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Bivalent transition metal complexes of coumarin-3-yl thiosemicarbazone derivatives: Spectroscopic, antibacterial activity and thermogravimetric studies

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ABSTRACT

Schiff base complexes of Cu(II), Co(II) and Ni(II) with two coumarin-3-yl thiosemicarbazone derivatives (1E)-1-(1-(2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (OCET) and (1E)-1-(1-(6-bromo-2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (BOCET) were synthesized by the reaction of Cu(II), Co(II) and Ni(II) chlorides with each mentioned ligand with molar ratio 1:2 metal-to-ligand. Both ligands and their metal complexes were characterized by different physicochemical methods, elemental analysis, molar conductivity, (UV-vis, Mass, Infrared, ¹H NMR spectra) and also thermal analysis (TG and DTG) techniques. The discussion of the outcome data of the prepared complexes indicate that the coumarin-3-yl thiosemicarbazone derivatives ligands behave as a bidentate ligand through both thione sulphur and azomethine nitrogen with 1:2 (metal:ligand) stoichiometry for all complexes. The molar conductance measurements proved that the complexes are electrolytes. The kinetic thermodynamic parameters such as: E^* , ΔH^* , ΔS^* and ΔG^* are calculated from the DTG curves, all complexes are more ordered except Ni(II) complexes. The antibacterial activity of the coumarin-3-yl thiosemicarbazone derivatives and their metal complexes was evaluated against some kinds of Gram positive and Gram negative bacteria.

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1. Introduction

Coumarins comprise a very large class of compounds found throughout the plant kingdom [1,2]. The coumarin derivatives are known to have diverse applications as anticoagulants, spasmolytics, anticancer drugs or as plant growth regulating agents [3,4]. Biological activity of coumarin nucleus and related derivatives [5,6] has a great important effects like antibacterial [7], antithrombotic and vasodilatory [8], antimutagenic [9], lipoxygenase and cyclooxygenase inhibition [10,11], scavenging of reactive oxygen species, and ntiumourigenic [12,13].

Several reviews summarize advances in various medicinal applications of metal complexes of coumarins [14,15]. As it was already reported in the literature the biological activity of some coumarin derivatives significantly enhances by binding to metal ions [16,17]. Generally, the increasing activities of the complexes are attributed to the synergistic effect that increases their lipophilicity [18]. A broad array of medicinal applications of metal complexes of coumarins has been investigated. It was found that in some cases the metal complexes obtained revealed higher biological activity than their ligands [19,20].

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Transition metal complexes of bis(thiosemicarbazone) ligands have been studied and attract attention against the antitumor activity [21,22]. In particular bis(thiosemicarbazone) complexes of copper(II) have been known for some time to be antitumor agents [23,24]. Because of their biological activity and analytical application, thiosemicarbazides and thiosemicarbazones, as well as their metal complexes have been the subject of many studies [25,26]. In this paper we are reported an efficient route for the synthesis of new Cu(II), Co(II) and Ni(II) complexes obtained from 3-(ethylidene thiosemicarbazide) coumarin and 6-bromo-3-(ethylidene thiosemicarbazide) coumarin. The thermal decomposition of their complexes is also used to infer the structure and the different thermodynamic activation parameters are calculated. The biological activity of these ligands and their metal complexes are evaluated.

2. Experimental

 $CuCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ and other chemicals were purchased from Fluka and Merck companies, and were used without further purification as received.

2.1. Synthesis of the Schiff base ligands

The coumarin thiosemicarbazone Schiff base ligands (Fig. 1) were synthesized according to the known condensation method [27]. The methanol solution (50 ml) of thiosemicarbazide was



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(1E)-1-(1-(2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide



(1E)-1-(1-(6-bromo-2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide

BOCET

Fig. 1. Structures of Schiff base OCET and BOCET ligands.

mixed with a solution of 3-acetyl coumarin or 6-bromo-(3-acetyl coumarin). The mixture was refluxed and stir magnetically for 4 h at 80 °C on a hot plate. After cooling, the solid Schiff base ligands were filtered, and the solid products were washed several times using methanol solvent. All organic impurities were removed by washing the products with small portions of diethyl ether. The ligands were recrystallized several times from ethyl alcohol and were dried in vacuo over calcium chloride. The purity of the ligands was evaluated by thin layer chromatography. Elemental analysis CHN, Mwt, color, m.p., yield and conductivity of Schiff base ligands were given in Table 1.

2.2. Synthesis of metal complexes

All of Cu(II), Co(II) and Ni(II) complexes were synthesized by adding of the appropriate metal chlorides (1.0 mmol, in 20 ml ethyl alcohol/water (50:50) volume to a hot solution of each thiosemicarbazone ligand (2.0 mmol, in 30 ml ethyl alcohol (95%)). The resulted color solutions were stirred and refluxed on a hot plate at 80 °C for 1 h. The volume of the resulted solution was reduced to half volume by evaporation. One day later, the colored solid complexes formed, were filtered, the solids washed with ethanol and diethyl ether and finally dried under vacuum. All complexes were prepared and isolated in amorphous shape.

2.3. Analyses

Elemental analyses (C, H, and N) were performed using a Perkin-Elmer CHN 2400 elemental analyzer. The content of metal ions was calculated gravimetrically as metal oxides. Molar conductance measurements of the OCET and BOCET ligands and their complexes with 1.0×10^{-3} mol/l in DMSO were carried out using Jenway 4010 conductivity meter. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method. ¹H NMR Varian 200 MHz spectrometer using DMSO as solvent, chemical shift are given in ppm relative to tetramethylsilane. Electron impact mass spectra were recorded on a Jeol, JMS, DX-303 mass spectrometer. The UV/vis, Spectra were obtained in DMSO solution $(1.0 \times 10^{-3}$ M) for the ligands OCET and BOCET and their six complexes with a Jenway 6405 Spectrophotometer using 1 cm quartz cell, in the range 200–600 nm. IR spectra (4000–400 cm⁻¹) were recorded as KBr pellets on Bruker FT-IR Spectrophotometer. Ther-

Table 1 Elemental analysis and physical	data of ligands OCET, BOCET	and their comp	lexes.								
Compounds	Empirical formula	Mwt g/mol	Color	M.p.	Yield (%)	$A_{ m m}~\Omega^{-1}~{ m cm^2}~{ m mol}^{-1}$	Content (calcula	ted) found			
							%C	H%	N%	%CI	%M
OCET	C ₁₂ H ₁₁ O ₂ N ₃ S	261.01	White	250	96	28	(55.16)55.32	(4.24)4.29	(16.08)15.89	I	I
[Cu(OCET) ₂]Cl ₂ ·H ₂ O	C ₂₄ H ₂₄ O ₅ N ₆ S ₂ Cl ₂ Cu	674.99	Pink	229	81	98	(42.70)42.24	(3.58)3.81	(12.45)12.27	(10.52)10.49	(9.41)10.44
[Co(OCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	C ₂₄ H ₃₀ O ₈ N ₆ S ₂ Cl ₂ Co	723.98	Brown	138	83	232	(38.82)39.10	(4.34)4.62	(11.32)11.06	(9.81)9.77	(7.94)6.31
$[Ni(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	C ₂₄ H ₃₀ O ₈ N ₆ S ₂ Cl ₂ Ni	723.64	Brown	245	82	172	(39.80)39.11	(4.18)4.43	(11.60)11.52	(9.81)9.79	(8.10)7.04
BOCET	$C_{12}H_{10}O_2N_3SBr$	338.97	Yellow	234	94	34	(42.37)42.22	(2.96)3.01	(12.35)12.64	I	I
[Cu(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·H ₂ O	C ₂₄ H ₂₆ O ₇ N ₆ S ₂ Br ₂ Cl ₂ Cu	868.89	Pink	150	85	187	(33.18) 33.82	(3.02)3.51	(9.67)9.99	(8.17)8.15	(7.31)8.41
[Co(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	C ₂₄ H ₂₈ O ₈ N ₆ S ₂ Br ₂ Cl ₂ Co	880.85	Brown	131	83	212	(32.67)33.12	(3.20)3.11	(9.532)9.55	(8.06)7.98	(6.68)5.90
[Ni(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	$C_{24}H_{28}O_8N_6S_2Br_2Cl_2Ni$	879.85	Brown	125	81	167	(32.67)32.84	(3.20)3.25	(9.53)9.22	(8.07)8.04	(6.68)7.30
111(POCET)2(1120)2)C12.21120	C2411280814602D12C12141	C0.610	וואסום	14.7	10	101	+0.20(10.20)	(7)()	77.C(CC.C)		+0.0(10.0)

mogravimetric analyses (TG/DTG) were carried out in the temperature range from 25 to 800 °C in a steam of nitrogen atmosphere using Shimadzu TGA 50H thermal analysis. The experimental conditions were: platinum crucible, nitrogen atmosphere with a 30 ml/min flow rate and a heating rate 10 °C/min.

2.4. Microbiological investigations

For these investigations the filter paper disc method was applied according to Gupta et al. [28]. The investigated isolates of bacteria were seeded in tubes with nutrient broth (NB). The seeded NB (1 cm³) was homogenized in the tubes with 9 cm³ of melted (45 °C) nutrient agar (NA). The homogeneous suspensions were poured into Petri dishes. The discs of filter paper (diameter 4 mm) were ranged on the cool medium. After cooling on the formed solid medium, 2×10^{-5} dm³ of the investigated compounds were applied using a micropipette. After incubation for 24 h in a thermostat at 25–27 °C, the inhibition (sterile) zone diameters (including disc) 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 Escherichia coli, Pseudomonas aeruginosa as Gram negative, Bacillus subtilis and Staphylococcus aureus as Gram positive. The concentration of each solution was 1.0×10^{-3} mol dm³. Commercial DMSO was employed to dissolve the tested samples.

3. Results and discussion

All the coumarin-3-yl thiosemicarbazone complexes show 1:2 metal:ligand stoichiometry ratio. The analytical data of the ligands and their metal complexes with the stoichiometries proposed are summarized in Table 1. The isolated solid complexes are stable in air and are insoluble in water and common organic solvents but soluble in DMF and DMSO. The molar conductance indicates that all the complexes are electrolytic in nature. The metal complexes are decomposed at different temperatures above 200 °C. Elemental analyses data were in a good agreement with those required for the suggested formula.

3.1. Molar conductivity of metal chelates

The molar conductivity values of the metal complexes in DMSO solvent (10^{-3} mol) were in the range $(98-232 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$.



Fig. 2. Infrared spectra of: A = OCET; $B = [Cu(OCET)_2]Cl_2 H_2O$; $C = [Co(OCET)_2 2H_2O]Cl_2 2H_2O$; $D = [Ni(OCET)_2 2H_2O]Cl_2 2H_2O$.



Fig. 3. Infrared spectra of: E = BOCET; F = [Cu(BOCET)₂·2H₂O]Cl₂·H₂O; G = [Co(BOCET)₂·2H₂O]Cl₂·2H₂O]Cl₂·2H₂O; H = [Ni(BOCET)₂·2H₂O]Cl₂·2H₂O.

Conductivity measurements have frequently been used in structural characterization of metal chelates (mode of coordination) within the limits of their solubility. These measurements were provided a method for testing the degree of ionization of the complexes. In case of the presence of anions outside the coordination sphere, the higher values of molar conductivity will be detected

Table 2

Infrared spectral data for OCET, BOCET ligands and their complexes (cm⁻¹).

Compounds	v(OH) hydrated H ₂ O	v(N–H) NH ₂	v(N–H) NH	<i>v</i> _s (C=0)	v _s (C=N)	$v_{as}(C=N)$	v(OH) coordinated H ₂ O	v _s (C=S)	v(M–N)	v(M-S)
OCET	-	3388	3235	1718(s)	1602(s)	1556(s)	-	762(s)	-	-
$[Cu(OCET)_2]Cl_2 \cdot H_2O$	3465(br)	3384	3234	1717(s)	1566(s)	1523(s)	860(m)	747(s)	431(w)	382(w)
$[Co(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	3471(br)	3387	3234	1716(s)	1557(s)	1539(s)	816(m)	750(s)	432(w)	380(w)
[Ni(OCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	3346(br)	3386	3233	1716(s)	1559(s)	1541(s)	862(m)	751(s)	431(w)	380(w)
BOCET	-	3408	2228	1723(s)	1590(s)	1546(s)	-	829(s)	-	-
[Cu(BOCET) ₂]Cl ₂ ·H ₂ O	3466(br)	3407	2227	1722(m)	1557(s)	1521(s)	770(m)	819(s)	458(w)	390(w)
[Co(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	3465(br)	3409	2227	1722(m)	1557(s)	1507(s)	770(m)	817(s)	457(w)	392(w)
$[Ni(BOCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	3466(br)	3408	2228	1720(m)	1540(s)	1507(s)	773(m)	817(s)	455(w)	391(w)



Fig. 4. HNMR spectra of OCET ligand.



Fig. 6. Mass spectra of BOCET ligand.

and vice versa [29]. It is clear from the conductivity data that the complexes present seem to be electrolytes, also the molar conductance values indicates that the anions were existed outside the coordination sphere.

3.2. Magnetic moments

Octahedral, d²sp³, Co(II) complexes are expected to have effective magnetic moment in the range 1.70–1.90 B.M. The cobalt complexes resulted have magnetic moment at 1.80 B.M.; thus the Co(II) complex is octahedral fashion. Ni(II) complexes gave a moment of 3.10 B.M. and hence assigned as octahedral, because of the square planar complexes of Ni(II) are a diamagnetic while tetrahedral complexes have moments in the range 3.20–4.10 B.M. [30]. For the Cu(II) in copper(II)/OCET complex the situation is detected at magnetic moment 1.82 B.M., thus the Cu(II) complex is square planar. But in case of Cu(II)/BOCET the magnetic moment is equal to 1.97 B.M. which assigned to octahedral geometry.

3.3. Infrared spectra

The most important bands in the infrared spectra (Figs. 2 and 3) of the both coumarin thiosemicarbazone ligands and their metal

NH₂ H_3 HN 0 m/z 261 -NHCSNH₂ m/z 186 -CO H₃ $\tilde{}$ m/z 158 -CO CH₃ Ň -CHCN m/z 132 m/z 91 (100%) -CH=CH

Scheme 1. Main fragments of OCET ligand.

m/z 65

complexes are presented in Table 2 along within their tentative assignment. The position of these bands are helpful to detected the bonding sites of both ligand molecules interacted with Cu(II), Co(II) and Ni(II). In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH–C=S functional group. The v(S-H) band at 2556 cm⁻¹ is absent from the IR spectra of the Schiff base ligands. At the same time the v(N-H) [31] band at 3235 cm⁻¹ is present, indicating that, in the solid state the ligands remain as the thione tautomer.

Infrared spectra of the ligands show strong bands in the region 1590–1602 cm⁻¹ and 1546–1565 cm⁻¹ which may be assigned to the symmetric and asymmetric v(C=N) [32] vibrations for OCET and BOCET ligands, respectively. These frequencies are shifted towards lower wavenumber by *ca*. 33–50 cm⁻¹ in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond [33,34] was detected by appearing frequencies in the region 431–458 cm⁻¹ from the IR data. Furthermore in the spectra of both ligands, the strong band observed at 762–829 cm⁻¹ was shifted to lower wavenumber by *ca*. 10–15 cm⁻¹ in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 380–395 cm⁻¹ which can be assigned to v(M-S) [35].

The spectra of the complexes exhibited a broad band's at \sim 3460 cm⁻¹ that are attributed to OH of crystal water molecules, while the bands observed at 770 and 860 cm⁻¹ for the complexes of OCET and BOCET ligands, respectively, are assigned to coordi-



Scheme 2. Main fragments of BOCET ligand.



Fig. 7. UV-vis spectra of OCET and BOCET and their complexes.

nated water molecule [36]. From the IR data, it can be inferred that the OCET and BOCET ligands involved in the complexation as a bidentate ligands which coordinated with metal ions through their thione sulphur and azomethine N atom.

3.4. HNMR spectra

¹H NMR spectra of both coumarin-3-yl thiosemicarbazone Schiff base ligands were performed in DMSO and the chemical shifts in ppm were recorded as follows:

Ligand((1E)-1-(1-(2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (OCET)): δ = 1.87 ppm (s, 3H, CH₃-C=N), δ = 8.58 ppm (s, 1H, NH-C=S), δ = 3.65 ppm (s, 2H, NH₂-C=S), δ = 7.25 ppm (m, 2H, Ar-H_{6,7}), δ = 7.34 ppm (m, 3H, Ar-H_{4,5,8}) (Fig. 4) and ligand((1E)-1-(1-(6-bromo-2-oxo-2H-chromen-3yl)ethylidene)thiosemicarbazide (BOCET)): δ = 1.96 ppm (s, 3H, CH₃-C=N), δ = 8.66 ppm (s, 1H, NH-C=S), δ = 3.84 ppm (s, 2H, NH₂-C=S), δ = 8.22 ppm (m, 1H, Ar-H₅), δ = 8.31 ppm (m, 1H, Ar-H₇), δ = 8.11 ppm (t, 1H, Ar-H₈), δ = 8.04 ppm (s, 1H, Ar-H₄).

By comparison between the free Schiff base ligands and their metal complexes, found that, the ¹H NMR signals of metal complexes located in the same places of their free ligands with decreasing in the intensity. This result proved that the absence of the participation of NH group in the complexation and also existed the C=S in thione feature.

3.5. Mass spectra

Mass spectra of the (1E)-1-(1-(2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (OCET) (Fig. 5) and (1E)-1-(1-(6-bromo-2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (BOCET) ligands (Fig. 6) confirm the proposed formula by detected the following peaks:

Ligand (OCET): appearance of the final peak at 261 amu $(C_{12}H_{11}O_2N_3S)$, calculated atomic mass 261 amu) and other peaks at 43, 75, 91, 132, 158 and 186 amu due to different fragment steps. The intensity of these peaks gives an idea about the stability of these fragments. Ligand(BOCET) has a molecular ion peak at 340 amu $(C_{12}H_{10}O_2N_3SBr)$, calculated atomic mass 340 amu) and other peaks at 65, 77, 91, 132, 186 and 264 amu assigned to the various fragments as discussed in Schemes 1 and 2.

3.6. Electronic spectra

The electronic spectra of OCET and BOCET ligands and their metal complexes in DMSO are shown in Fig. 7 and the spectral data

Table 3

Electronic spectra of OCET, BOCET ligands and their metal complexes.

	-	=	
Compounds	λ_{\max} (nm)	$\epsilon ({ m mol}^{-1}{ m cm}^{-1})$	Assignment
OCET	260	1330	$\pi - \pi^*$
	335	1100	$n - \pi^*$
$[Cu(OCET)_2]Cl_2 \cdot H_2O$	265	2250	$\pi - \pi^*$
	330	1810	$n - \pi^*$
$[Co(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	265	1130	$\pi - \pi^*$
	330	600	$n - \pi^*$
$[Ni(OCET)_2(H_2O)_2]Cl_2\cdot 2H_2O$	250	2720	$\pi - \pi^*$
	335	2260	$n - \pi^*$
BOCET	260	2650	$\pi - \pi^*$
	340	2220	$n - \pi^*$
$[Cu(BOCET)_2(H_2O)_2]Cl_2 \cdot H_2O$	255	2710	$\pi - \pi^*$
$[Co(BOCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	245	2230	$\pi - \pi^*$
	350	810	$n - \pi^*$
$[Ni(BOCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	245	1150	$\pi - \pi^*$
	375	320	$n - \pi^*$

are listed in Table 3. The bands in the range 200–450 nm can be assigned to π – π^* and/or n– π^* interaligand transition. There are two detected absorption bands at around 260 and 340 nm assigned to π – π^* and n– π^* interaligand transition, respectively, in the electronic spectra of both ligand. These transition also found in the spectra of the resulted complexes with small shifted and hyper-chromically effect.

3.7. Thermogravimetric analysis (TGA)

The TGA curves of the Schiff base complexes (Fig. 8) were carried out within a temperature range from room temperature up to 800 °C. The thermal decomposition data of both ligands and their metal complexes are listed in Table 4. The data from thermogravimetric analysis clearly indicated that the decomposition of the complexes proceeds in several steps. Hydration water molecules were lost in between 30 °C and 150 °C. The coordinated water molecules and chlorides ions were liberated in between 250 °C and 350 °C, finally the metal oxides were formed above 600 °C for Cu(II), Co(II) and Ni(II) complexes. The decomposition was complete at ≥ 600 °C for all complexes. The degradation pathway for all complexes may be represented as follows.

$$\begin{split} & [\mathsf{M}(\mathsf{L})_{2}(\mathsf{H}_{2}\mathsf{O})_{2}] \cdot \mathsf{Cl}_{2} \cdot n\mathsf{H}_{2}\mathsf{O} \xrightarrow{30-150 \,\,^{\circ}\mathsf{C}} \ [\mathsf{M}(\mathsf{L})_{2}(\mathsf{H}_{2}\mathsf{O})_{2}] \cdot \mathsf{CL}_{2} + n\mathsf{H}_{2}\mathsf{O} \\ & [\mathsf{M}(\mathsf{L})_{2}(\mathsf{H}_{2}\mathsf{O})_{2}] \cdot \mathsf{CL}_{2} \xrightarrow{150-600 \,\,^{\circ}} 2\mathsf{H}_{2}\mathsf{O} + \mathsf{CL}_{2} + \mathsf{MO} \text{ or } \mathsf{M}_{2}\mathsf{O}_{3} \\ & \mathsf{where} \, \mathsf{M}_{2} - \mathsf{Cu} \,\,\mathsf{Ce} \,\,\mathsf{er} \,\,\mathsf{Ni}_{2} \,\,\mathsf{n}_{2} = 1 \,\,\mathsf{er} \,\,\mathsf{C}_{2} \end{split}$$

where M = Cu, Co or Ni; n = 1 or 2).

3.7.1. OCET and BOCET ligands

The (1E)-1-(1-(2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (OCET) melts at 250 °C with simultaneous decomposition. The two main degradation peaks were observed at 304 and 560 °C in the TG profile. The decomposition occurs with a mass loss of 39.11% and its calculated value is 40.0% for the first step and 61.20% and its calculated value 60.38% for second step.

The (1E)-1-(1-(6-bromo-2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (BOCET) melts at 234 °C with simultaneous decomposition. The two main degradation peaks were observed at 300 and 560 °C in the TG profile. The decomposition occurs with a mass loss of 31.24% and its calculated value is 30.67% for the first step and 68.80% and its calculated value 69.32% for second step.

3.7.2. $[Cu(OCET)_2]Cl_2 H_2O$ and $[Cu(BOCET)_2(H_2O)_2]Cl_2 H_2O$

Thermal analysis curves of Cu(II) complex show that decomposition take places in three stages in temperature range 35–800 °C (DTG_{max} 100, 280 and 604 °C) and (75, 240 and 510) for OCET and BOCET ligands, respectively. The TG curve of the Cu(II) complex of OCET ligand show a weight loss (found: 2.53%, calcd: 2.66%) between 35 and 175 °C corresponding to the loss of one crystal water molecule. The second stage show a weight loss (found: 29.33%, calcd: 28.27%) between 175 and 510 °C corresponding to the loss two chloride ion and organic moiety (C₄H₄N₄S₂). The final product formed at 800 °C, consist of copper oxide and two carbon atoms, interpretive for no sufficiently of oxygen atoms encouraged the liberated carbon as monoxide or dioxide.

The TG curve of the Cu(II) complex of BOCET ligand show a weight loss (found: 2.22%, calcd: 2.07%) between 25 and 120 °C corresponding to the loss of one crystal water molecule. The second stage show a weight loss (found: 32.42%, calcd: 32.09%) between 120 and 350 °C corresponding to the loss two coordinate water molecules, two chloride ion and organic moiety (C₄H₄N₄S₂). The third stage show a weight loss (found: 55.84%, calcd: 56.50%) between 350 and 550 °C corresponding to the loss two bromide ion and organic moiety (C₂₀H₁₆O₃N₂). The final product formed at 800 °C, consist of copper oxide (found: 9.52%, calcd: 9.09%).



Fig. 8. TGA diagram of OCET, BOCET ligand and their metal complexes.

3.7.3. [Co(OCET)₂(H₂O)₂]Cl₂·2H₂O and [Co(BOCET)₂(H₂O)₂]Cl₂·2H₂O The diagrams of Co(OCET)₂(H₂O)₂]Cl₂·2H₂O and [Co(BOCET)₂ (H₂O)₂]Cl₂·2H₂O reveals mass loss in temperature range 30–800 °C;

three or four stages are shown in the pyrolysis curve at $(DTG_{max} 100, 280 \text{ and } 604 \,^{\circ}\text{C})$ and $(DTG_{max} 75, 250, 430 \text{ and } 645 \,^{\circ}\text{C})$ for [Co $(OCET)_2(H_2O)_2$]Cl₂·2H₂O and [Co(BOCET)_2(H_2O)_2]Cl_2·2H_2O, respectively.

Table 4 Thermal decomposition of the OCET, BOCET ligands and their metal complexes.

Compounds	Steps	Temperature range	DTG peaks	Weight loss (calc.) found %	Assignment
OCET	1st 2nd	189–325 325–600	304 560	(40.00)39.11 (60.38)61.20	$C_2H_6N_3S$ $C_{10}H_5O_2$
[Cu(OCET) ₂]Cl ₂ ·H ₂ O	1st 2nd 3rd	35–175 175–510 510–657	75 230 502	(2.66)2.53 (28.27)29.33 (53.03)52.63 (15.24)15.51	H_2O 2Cl + $H_4N_4S_2$ $C_{22}H_{18}N_2O_3$ CuO + 2C
$[Co(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	1st 2nd 3rd	35–175 175–510 510–657	100 280 604	(4.96)5.19 (38.51)38.0 (45.02)45.98 (11.20)10.83	$\begin{array}{l} 2H_2O\\ 2Cl+2H_2O+C_4H_4N_4S_2\\ C_{20}H_{18}N_2O_{2.5}\\ 1/2Co_2O_3 \end{array}$
[Ni(OCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	1st 2nd 3rd 4th	30-120 120-260 260-460 460-560	75 234 417 507	(4.97)4.94 (14.78)15.17 (31.23)30.68 (38.69)38.17 (10.36)11.04	2H ₂ O 2H ₂ O + 2Cl C ₆ H ₆ N ₆ S ₂ C ₁₈ H ₁₆ O ₃ NiO
BOCET	1st 2nd	220–350 350–600	300 560	(30.67)31.24 (69.32)68.80	$C_2H_6N_3S$ $C_{10}H_4O_2Br$
[Cu(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·H ₂ O	1st 2nd 3rd	25–120 120–350 350–550	75 240 510	(2.07)2.22 (32.09)32.42 (56.50)55.84 (9.09)9.52	$\begin{array}{l} H_2 O \\ 2 C l + 2 H_2 O + C_4 H_4 N_4 S_2 \\ 2 B r + C_{20} H_{16} O_3 N_2 \\ C u O \end{array}$
[Co(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	1st 2nd 3rd 4th	30–120 120–350 350–500 500–710	75 250 430 645	(4.08)4.32 (12.13)12.64 (17.02)17.86 (57.20)56.79 (9.42)8.39	$\begin{array}{l} 2H_2O\\ 2CI + 2H_2O\\ C_2H_6N_4S_2\\ 2Br + C_{22}H_{14}N_2O_{2.5}\\ 1/2Co_2O_3 \end{array}$
[Ni(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	1st 2nd 3rd	30–160 160–500 500–680	75 195 658	(4.09)4.60 (35.82)35.22 (51.64)50.99 (8.53)9.19	2H ₂ O 2Cl + 2H ₂ O + C ₄ H ₁₂ N ₆ S ₂ C ₂₀ H ₈ O ₃ Br ₂ NiO

For $[Co(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$, the first stage corresponding to the dehydration of two water molecules (found: 5.19%, calcd: 4.96%). The second stage was discussed concerning to the loss of two uncoordinated chloride ions, two coordinated water molecules and organic moiety (C₄H₄N₄S₂) weight loss (found: 15.17%, calcd: 14.78%).

In case of $[Co(BOCET)_2(H_2O)_2]Cl_2\cdot 2H_2O$, the first stage corresponding to the dehydration of two water molecules (found: 4.32%, calcd: 4.08%). The second stage show weight loss (found: 12.64%, calcd: 12.13%) corresponding to the loss of two uncoordinated chloride ions and two coordinated water molecules. The final decomposition product is $1/2Co_2O_3$, the overall weight loss (found: 11.04%, calcd: 10.36%) and (found: 8.39%, calcd: 9.42%) for $[Co(OCET)_2(H_2O)_2]Cl_2\cdot 2H_2O$ and $[Co(BOCET)_2(H_2O)_2]Cl_2\cdot 2H_2O$, respectively.

3.7.4. [Ni(OCET)₂(H₂O)₂]Cl₂·2H₂O and [Ni(BOCET)₂(H₂O)₂]Cl₂·2H₂O

Thermal decomposition of $[Ni(OCET)_2 \cdot 2H_2O]Cl_2 \cdot 2H_2O$ and $[Ni(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ and $[Ni(BOCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ proceeds in three or four ranged main stages in temperature range 30–800 °C (DTG_{max} 75, 234, 417 and 507 °C) and (DTG_{max} 75, 195 and 658 °C) for $[Ni(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ and $[Ni(BO-CET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$, respectively.

For $[Ni(OCET)_2(H_2O)_2]Cl_2\cdot 2H_2O$, the first stage show a weight loss (found: 4.94%, calcd: 4.97%), corresponding to the loss of two crystal water molecules. The second stage show a weight loss (found: 15.17%, calcd: 14.78%), corresponding to the loss of two uncoordinated chloride ions and two coordinated water molecules.

For $[Ni(BOCET)_2(H_2O)_2]Cl_2\cdot 2H_2O$, the first stage show a weight loss (found: 4.60%, calcd: 4.09%), corresponding to the loss of two crystal water molecules. The second stage show a weight loss (found: 35.22%, calcd: 35.82%), corresponding to

the loss of two uncoordinated chloride ions, two coordinated water molecules and organic moiety $(C_4H_{12}N_6S_2)$. The final products, formed at 800 °C, consist of nickel oxide a weight loss (found: 11.04%, calcd: 10.36%) and (found: 9.19%, calcd: 8.53%) for $[Ni(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ and $[Ni(BOCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$, respectively.

3.8. Kinetic studies

Several equations [37–44] have been proposed as means of analyzing a TG curve and obtaining values for kinetic parameters. Many authors [37–43] have discussed the advantages of this method over the conventional isothermal method. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion [44], using

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

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 mechanism of decomposition. 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

$$k = Ae^{-E^*/RT}$$
(2)

where *R* is the gas constant in (J mol⁻¹ K⁻¹). Substituting Eq. (2) into Eq. (1), we get $\frac{d\alpha}{dt} = \left(\frac{A}{\phi e^{-F^*/R^*}}\right) f(\alpha)$ where ϕ is the linear heating rate dT/dt. On integration and approximation, this equation can be obtained in the following form

$$\ln g(\alpha) = -\frac{E^*}{RT} + \ln \left[\frac{AR}{\varphi E^*}\right]$$



Fig. 9. Horowtiz-Metzger (HM) and Coats-Redfern (CR) of OCET, BOCET and their metal complexes.



Fig. 9 (continued)

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 and has no closed for solution. 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 [37] integral method of Coat and Redfern [40], the approximation method of Horowitz and Metzger [42]. In the present investigation, the general thermal behaviors of the prepared complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in Fig. 9 and Table 5. The kinetic parameters have been evaluated using the following methods and the results obtained by these methods are well agreement with each other. The following two methods are discussed in brief.

3.8.1. Coats-Redfern equation

The Coats–Redfern equation, which is a typical integral method, can be represented as:

$$\int_0^{\alpha} \frac{d\alpha}{\left(1-\alpha\right)^n} = \frac{A}{\alpha} \int_{T_1}^{T_2} \exp\left(\frac{-E^*}{RT}\right) dt$$

For convenience of integration the lower limit T_1 is usually taken as zero. This equation on integration gives.

$\ln[-\ln(1-\alpha)/T^2] = -E^*/RT + \ln[AR/\varphi E^*]$

A plot of left-hand side (LHS) against 1/T was drawn. E^* is the energy of activation in J mol⁻¹ and calculated from the slop and A in (S⁻¹) from the intercept value. The entropy of activation in (J K⁻¹ mol⁻¹) was calculated by using the equation:

$$\Delta S^* = R \ln \left(\frac{Ah}{K_{\rm B} T_{\rm S}} \right) \tag{3}$$

where $k_{\rm B}$ is the Boltzmann constant, *h* is the Plank's constant and $T_{\rm S}$ is the DTG peak temperature [45].

3.8.2. Horowitz-Metzger equation

The Horowitz–Metzger equation is an illustrative of the approximation methods. These authors derived the relation:

$$\log\left[\frac{\left\{1 - (1 - \alpha)^{1-n}\right\}}{(1 - n)}\right] = \frac{E^*\theta}{2.303RT_{\rm S}^2} \text{ for } n \neq 1$$
(4)

Table 5

Thermodynamic data of the thermal decomposition of OCET, BOCET ligands and their complexes.

Complexes	Stage	Method	Parameter					
			E (J mol ⁻¹)	A (s ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔH (J mol ⁻¹)	$\Delta G (J \text{ mol}^{-1})$	
OCET	2nd	CR HM	$\begin{array}{c} 2.41\times 10^5 \\ 2.40\times 10^5 \end{array}$	$\begin{array}{c} 1.55 \times 10^{13} \\ 1.24 \times 10^{13} \end{array}$	-96.7 -28.2	$\begin{array}{c} 2.34\times10^5\\ 2.34\times10^5\end{array}$	$\begin{array}{c} 2.35\times10^5\\ 2.36\times10^5\end{array}$	0.99354 0.99651
[Cu(OCET) ₂]Cl ₂ ·H ₂ O	2nd	CR HM	$\begin{array}{c} 9.98\times10^4 \\ 1.13\times10^2 \end{array}$	$\begin{array}{c} 1.08\times10^{4}\\ 2.24\times10^{5}\end{array}$	-176 -150	$\begin{array}{c} 9.33\times10^4 \\ 1.06\times10^5 \end{array}$	$\begin{array}{c} 2.30\times10^5\\ 2.23\times10^5\end{array}$	0.99647 0.99994
$[Co(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	2nd	CR HM	$\begin{array}{c} 1.99\times10^5\\ 2.13\times10^5\end{array}$	$\begin{array}{l} 4.32 \times 10^{9} \\ 4.30 \times 10^{10} \end{array}$	-69.4 -50.3	$\begin{array}{c} 1.92\times10^5\\ 2.06\times10^5\end{array}$	$\begin{array}{c} 2.53\times10^5\\ 2.50\times10^5\end{array}$	0.99809 0.99937
$[Ni(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	2nd	CR HM	$\begin{array}{c} 3.04\times10^5\\ 3.07\times10^5\end{array}$	$\begin{array}{c} 1.01 \times 10^{18} \\ 5.13 \times 10^{18} \end{array}$	91.8 105	$\begin{array}{c} 2.98\times10^5\\ 3.0\times10^5 \end{array}$	$\begin{array}{c} 2.26\times10^5\\ 2.18\times10^5\end{array}$	0.99647 0.99783
BOCET	2nd	CR HM	$\begin{array}{c} 3.35\times10^5\\ 3.24\times10^5\end{array}$	$\begin{array}{c} 2.30 \times 10^{19} \\ 2.72 \times 10^{18} \end{array}$	117 99.4	$\begin{array}{l} 3.28\times10^5\\ 3.17\times10^5\end{array}$	$\begin{array}{c} 2.30\times10^5\\ 2.34\times10^5\end{array}$	0.99562 0.99759
$[Cu(BOCET)_2(H_2O)_2]Cl_2 \cdot H_2O$	2nd	CR HM	$\begin{array}{c} 1.19\times10^5\\ 1.40\times10^5\end{array}$	$\begin{array}{l} 4.30\times10^5\\ 1.52\times10^7\end{array}$	-145 -115	$\begin{array}{c} 1.12\times10^5\\ 1.34\times10^5\end{array}$	$\begin{array}{c} 2.26\times10^5\\ 2.24\times10^5\end{array}$	0.99487 0.99951
[Co(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	2nd	CR HM	$\begin{array}{c} 1.88\times10^5\\ 2.03\times10^5\end{array}$	$\begin{array}{c} 3.22\times10^8\\ 2.64\times10^9\end{array}$	-91.4 -73.9	$\begin{array}{c} 1.80\times10^5\\ 1.96\times10^5\end{array}$	$\begin{array}{c} 2.64\times10^5\\ 2.63\times10^5\end{array}$	0.99505 0.99822
[Ni(BOCET) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	2nd	CR HM	$\begin{array}{c} 4.05\times10^5\\ 3.92\times10^5\end{array}$	$\begin{array}{c} 1.13 \times 10^{21} \\ 1.41 \times 10^{20} \end{array}$	149 131	$\begin{array}{l} 3.97\times10^5\\ 3.85\times10^5\end{array}$	$\begin{array}{c} 2.58\times10^5\\ 2.62\times10^5\end{array}$	0.99656 0.99808

when n = 1, the LHS of Eq. (4) would be $\log[-\log(1 - \alpha)]$. For a first-order kinetic process the Horowitz–Metzger equation may be written in the form:

$$\log\left[\log\left(\frac{w_{\alpha}}{w_{\gamma}}\right)\right] = \frac{E^*\theta}{2.303RT_{\rm S}^2} - \log 2.303$$

where $\theta = T - T_s$, $w_{\gamma} = w_{\alpha} - w$, $w_{\alpha} = mass$ loss at the completion of the reaction; w = mass loss up to time *t*. The plot of $\log[\log(w\alpha/w\gamma)]$ versus θ was drawn and found to be linear from the slope of which E^* was calculated. The pre-exponential factor, *A*, was calculated from the equation:

$$\frac{E^*}{RT_{\rm S}^2} = \frac{A}{\left[\varphi \exp(-E^*/RT_{\rm S})\right]}$$

The entropy of activation, ΔS^* , was calculated from Eq. (3). The enthalpy activation, ΔH^* , and Gibbs free energy, ΔG^* , were calculated from; $\Delta H^* = E^* - RT$ and $\Delta G^* = \Delta H^* - T\Delta S^*$, respectively.

The calculated values of E^* , A, ΔS^* , ΔH^* and ΔG^* for the decomposition steps are given in Table 5. According to the kinetic data obtained from DTG curves, all the complexes have –ve entropy except Ni(II) complexes of OCET and BOCET ligands. Which indicates that activated complexes have more order systems than reactants except Ni(II) complexes. Based on the activation energy values, Co(II) and Ni(II) complexes have nearly the same thermal stability due to they are isostructural.

Table 6

Antibacterial activity data of OCET, BOCET ligands and their metal complexes, inhibition zone (mm).

Compound	Bacillus subtili G+	Staphylococcus aureus G+	Escherichia coli G–	Pseudomonas aeruginosa G–
OCET	13	17	16	14
$[Cu(OCET)_2]Cl_2 \cdot H_2O$	13	12	13	13
$[Co(OCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	18	18	17	18
$[Ni(OCET)_2(H_2O)_2]Cl_2\cdot 2H_2O$	17	16	15	17
BOCET	17	17	17	18
$[Cu(BOCET)_2(H_2O)_2]Cl_2 \cdot H_2O$	14	15	17	15
$[Co(BOCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	16	18	18	17
$[Ni(BOCET)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	18	15	15	17

Fig. 10. The inhibition zone of OCET, BOCET ligands and their Cu(II), Co(II) and Ni(II) complexes on some kinds of bacterial.

3.9. Microbiological investigation

The results of antibacterial actives in vitro of the ligand and all their complexes are shown in Table 6 and Fig. 10. From the results we can see that all the test compounds have high activity antibac-

Fig. 11. Suggested structure of the Schiff base complexes.

terial on Gram positive (*Bacillus subtili, S. aureus*) also toward Gram negative (*E. coli, P. aeruginosa*), but the activity on Gram negative more than Gram positive.

3.10. Structure of the complexes

Finally, it is concluded that from elemental analysis, IR and ${}^{1}H$ NMR spectra, the Schiff base ligands behave as a bidentate ligand coordinated to the metal ions Cu(II), Co(II) and Ni(II) through the thione CS group and azomethine group (Fig. 11).

4. Conclusions

The structures of the complexes of Schiff bases OCET and BOCET, with Cu(II), Co(II) and Ni(II) ions were interpretive by elemental analyses, IR, NMR, molar conductance, magnetic, UV–vis, mass, and thermal analysis data. Therefore, from the IR spectra, it is concluded that OCET and BOCET behaves as a neutral bidentate ligand, coordinated to the metal ions via azomethine N and thione S. From the molar conductance data, it was found that all the M(II)

chelates are considered as 1:2 electrolytes. The ¹H NMR spectra of the free ligands show that the SH signal is absence in the spectra of OCET and BOCET ligands this indicating that the SH proton not exist and both ligands located as thione feature. On the basis of the magnetic measurements octahedral geometry are suggested for all investigated complexes except for Cu(II)/OCET complex is a square planner. The synthesized ligands in comparison to their metal complexes, were also screened for their antibacterial activity against bacterial species, *E. coli*, *P. aeruginosa* as Gram negative, *B. subtilis* and *S. aureus* as Gram positive. The activity data show the metal complexes to be more potent antibacterials than the parent Schiff base ligands against one or more bacterial species.

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