. Enzym. Inhib. Med. Chem*., 2006, vol. 21(5), p. 557.
4. Cozzi, P.G., *Chem. Soc. Rev*., 2004, vol. 33, p. 410.
5. Jarrahpour, A.A. and Zarei, M., *Molbank*, 2004, p. M377.
6. Chandra, S. and Sangeetika, J., *J. Indian Chem. Soc*., 2004, vol. 81, p. 203.
7. More, P.G. and Bhalvankar, R.B., *J. Indian Chem. Soc*., 2004, vol. 81, p. 13.
8. Yildiz, M., Dulger, B., Koyuncu, S.Y., and Yapici, B.M., *J. Indian Chem. Soc*., 2004, vol. 81, p. 7.
9. Islam, M.S., Farooque, M.A., Bodruddoza, M.A.K., Mosaddik, M.A., and Alam, M.S., *J. Biol. Sci*., 2002, vol. 2(12), p. 797.
10. Ferrari, M.B., Capacchi, S., Pelosi, G., Reffo, G., Tarasconi, P., Albertini, R., Pinelli, S., and Lunghi, P., *Inorg. Chim. Acta*, 1999, vol. 286(2), p. 134.
11. Chohan, Z.H., Pervez, H., Khan, K.M., Rauf, A., and Supuran, C.T., *J. Enzyme Inhib. Med. Chem*., 2004, vol. 19(1), p. 51.
12. Canpolat, E. and Kaya, M., *J. Coord. Chem*., 2004, vol. 57(14), p. 1217.
13. Refat, M.S., *J. Mol. Struct*., 2013, vol. 1037, p. 170.
14. Barnum, W., *J. Inorg. Nucl. Chem*., 1961, vol. 21, p. 221.
15. Holm, R.H. and Cotton, F.A., *J. Am. Chem. Soc*., 1958, vol. 80, p. 5658.
16. Cotton, F.A. and Wilkinson, C.W., *Advanced Inorganic Chemistry*, 3rd ed, New York: Interscience Publishers, 1972.
17. Roy, R., Saha, M.C., and Roy, P.S., *Trans. Met. Chem*., 1990, vol. 51, p. 5110.
18. Corbi, P.P., Cagnin, F., Sabeh, L.P.B., Massabni, A.C., and Costa-Neto, C.M., *Spectrochim. Acta part A*, 2007, vol. 66, p. 1171.
19. Freeman E.S. and Carroll, B., *J. Phys. Chem*., 1958, vol. 62, p. 394.
20. Sestak, J., Satava, V., and Wendlandt, W.W., *Thermochim. Acta*, 1973, vol. 7, p. 333.
21. Coats, A.W. and Redfern, J.P., *Nature*, 1964, vol. 201, p. 68.
22. Ozawa, T., *Bull. Chem. Soc. Jpn*., 1965, vol. 38, p. 1881.
23. Wendlandt, W.W., *Thermal Methods of Analysis*, New York: Wiley, 1974.
24. Horowitz, H.W. and Metzger, G., *Anal. Chem*., 1963, vol. 35, p. 1464.
25. Flynn, J.H. and Wall, L.A., *Polym. Lett*., 1966, vol. 4, p. 323.
26. Kofstad, P., *Nature*, 1957, vol. 179, p. 1362.