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Biheterocyclic ligands: synthesis, characterization and coordinating properties of bis(4-amino-5-mercapto-1,2,4-triazol-3-yl) alkanes with transition metal ions and their thermokinetic and biological studies

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Abstract: The Co(II), Ni(II) and Cu(II) metal ions complexes of *Bis(4-amino-5-mercapto-1,2,4-triazol-3-yl) alkanes* (BATs) have been prepared and characterized by elemental analysis, conductivity measurements infrared, magnetic susceptibility, the electronic spectral data and thermal studies. Based on spectral and magnetic results, the ligands are tetradentate coordinating through the N and S-atoms of BATs; six-coordinated octahedral or distorted octahedral and some times four-coordinated square planar were proposed for these complexes. Activation energies computed for the thermal decomposition steps were compared. The ligands and their metal complexes were tested in *vitro* for their biological effects. Their activities against two gram-positive, two gram-negative bacteria and two fungal species were found to vary from moderate to very strong.

Keywords: Biheterocyclic Ligands; Co(II), Ni(II) and Cu(II) complexes; Synthesis; Characterization; Thermal Degradation; Kinetic Parameters; Biological Activities.

Introduction

In recent years, considerable attention has been paid to the synthesis of biheterocyclic compounds that play a significant role in many pharmacological, biological activities, therapeutic effect and plant growth [1-7]. Antimicrobial activities of some new biheterocyclic compounds were reported recently [5]. Antibacterial activities of biheterocyclic compounds are much better than that of heterocyclic [8]. Biheterocyclic compounds act as a powerful chelating agent, forming stable coordination polymers, complexes with various transition metals, trace elements, lanthanide(III), uranium(VI) and thorium(VI) ions [9-12] Based on spectral and thermal studies, a coordination number of seven was proposed for niobium(V) complexes with biheterocyclic ligand [13]. Six-coordination octahedral structures for some transition metal ions complexes of biheterocyclic ligands were determined by magnetic susceptibility measurements, and infrared and electronic spectral data [14].

In 1999, the synthesis of the biheterocyclic compounds of interest, *Bis(4-amino-5-mercapto-1,2,4-triazol-3-yl) alkanes,* (BATs) were first reported [7] by P. F. Xu *et al* . The characteristic structure of the BATs (i.e. BAT1, BAT2, BAT3 and BAT4) is apparent in the existence of the sulfur of thione and nitrogen of amino groups on both sides of a molecule. This makes the compounds (BATs) electron-rich ligands. However, literature survey has revealed that no attempt has been made to study the complexes of some transition metal ions with the above mentioned ligand compounds. It is a thought of interest to study the synthesis and characterization of the Co(II), Ni(II) and Cu(II) complexes of BATs ligands. The processes of thermal degradation of these metal complexes have been investigated by thermoanalytical (TG, DTG) and Coats-Redfern integral method [15] has been used to determine the associated kinetic parameters for the successive steps in the decomposition sequence.

Some literatures [16-18] indicated that in some transition metal complexes with heterocyclic or biheterocyclic are biologically more active than the free ligands. Therefore, the biological activities of the ligands BATs and their metal complexes of the Co(II), Ni(II) and Cu(II) are tested against four strains of bacteria (i.e. two gram-positive and two gram-negative bacteria) and against two fungal species. The effect of the methylene group number between two heterocyclic rings on the biological activity [19] is considered.

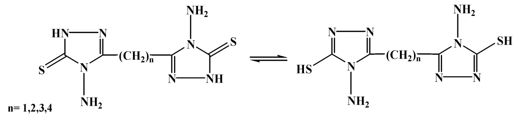
Experimental

Materials

All chemicals, solvents, indicators, metal(II) chlorides, and starting materials required and used as appropriate, were commercially available from BDH and Aldrich chemical Co.

Synthesis of the ligands

The ligands *1,1 bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)methane* (BAT1), *1,2 bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)ethane* (BAT2), *1,3 bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)propane* (BAT3) and *1,4 bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)butane* (BAT4) were prepared and purified according to the procedures reported in the literature [7]. All the prepared ligands collected after recrystallization show single spots on their thin layer chromatography with satisfactory R_f values. These ligands are stable in atmospheric conditions, insoluble in water, completely soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO) and partially soluble in ethanol, acetone and carbon tetrachloride. The elemental data and physical properties of these ligands are given in Table (1). The chemical structures of the ligands of interest under investigation are:



When

n = 1: 1,1 bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)methane (BAT1)

n = 2: 1,2 bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)ethane (BAT2)

n = 3: 1,3 bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)propane (BAT3)

n = 4: 1,4 bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)butane (BAT4)

Preparation of the complexes

For metal ion of Co(II), Ni(II) and Cu(II), complexes with the various ligands of interest (BAT1, BAT2, BAT3 and BAT4) were synthesized and collected pure after recrystallization.

In general, 0.01 mol of each ligand (BAT1=2.44 g, BAT2=2.58 g, BAT3=2.72 g and BAT4=2.86 g) was dissolved warm in 100 ml ethanol by warming up the solution. As 1: 2 mole ratio was adopted, a 0.02 mol metal chloride ($CoCl_2.6H_2O$=4.758 g, $NiCl_2.6H_2O$=4.754 g and $CuCl_2.2H_2O$= 3.4108 g) in 50 ml ethanol was added dropwise to the 0.01 mol ligand solution. The solution mixture was refluxed (3-4 hours) until precipitation occurred. The precipitates obtained were filtered off and recrystallized from ethanol and their yield percent are given in Table 1.

Chemical and physical measurements

Stuart scientific electrothermal melting point apparatus was used in measuring the melting point of the ligands and their complexes. Metal content was estimated using Perkin-Elmer 2380 atomic absorption spectrophotometer, and chloride was determined gravimetrically using standard method [20]. Carbon, hydrogen, nitro-

Table 1. Analytical and Physical data of the BATs ligands and their Co(II), Ni(II) and Cu (II) complexes.

Compound	Color	M.P °C	Yield %	Λ_m mS cm^{2}mol^{-1}	R_f	Elemental Analysis, Found (calculated)%					
						C	H	N	S	M	Cl
BAT1 $C_5H_8N_8S_2$	Yellowish white	290	69	0.23	0.11	24.9 (24.6)	3.5 (3.3)	45.8 (45.9)	26.7 (26.2)	-	-
BAT2 $C_6H_{10}N_8S_2$	White	248	77	0.20	0.30	28.1 (27.9)	3.4 (3.9)	43.7 (43.4)	25.0 (24.8)	-	-
BAT3 $C_7H_{12}N_8S_2$	White	227	95	0.15	0.38	31.2 (30.9)	4.1 (4.4)	41.3 (41.2)	23.8 (23.5)	-	-
BAT4 $C_8H_{14}N_8S_2$	White	239	80	0.13	0.15	33.3 (33.6)	5.1 (4.9)	39.0 (39.2)	22.1 (22.4)	-	-
$[Co_2(BAT1)Cl_4]$ $\cdot H_2O \cdot 1/3C_2H_5OH$	Dark brawn	>350 dec	49	3.7	0.11	12.7 (12.7)	2.0 (2.2)	21.5 (21.0)	12.0 (11.9)	21.5 (21.9)	26.0 (26.4)
$[Co_2(BAT2)Cl_4]$ $\cdot 3/4H_2O \cdot 1/2C_2H_5OH$	Dark gray	257	55	4.1	0.32	15.1 (15.2)	2.9 (2.6)	20.7 (20.2)	12.0 (11.6)	21.8 (21.3)	26.0 (25.6)
$[Co_2(BAT3)(H_2O)_4Cl_4]$ $\cdot 1/4H_2O \cdot 1/3C_2H_5OH$	Gray	> 350 dec	63	4.8	0.34	14.8 (14.8)	3.7 (3.6)	18.0 (18.0)	10.1 (10.3)	19.0 (18.9)	23.0 (22.7)
$[Co_2(BAT4)(H_2O)_4Cl_4]$ $\cdot C_2H_5OH$	Brown	320	42	5.1	0.14	18.0 (18.1)	4.9 (4.2)	16.9 (16.6)	10.0 (9.6)	18.0 (17.7)	21.0 (21.4)
$[Ni_2(BAT1)Cl_4] \cdot H_2O$	Grassy green	> 350	61	6.3	0.12	11.0 (11.5)	2.2 (1.9)	21.9 (21.5)	3.5 (3.1)	22.9 (22.5)	27.0 (27.2)
$[Ni_2(BAT2)(H_2O)_4Cl_4]$ $\cdot 3/4H_2O \cdot C_2H_5OH$	Light green	> 350	48	6.1	0.29	14.9 (14.8)	3.4 (3.9)	17.6 (17.3)	9.3 (9.9)	18.2 (17.9)	22.0 (21.9)
$[Ni_2(BAT3)(H_2O)_4Cl_4]$ $\cdot H_2O \cdot 1/5C_2H_5OH$	Grassy green	> 350	61	6.0	0.37	14.5 (14.1)	3.8 (3.7)	18.0 (17.8)	9.9 (10.2)	18.1 (18.6)	22.1 (22.5)
$[Ni_2(BAT4)(H_2O)_4Cl_4]$ $\cdot 1/2H_2O \cdot 1/2C_2H_5OH$	Grassy green	> 350	39	5.9	0.13	16.9 (16.6)	3.8 (4.0)	17.9 (17.3)	9.3 (9.9)	18.7 (18.1)	22.2 (21.8)
$[Cu_2(BAT1)Cl_4]$ $.3/2H_2O$	Dark brawn	> 350	75	9.2	0.12	10.9 (11.0)	1.8 (2.0)	19.8 (20.3)	11.9 (11.9)	24.0 (23.5)	26.5 (26.3)
$[Cu_2(_4BAT2)Cl_{4.}]$ $\cdot 5/2\ H_2O$	Dark brawn	242	72	9.6	0.19	12.2 (12.6)	2.9 (2.6)	19.8 (19.6)	11.5 (11.2)	22.0 (22.2)	25.0 (24.8)
$[Cu_2(BAT3)(H_2O)_4Cl_4]$ $\cdot 3/2H_2O \cdot 1/4C_2H_5OH$	Dark brawn	> 350	85	10.5	0.35	13.5 (13.8)	3.5 (3.8)	16.9 (17.2)	10.0 (9.8)	19.6 (19.5)	21.9 (21.9)
$[Cu_2(BAT4)(H_2O)_4Cl_4]$ $\cdot 1/4H_2O$	Dark brawn	260	50	10.9	0.12	15.1 (15.2)	3.4 (3.6)	17.2 (17.7)	9.9 (10.1)	20.3 (20.1)	22.2 (22.5)

R_f = retention factor in Thin Layer Chromatography

gen and sulfur analysis were determined microanalytically using a Vario EL Fab. CHNS Nr.11042023 instrument. Thin Layer Chromatography (TLC) was carried out on Silica Gel GF_{254} plates (mn-kieselgel G., 0.2 mm thickness) with a 3:1 v/v ethylacetate / petroleum ether solution as eluent. The plates were scanned under ultraviolet light 254 nm lamp [21].

The molar conductance of 10^{-3} M solutions of the ligands and their metal complexes in DMF solvent were measured on a HACH conductivity meter model sens ion 5. All the measurements were taken at room temperature on freshly prepared solutions.

The electronic spectra of the ligands and their complexes were recorded in nujol mulls in the range 200-1100 nm on a Perkin Elmer Lambda 35 UV/Vis spectrometer. IR spectra of these compounds were recorded on Shimadzu DR-8001 infrared spectrophotometer in KBr pellets.

Magnetic susceptibility measurements of the solid complexes were carried out at room temperature using a Johnson Metthey and Sherwood magnetic susceptibility balance, and the data collected were processed in accordance with an earlier report [22]. Diamagnetic corrections were carried out using standard Pascal's constants.

Thermogravimetric Analysis (TGA) experiment was conducted using TGA-50H thermal analyzers. All experiments were performed using a single use top loading platinum sample pan under nitrogen atmosphere at a flow rate of 30 ml/min and a 10°C/min heating rate in the temperature range 25-800°C. The data were extracted from the TG curves for each decomposition step with the assistance of the DTG curves and hence kinetic parameters of decomposition were evaluated using the Coats-Redfern method [15], as appropriate.

Biological screening

The ligands and their metal complexes were tested for their antimicrobial activity against four species of bacteria (*Staphylococcus aureus, Streptococcus pyogenes, Haemophilus influenzae*, *Pseudomonas aeruginosa*), and two fungal species (*Aspergillus flavus* and *Candida albicans*) using filter paper disc method [23].The diameters of inhibition zones (mm) were measured at the end of an incubation period of 24 hours at 37 °C for bacteria, and 4 days at 28 °C for fungi. Discs saturated with DMSO are used as solvent control. Ampicillin 25 μg/ml was used as a reference substance for bacteria and 30 μg/ml Mycostatin for fungi [6, 21].

Results and discussion

Table 1 compares the elemental analysis, molar conductance and some other physical properties of the BATs ligands and their metals complexes under investigation. The prepared metals complexes show single spots on their thin layer chromatography with satisfactory R_f values (Table 1), indicating their purity [24]. All the complexes are colored, quite stable in atmospheric conditions and insoluble in water and ethanol, but most of them are partially soluble in acetone, Chloroform, Carbon tetrachloride, DMF and DMSO. Most of the complexes have high melting points (>350°C) and do not melt but decompose at higher temperature. However, few of them melt and their melting points appear at the 242-320°C range.

The proposed empirical formulae of the complexes are in good agreement with the stoichiometry of 2:1, metal : ligand concluded from their analytical data (Table 1) and the thermogravimetric analysis results (Tables 4 and 5). The molar conductance values (Table 1) of 10^{-3}M solutions in DMF solvent are in the range of 3.7-10.9 mS cm^{2}mol^{-1}, indicating a non-electrolytic behavior of these metal complexes and clearly suggest the coordination of the anions with the metal ions [25]. The ligands and their metal ions complexes are characterized by elemental analysis, molar conductance, IR spectra, electronic spectra, magnetic susceptibility and with assistance of thermal analysis (Tables 1-5).

Infrared spectra studies

Table 2 shows the significant IR absorp-

Table 2. Significant IR spectral bands (cm^{-1}) of the BATs and their metal complexes

Compound	ν(NH$_2$)	ν(OH) H$_2$O	νCH-aliph.	ν(C=N)	ν(C=S)	ν(N-N)	Thioamide Bands				ν(M-O)	ν(M-N)	ν(M-S)	ν(M-Cl)
							I	II	III	IV				
BAT1	3308, 3204	-	2955	1622	1244	1044	1581	1302	982	750	-	-	-	-
$[Co_2(BAT1)Cl_4]\cdot H_2O\cdot\frac{1}{3}C_2H_5OH$	3225	3391	2955	1564	1227	924	1564	1294	924	695	426	406	350	347
$[Ni_2(BAT1)Cl_4]\cdot H_2O$	3225	3433	2955	1514	1217	928	1564	1294	928	675	426	405	350	
$[Cu_2(BAT1)Cl_4]\cdot 1\frac{1}{2}H_2O$	3287, 3163	3454	2955	1514	1228	928	1568	1294	928	675	-	405	350	347
BAT2	3308, 3277	-	2948	1621	1253	1032	1570	1319	970	781	-	-	-	-
$[Co_2(BAT2)Cl_4]\cdot\frac{3}{4}H_2O\cdot\frac{1}{2}C_2H_5OH$	3225	3391	2976	1617	1232	950	1560	1314	930	692	476	402	350	340
$[Ni_2(BAT2)(H_2O)_4Cl_4]\cdot\frac{3}{4}H_2O\cdot C_2H_5OH$	3267, 3163	3412	2935	1568	1165	970	1568	1317	974	742	435	405	352	329
$[Cu_2(BAT2)Cl_4]\cdot 2\frac{1}{2}H_2O$	3287, 3184	3454	2934	1611	1215	974	1558	1318	974	742	440	400	351	325
BAT3	3308, 3267	-	2934	1626	1248	1028	1581	1327	982	745	-	-	-	-
$[Co_2(BAT3)(H_2O)_4Cl_4]\cdot\frac{1}{4}H_2O\cdot\frac{1}{3}C_2H_5OH$	3204	3391	2934	1622	1232	992	1547	1311	980	692	480	400	351	347
$[Ni_2(BAT3)(H_2O)_4Cl_4]\cdot H_2O\cdot 1/5C_2H_5OH$	3184	3412	2955	1622	1231	982	1514	1323	982	692	430	400	355	334
$[Cu_2(BAT3)(H_2O)_4Cl_4]\cdot 1\frac{1}{2}H_2O\cdot\frac{1}{4}C_2H_5OH$	3287, 3184	3474	2955	1622	1232	974	1558	1323	974	675	427	405	384	359
BAT4	3308, 3204	-	2955	1622	1240	1027	1581	1323	920	754	-	-	-	-
$[Co_2(BAT4)(H_2O)_4Cl_4]\cdot C_2H_5OH$	3204, 3142	3427	2934	1564	1232	995	1564	1323	908	737	426	405	385	355
$[Ni_2(BAT4)(H_2O)_4Cl_4]\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}C_2H_5OH$	3225	3371	2934	1615	1230	1000	1547	1323	905	735	426	405	382	341
$[Cu_2(BAT4)(H_2O)_4Cl_4]\cdot\frac{1}{4}H_2O$	3308, 3184	3412	2934	1613	1229	1000	1541	1323	909	735	426	405	380	355

tion bands of the BATs ligands and their twelve complexes. The IR spectra of BAT1, BAT2, BAT3 and BAT4 accord with the literature [7]. A broad IR band in the range 3142-3474 cm^{-1} in the complexes is attributed to the overlapping vibration of $\nu NH(NH_2)$ with that of $\nu OH(H_2O)$ of coordinated water [26]. Coordinated water shows metal-oxygen ν(M-O) stretching vibration in the 426-480 cm^{-1} [27].

The appearance of the four thioamide bands (I-IV) at 1570 - 1581, 1302 - 1327, 920 - 982 and 745 - 781 cm^{-1} [27], refutes the presence of the bands in the 2400-2600 cm^{-1} regions and at 606 cm^{-1} due to ν(SH) and ν(C-S), respectively [28] confirming that the ligands of BATs exist mainly in the thione form [5].These four thioamide bands of the ligands are compared with those of their complexes in Table 2, indicating the shift due to complexation. The bands at 1240-1253 cm^{-1} in the spectra of the ligands assigned to ν(C=S) is lowered by 8-88 cm^{-1} in the spectra of the complexes, indicating involvement of thione groups sulfur in the coordination. This leads to new bands in the region 350-385 cm^{-1} tentatively assigned to M-S vibration [27].

The shift to lower frequency of the amino group by 20-124 cm^{-1} may suggest the participation of the nitrogen atom in the complexation. The bands at 1027-1044 cm^{-1} due to ν(N-N) in the free ligands are shifted to lower frequencies by 27-120 cm^{-1} in the complexes formation spectra [29], confirming the coordination through the nitrogen atoms . In addition, the shift in ν(C=N), for C=N being adjacent to N-N in the molecular structure, is to lower frequency by 4-108 cm^{-1} [13]. Coordination through the amino groups nitrogen is consistent with new bands in the 400-406 cm^{-1}, assignable to the ν(M-N) vibration [23, 27, 30]. The new band at the low frequency 325-359 cm^{-1} is assigned to ν(M-Cl). The above findings indicate the tetradentate (N and S donor atoms) nature of ligands, enhancing the coordination of two metal ions with one ligand molecule.

Electronic and magnetic studies

Table 3 compares the magnetic moments, electronic spectral data and ligand field parameters of the Co(II), Ni(II) and Cu(II) complexes with the ligands of BATs. The electronic spectrum of the ligands BAT2 and BAT3 exhibit their two absorption maxima in the ranges 42194 - 33333 cm^{-1} and 42373-33112 cm^{-1}, assignable to $\pi \rightarrow \pi^*$ (K-band) and $n \rightarrow \pi^*$ (R-band) transitions [27], respectively, (Table 3).

From the electronic spectra and magnetic moment data the structures and geometries of these Co(II), Ni(II) and Cu(II) complexes are identified and interpreted, as illustrated in structures I and II and given in Table (3). The electronic spectrum of the Co(II) complexes,

Table 3. Magnetic moment, electronic spectral data in Nujol mull and ligand field parameters for the BATs and their Complexes.

Compound	μ_{eff} (B.M.)	UV bands (cm^{-1})		L→M charge transfer (cm^{-1})	*d-d* transition bands (cm^{-1})	ν_1 (cm^{-1})	Ligand field parameters				Supposed structure
		$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$				B (cm^{-1})	β	$10Dq$ (cm^{-1})	ν_2/ν_1	
BAT2	-	42194	33333	-	-	-	-	-	-	-	-
$[Co_2(BAT2)Cl_4]\cdot\frac{3}{4}H_2O\cdot\frac{1}{2}C_2H_5OH$	2.10	44053	-	23041^b	20000,16779,14881 ,12255	-	-	-	-	-	Square planer
$[Ni_2(BAT2)(H_2O)_4Cl_4]\cdot\frac{3}{4}H_2O\cdot C_2H_5OH$	3.08	40161	33333	28409^b	22831,18797,14245	9901	795	0.76	9901	1.89	Octahedral
$[Cu_2(BAT2)Cl_4]\cdot 2\frac{1}{2}\ H_2O$	1.41	41152	33300	28421^c, 25126^a, 20661^b	16778	-	-	-	-	-	Square planar
BAT3	-	42373	33112	-	-	-	-	-	-	-	-
$[Co_2(BAT3)(H_2O)_4Cl_4]\cdot\frac{1}{4}H_2O\cdot\frac{1}{3}C_2H_5OH$	4.27	39370	33113	25000^b	19231, 14837	6948	889	0.92	7889	2.14	Octahedral
$[Ni_2(BAT3)(H_2O)_4Cl_4]\cdot H_2O\cdot 1/5C_2H_5OH$	2.86	39370	33113	27855^b	25000, 18382,14577	8767	885	0.85	8767	1.66	Octahedral
$[Cu_2(BAT3)(H_2O)_4Cl_4]\cdot 1\frac{1}{2}H_2O\cdot\frac{1}{4}C_2H_5OH$	1.45	41841	33112	28409^c, 24876^a, 21736^b	18797, 13736	-	-	-	-	-	Distorted Octahedral

a: O→M Charge transfer , b: S→M Charge transfer, c: d →π* Charge transfer.

$[Co_2(BAT3)(H_2O)_4Cl_4]\cdot 1/4H_2O\cdot 1/3C_2H_5OH$ is indicated by the absorption bands at 19231 cm^{-1} and 14837 cm^{-1} due to the $^4T_{1g}\rightarrow {}^4T_{1g}(P)$ (ν_3) and $^4T_{1g}\rightarrow {}^4A_{2g}$ (ν_2) transitions [31], respectively, suggesting octahedral geometry (structure I).

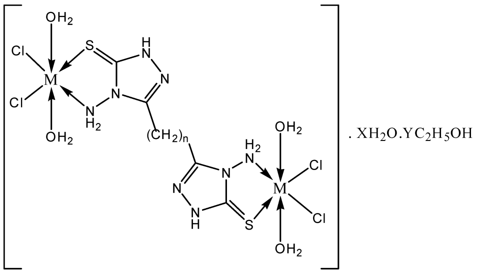
Due to instrumental limitation, the values of ν_2 and ν_3 obtained from the electronic spectra are used to calculate the third transition, $^4T_{1g}\rightarrow {}^4T_{2g}(F)$ (ν_1) band by the equations used for the d^7 system [32] and found to be 6948 cm^{-1}. From these transition bands the ligands field parameters (Table 3) calculated for the Co(II) complex of BAT3 ligand are B = 889 cm^{-1}, β = 0.92, $10Dq$ = 7889 cm^{-1} and ν_2/ν_1 = 2.14 , respectively. Reduction of the B value of the free ion from 971 cm^{-1} to 889 cm^{-1} (i.e. β from 1 to 0.92) on the complexation indicates the covalent character of metal-to-ligand bonds [33]. The lower is the value the greater is the covalency.

The Co(II) complexes, $[Co_2(BAT3)(H_2O)_4Cl_4]\cdot 1/4H_2O\cdot 1/3C_2H_5OH]$ and $Co_2(BAT4)(H_2O)_4Cl_4]\cdot C_2H_5OH$ have magnetic moments of 4.27 and 4.82 B.M., respectively, which lie in the range reported [34] for an octahedral geometry around the Co(II) ion (structure I). However, the subnormal magnetic moments of the Co(II) chelates reflect a behavior of the binuclear complexes [30]. The 4.27 B.M. value is lower than that previously reported [35]. However, magnetic moments lower than 4.80 B.M for the octahedral Co(II) complexes has been observed [36]. The anomalous magnetic moment suggests a low-symmetry around the cobalt (II) ion [37]. Moreover, the gray and brown colors of the complexes are in good agreement with those reported for octahedral Co(II) complexes [33].

The observed charge transfer band recorded for the complex of BAT3 at 25,000 cm^{-1} is mainly due to S→Co [27, 32]. This charge transfer transitions probably from the π-orbitals of the donor atoms to the metal ion. The UV bands, $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$, of the ligand most likely moves to lower energy on complexation [29].

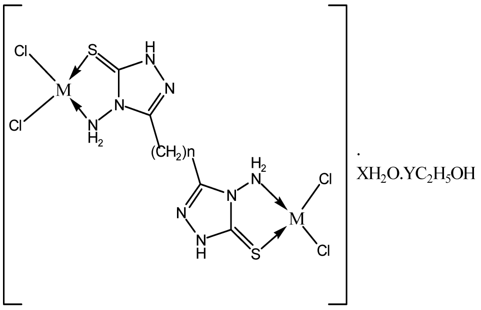
The other Co(II) complexes, $[Co_2(BAT1)Cl_4]\cdot H_2O\cdot 1/3C_2H_5OH$ and

$[Co_2(BAT2)Cl_4]\cdot 3/4H_2O\cdot 1/2C_2H_5OH$ have a magnetic moments (2.67 and 2.10 B.M, respectively) which fall in the region reported for one unpaired electron existing in both square-planer and low spin octahedral geometries [27]. The absence of octahedral characteristic bands spectra excludes the low spin octahedral configuration, whereas the existence of a broad band at 20,000 cm^{-1} in the $[Co_2(BAT2)Cl_4]\cdot 3/4H_2O\cdot 1/2C_2H_5OH$ electronic spectrum may suggest a square-planer geometry (structure II). Also, the existence of the three bands at 12,255, 14,881 and 16,779 cm^{-1} confirms the proposed geometry [27, 32]. These observations together with the magnetic moment value (2.10 B.M.) support the presence of a square planar environment around the cobalt (II) ion [32].



M=Co^{2+}: n = 3, 4; X = 0.25, 0; Y = 0.33, 1
M=Ni^{2+}: n = 2,3,4; X = 0.75,1,0.5; Y = 1,0.2,0.5
M=Cu^{2+}: n = 3, 4; X = 1.5,0.25; Y = 0.25,0

Structure I



M=Co^{2+}: n = 1, 2; X = 1, 0.75; Y = 0.33, 0.5
M=Ni^{2+} : n = 1; X = 1; Y= 0
M=Cu^{2+}: n = 1, 2; X = 1.5, 2.25; Y=0, 0

Structure II

Nickel(II) complexes

The complexes $[Ni_2(BAT2)(H_2O)_4Cl_4]\cdot 3/4H_2O\cdot C_2H_5OH]$, $[Ni_2(BAT3)(H_2O)_4Cl_4]\cdot H_2O\cdot 1/5C_2H_5OH$ and $[Ni_2(BAT4)(H_2O)_4Cl_4]\cdot 1/2H_2O\cdot 1/2C_2H_5OH]$ have magnetic moments of 3.08, 2.86 and 3.00 B.M., respectively. They lie in the range reported [34] for an octahedral geometry around the Ni(II) ion with a $^3A_{2g}$ ground term (structure I).

The nickel (II) complexes, $[Ni_2(BAT2)(H_2O)_4Cl_4]\cdot3/4H_2O\cdot C_2H_5OH$ and $[Ni_2(BAT3)(H_2O)_4Cl_4]\cdot H_2O\cdot1/5C_2H_5OH$, electronic spectra indicate two absorption bands in the regions 22831-25000 and 14577-18797 cm^{-1} for ν_3 and ν_2 transitions [$^3A_{2g}\rightarrow{}^3T_{1g}(P)$ (ν_3) and $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (ν_2)] and the third ν_1 transition [$^3A_{2g}\rightarrow{}^3T_{2g}$ (ν_1)] band is estimated (8767-9901cm^{-1}) using equations for the d^8 system [32]. These transitions suggest an octahedral geometry (structure I) for Ni (II) complex [31].

The ligand field parameters: (B =795-885 cm^{-1} , β = 0.76-0.85, 10Dq = 8767-9901 cm^{-1} and ν_2/ν_1 = 1.66-1.89) worked out for this complex (Table 3) lie in the same range as reported for an octahedral structure around Ni(II) ions [32]. Reduction of the B value of the free ion from 1041 cm^{-1} to 795-885 cm^{-1} due to complex formation indicates the covalent character of metal-to-ligand bonds [33]. The green color of this complex is an additional evidence for an octahedral structure [27].

The $[Ni_2(BAT1)Cl_4]\cdot H_2O$ complex is diamagnetic, which factually supports (structure II) square-planar geometry [30]. The commonly square-planar Ni(II) complexes are orange or red but a few have purple or green colors [32].

Copper(II) complexes

The complexes $[Cu_2(BAT3)(H_2O)_4Cl_4]\cdot3/2H_2O\cdot1/4C_2H_5OH$ and $[Cu_2(BAT4)(H_2O)_4Cl_4]\cdot1/4H_2O$ possess magnetic moments (1.45 and 1.58 B.M., respectively) found to be within the range reported for the d^9-system containing one unpaired electron [38], and assignable to a distorted octahedral geometry (structure I). The dark brown color of these complexes supports the proposed geometry [38].

The electronic spectrum of $[Cu_2(BAT3)(H_2O)_4Cl_4]\cdot3/2H_2O\cdot1/4C_2H_5OH$, show weak shoulders at 18,797 cm^{-1} and 13,736 cm^{-1}. These bands are due to $^2B_{1g}\rightarrow{}^2E_g$ and $^2B_{1g}\rightarrow{}^2A_{1g}$ transitions in a distorted octahedral geometry [30, 32]. The broadness of the observed band may be due to Jahn-Teller effect [39], which enhances the distortion of the octahedral geometry.

The magnetic moments of the $[Cu_2(BAT1)Cl_4]\cdot3/2H_2O$ and $[Cu_2(_4BAT2)Cl_{4.}]\cdot5/2\ H_2O$ complexes are 1.85 and 1.41 B.M., respectively. These values lie in the range reported [39] for a square-planar geometry (structure II). The lower value of μ_{eff} (1.45, 1.58 and 1.41 B.M.) than that calculated (1.73B.M.) for one unpaired electron is normal and expected if binuclear complexes are considered [30]. Thus, in general a decrease in the magnetic moment below the spin-only value (1.73B.M.) may be attributed to molecular association taking place to form bi-or poly nuclear molecules [40]. Little changes in the ligands bands ($\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$) energies are detected on complexation [29]. It is proved that the bands observed at 20661 and 21736 cm^{-1} are assigned to S→Cu(II) transition [27], and that at 28421 and 28409 cm^{-1} may be assigned to $d\rightarrow\pi^*$ [41].

Thermal analysis

Tables 4 and 5 compare the characteristic thermal and kinetic parameters determined for each step in the decomposition sequence of the complexes. It can be seen clearly (Tables 4 and 5) that the mass losses (Δm%) obtained from the TG curves and that calculated for the corresponding molecule or molecules are in good agreement as is the case for all of these complexes. However, as the compositions of the final decomposition products (i.e. final residues) are not proved, ill-defined final states are considered for the thermal decomposition of these six complexes. The integral method used is the Coats-Redfern equation [15] for reaction order n ≠1, which when linearised for a correctly chosen n yields the activation energy from the slope;

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\log\frac{ZR}{qE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT}$$

where: α = fraction of weight loss, T = temperature (K), n = order of reaction, Z = pre-exponential factor, R = molar gas constant, E_a = activation energy and q = heating rate.

The TGA (TG and DTG) curves recorded for the BAT2 and BAT3 ligands are given in Figure 1.The BAT2 and BAT3 ligands exhibit almost similar thermal decomposition process and the resulting mass loss (Δm %), order reaction (n), activation energy (E_a), initial (T_i), final

Table 4. Characteristic parameters of thermal decomposition (10°C min^{-1}) for Co(II), Ni(II) and Cu(II) complexes of BAT2.

Comp.	Step	TGA				n	E_a/ kJ mole^{-1}	Reaction
		Δm% found (calc.)	T_i/°C	T_f/°C	T_{DTG}			
BAT2	1	19	130	281	249	1.9	234	- [19% of Ligand]
	2	24	281	410	324	2.6	201	- [24% of Ligand]
	Total mass loss = 84.5% and Final residue = 15.5%; at 800 °C							
Co-BAT2	1	6.70 (6.60)	34	153	69	2.5	72	-[0. 5EtOH + 0.75H_2O]
	2	25.70 (25.60)	169	367	267	2.2	102	- 4 Cl
	3	10.60 (10.70)	367	499	455	1.2	123	-[23% of bb^a]
	4	10.80 (10.70)	499	648	540	2.4	237	-[23% of bb^a]
	5	13.00 (13.00)	648	781	718	1.2	316	-[28% of bb^a]
	Final residue (2 Co + 26% of bb^a): 33.20% (33.40%)							
Ni -BAT2	1	14.70 (14.72)	33	180	81	2.1	53	-[EtOH+0.75H_2O+2H_2O]
	2	22.10 (21.95)	180	400	327	1.1	53	-[2H_2O+ 3Cl]
	3	35.30 (35.29)	400	608	503	1.2	109	-[Cl +75% of bb^a]
	Final residue (2 Ni + 25% of bb^a): 27.90% (28.04%)							
Cu -BAT2	1	7.80 (7.90)	32	182	72	5	94	- 2.5 H_2O
	2	24.60 (24.80)	182	360	256	2.6	103	- 4Cl
	3	11.50 (11.70)	360	538	399	2.7	132	-[26% of bb^a]
	4	23.40 (23.50)	538	800	715	0.8	98	-[52 % of bb^a]
	Final residue (2 Cu + 22% of bb^a): 32.70% (32.10%)							

[a] bb; Backbone components

(T_f) and maximum rate (T_{DTG}) temperatures of mass loss are given in Tables 4 and 5. The ligands BAT2 and BAT3 start losing 43% and 49% of their masses in two rapid and consecutive steps in the 130-414°C range, followed by slow and continuous bleeding of 41.5% and 29.8% mass losses in the 262-800°C range with 15.5% and 21.2% residual mass at the end of the reaction (800°C), respectively. In the two apparent consecutive-steps, the strongly sharp peaks (T_{DTG}) at 249°C and 324°C due to the rapid and consecutive 19% and 24% mass losses with activation energies 234 kJ mol^{-1} and 201 kJ mol^{-1} observed for the BAT2 ligand are more or less comparable with that at 230°C and 295°C with 19% and 30% mass losses and activation energies of 186 kJ mol^{-1} and 184 kJ mol^{-1} observed for BAT3 ligand.

The TG/DTG curves of the metal-complexes in Figures 2 and 3 reveal that with overlapping steps being various, three, four or five steps in the sequential decomposition of BAT2 and BAT3 metal-complexes are observed. The

Table 5. Characteristic parameters of thermal decomposition (10°C min^{-1}) for Co(II), Ni(II) and Cu(II) complexes of BAT3.

Comp.	Step	TGA				n	E_a/ kJ mole^{-1}	Reaction
		Δm% found (calc.)	T_i/°C	T_f/°C	T_{DTG}			
BAT3	1	19	180	262	230	1.5	186	- [19% of Ligand]
	2	30	262	414	295	3.1	184	- [30% of Ligand]
	Total mass loss = 78.8% and Final residue = 21.2%; at 800 °C							
Co-BAT3	1	14.60 (14.80)	23	229	69	3.6	64	-[0.33EtOH +4.25H_2O]
	2	5.60 (5.70)	229	315	286	1.4	167	- Cl
	3	11.50 (11.40)	315	414	355	2.1	191	-2 Cl
	4	12.60 (12.50)	414	526	460	2	233	- [Cl + 15.5% of bb^a]
	5	29.40 (29.50)	526	800	662	1.4	141	- [67.5% of bb^a]
	Final residue (2 Co + 17% of bb^a): 26.30% (26.10%)							
Ni-BAT3	1	15.70 (15.80)	34	275	66	3.7	58	-[0.2EtOH+ 5H_2O]
	2	5.57 (5.62)	275	358	321	2.4	198	-Cl
	3	11.20 (11.30)	358	420	370	2.2	282	-2Cl
	4	12.63 (12.61)	420	538	437	3.8	314	-[Cl + 16.2% of bb^a]
	5	25.60 (25.50)	538	796	669	3	170	-[59 % of bb^a]
	Final residue (2 Ni + 24.8% of bb^a): 29.30% (29.17%)							
Cu-BAT3	1	5.60 (5.91)	34	101	62	2	94	-[0.25EtOH+1.5 H_2O]
	2	27.70 (27.38)	112	340	211	2	63	-[4H_2O + 3Cl]
	3	13.70 (13.79)	340	500	377	3.4	149	-[Cl + 20% of bb^a]
	4	24.20 (24.22)	500	744	554	3.2	242	-[58 % of bb^a]
	Final residue (2 Cu + 22% of bb^a): 28.80% (28.70%)							

[a] bb; Backbone components

first decomposition steps of both ligands complexes between 23-275°C with mass losses ranging from 5.60 to 15.70% correspond to the co-evolution of solvent with various number of adsorbed or/and coordinated water molecules (cal. 5.70-15.80%), and as a result broad peaks either due to peaks overlapping or a gradual extending end (T_f) is observed. The corresponding activation energy values of these steps range between 53 to 94 kJ mol^{-1}.

The second-step of decomposition in the 112-400°C range indicates the mass losses between 5.57 and 27.70% may be due to either the release of various ratio of coordinated water molecules

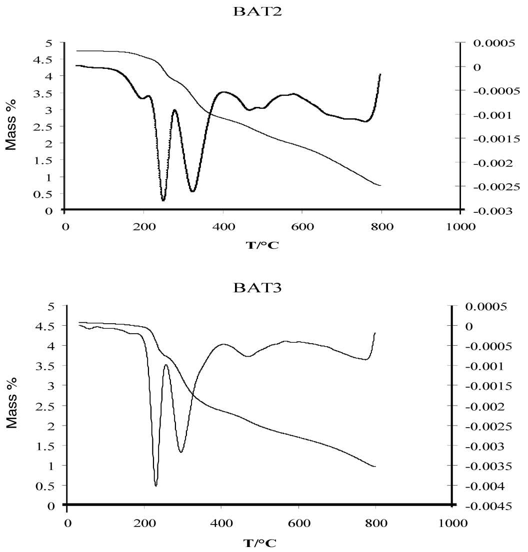


Figure 1. The TG and DTG thermograms of the BAT2 and BAT3 ligands in nitrogen at the heating of 10°C min^{-1}.

together with chloride atoms or various number of chloride atoms (cal. 5.62-27.38%). These second-steps show overlapping steps of either a very rapid or a gradual mass loss with activation energy falls in the 53-198 kJ mol^{-1} range.

The third-step of these complexes occurs at the 315-608°C range with a gradual mass loss ranging from 10.60 to 35.30%. This corresponds to either the release of two chloride atoms, one chloride atom along with various percent of backbone components or various percent of backbone components (cal. 10.70 to 35.29%) with activation energies between 109-282 kJ mol^{-1}. The third-step (400-608°C) is an end of reaction step for the decomposition of Ni-BAT2 complex leaving a 27.90% mass loss that is in consistent with the final product (cal. 28.04%) of an ill-defined final state.

The fourth-step at the 414-648°C range is assigned to the removal of one chloride atom along with 15.5% of the backbone components (found 12.60%, cal. 12.50%), one chloride atom along with 16.2% of the backbone components (found 12.63%, cal. 12.61%) and 23% of the backbone components (found 10.80%, cal. 10.70%) in the decomposition process of Co-BAT3, Ni-BAT3 and Co-BAT2 complexes with activation energy of 233, 314 and 237 kJ mol^{-1}, respectively.

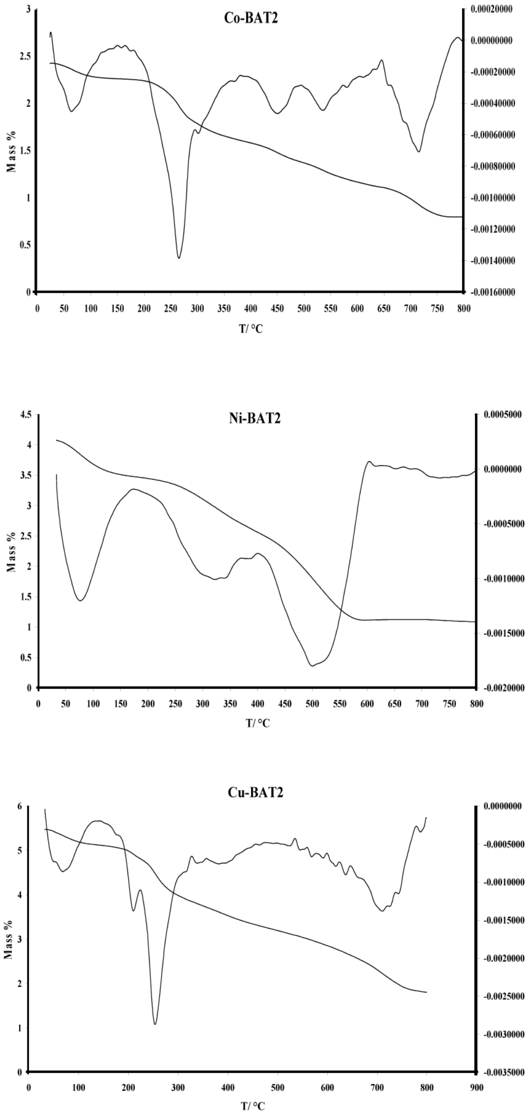


Figure 2. The TG and DTG thermograms of the Co, Ni and Cu complexes with BAT2 ligand in nitrogen at the heating of 10°C min^{-1}.

In the contrary, this fourth-step in the 499-800°C range is the end of decomposition of Cu-BAT2 and Cu-BAT3 complexes for eliminating the remaining 52% (found 23.40%, cal. 23.50%) and 58% (found 24.20%, cal. 24.22%) of the backbone components with the deposition of ill-defined final residues 32.70% (cal. 32.10%) and 28.80% (cal. 28.70%) at the end of the reactions, respectively. Their activation energies found to

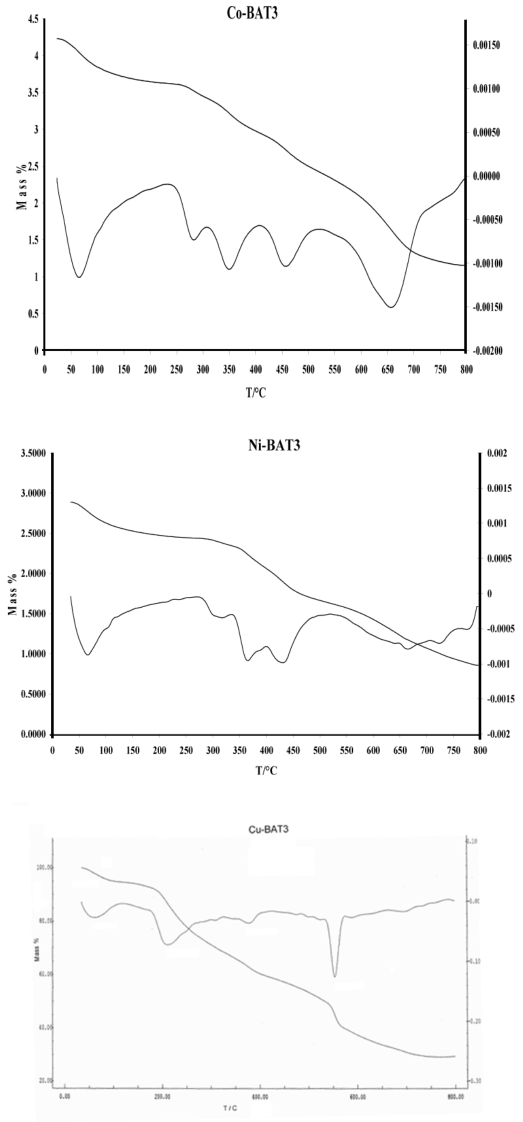


Figure 3. The TG and DTG thermograms of the Co, Ni and Cu complexes with BAT3 ligand in nitrogen at the heating of 10°C min^{-1}.

be 98 and 242 kJ mol^{-1}, respectively. It is found that the release of the coordinated water molecules and chloride atoms fairly accord with literature [42, 43].

However, in the fifth-step of the 526-800°C range, the Co-BAT2, Co-BAT3 and Ni-BAT3 decompose completely by losing the remaining 28% (found 13.0%, cal 13.0%), 67.5% (found 29.40%, cal 29.50%) and 59% (found 25.60%, cal 25.50%) of their backbone components with the deposition of ill-defined final products 33.20% (cal. 33.40%), 26.30% (cal. 26.10%) and 29.30% (cal. 29.17%), and the associated activation energies are 316, 141 and 170 kJ mol^{-1}, respectively.

It can be concluded that the thermal decomposition of these six complexes is of a variety of degrees of similarity (Table 4 and 5). For instant, the first, second and third steps in the sequential decomposition of the square-planar complexes of Co-BAT2 and Cu-BAT2 are of very close thermal and kinetic parameters. This is, maybe, due to similar nature of decomposition process, i.e. similar mechanism and kinetics of the decomposition reaction that took place in the first three steps of the Co-BAT2 and Cu-BAT2 complexes. Acceptable similarities in the thermal and kinetic parameters are observed for the five steps in the decomposition sequence of the Co-BAT3 and Ni-BAT3 octahedral complexes. However, this is inconsistent with the thermal decomposition of the octahedral complexes of Ni-BAT2 and Cu-BAT3 with their three and four steps in the decomposition process.

Biological activity

The ligands BAT1, BAT2, BAT3 and BAT4 under investigation and their Co(II) Ni(II) and Cu(II) complexes were screened *in vitro* for their antibacterial activity against four strains of bacteria, i.e. two gram-positive bacteria (*Staphylococcus aureus, Streptococcus pyogenes)* and two gram-negative bacteria (*Haemophilus influenzae*, *Pseudomonas aeruginosa*), and two fungal species (*Aspergillus flavus* and *Candida albicans*). Discs saturated with DMSO solvent, which show no zone of inhibition (-) were used as control and the results of the antibacterial and antifungal activities were summarized in Table 6.

The ligands BAT1, BAT2, BAT3 and BAT4 and their Co(II), Ni(II) and Cu(II) complexes are found to possess various antibacterial and antifungal activities towards the strains of the bacteria and the fungal species used. However, no inhibition zone is observed for the ligands BAT3 and BAT4 against the gram-posi-

Table 6. Effect of the ligands and their Co(II), Ni(II) and Cu(II) Complexes on the growth of Bacteria and Fungi (Zone of inhibition in mm).

Compound (1000 µg/ml)	Bacteria				Fungi	
	gram-positive		gram-negative		*Aspergillus flavus*	*Candida albicans*
	Staphylococcus aureus	*Streptococcus pyogenes*	*Haemophilus influenzae*	*Pseudomonas aeruginosa*		
BAT1	+	+	+	+	+	+
BAT2	+++	++	+	+	++	+
BAT3	-	-	++	+	++	++
BAT4	-	-	+	+	+	+
Co-BAT1	++	+	+	+	+	+
Co-BAT2	++	+++	+	+	+	+
Co-BAT3	+	++	+	+	+	+
Co-BAT4	+	+	+	+	+	+
Ni -BAT1	++	+	+	+	+	+
Ni -BAT2	++	+++	+	+	++	++
Ni -BAT3	++	+	+	+	+	+
Ni -BAT4	+	+	+	+	+	+
Cu -BAT1	++	+	+	+	+	+
Cu -BAT2	++	++	++	+	++	+
Cu -BAT3	++	-	+	++	+	+
Cu -BAT4	+	+	+	+	+	+
Ampicillin 25 µg/ml	+	+	+	+		
Mycostatin 30 µg/ml					+++	+++

(-) No zones of inhibition were observed.
Moderately sensitive (+), Inhibition zones of 7-10 mm.
Sensitive (++), Inhibition zones of 11-14 mm.
Highly sensitive (+++), Inhibition zones of 15-20 mm

tive bacteria and only for the complex Cu-BAT3 against *Streptococcus pyogene*. The highest activity observed is for the BAT2 against *Staphylococcus aureus* and for the Co(II) and Ni(II) complexes of BAT2 towards *Streptococcus pyogene*. Apart from the above-mentioned ligands and complexes, the remaining ligands and metal complexes exhibit moderate to high antibacterial activity.

Apart from the ligands and metal complexes that possess a high activity against *Aspergillus flavus* and *Candida albicans*, all the rest of the ligands and the complexes exhibit moderate antifungal activities against the fungi tested.

It has been reported [16-18] that complexes of some heterocyclic ligands with transition metals increase their biological activities. This can be seen relatively more in the higher activity of the metals complexes towards *Staphylococcus aureus* than the free ligands, but slightly less against *Streptococcus pyogene*. In contrast, increasing the number of methylene groups between two heterocyclic rings may decrease the antibacterial activity of these compounds [19]. Close examination of the antibacterial activity of the ligands and their metal complexes reveals that the ligand BAT4 with the highest methylene groups and its metal complexes possess the lowest antibacterial activity against gram-positive bacteria than the others.

Conclusion

Based on the analytical data and the TGA results, the formulae and the stoichiometry of the prepared BATs ligands and their Co(II) , Ni(II) and Cu(II) metal complexes are suggested. The IR spectral studies indicate neutral tetradentate behavior of the ligands coordinating through the amine group nitrogen and thione form sulphur. The molar conductance values show the non-electrolytic nature of the complexes. The spectral and magnetic results reveal an octahedral geometry (structure I) for some of the complexes and a square-planer (structure II) for the others.

Generally, the metal-complexes of a particular ligand with various metals exhibit various thermal decomposition behavior, and the kinetic parameters for the successive steps in the decomposition sequence are determined. The inconsistent biological activities observed again the four strains of bacteria and the two fungal species reflect various degrees effect nature of these metal-complexes.

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