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Antimicrobial Activity Studies of the Metal Complexes Derived from Cyclobutane-Substituted Thiazole Carbamate Ligands

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ABSTRACT: *Two novel monodentate carbamate ligands derived mainly from 4-(1-methyl-1-phenylcyclobutyl-3-yl)-2-aminothiazole and 4-(1-phenyl-1-methylcyclobutane-3-yl)-2-(N-methyl)aminothiazole, have been prepared. The ligands and their metal complexes have been characterized by elemental analyses, IR, ^{13}C, and ^1H NMR spectra, as well as UV–Vis, and magnetic susceptibility measurements. Both ligands contain 1 mole of water of crystallization and all complexes are mononuclear. Antimicrobial activities of the ligands and their complexes have been screened against the Bacillus subtitis IMG 22 (bacteria), Micrococcus luteus LA 2971 (bacteria), Escherichia coli DM (bacteria), Staphylococcus aureus COWAN I (bacteria), Saccharamyces cerevisiae UGA 102 (yeast), and Candida albicans CCM 314 (yeast). Thermal properties of the ligands and their complexes have been studied by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC).* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:665–670, 2001

INTRODUCTION

Metal complexes of dithiocarbamic acid and its derivatives are a subject of growing interest [1]. In fact, the transition metal complexes of dithiocarbamates and related ligands have been the focus of research for about 100 years. These complexes have good lubricant, antioxidant, antiwear, and antidote properties.

Some dithiocarbamates exhibit fungicidal, pesticidal, and bacteriological activities and are also used as a sulfide precursor for technological purposes [2]. It is well known that 3-substituted cyclobutanecarboxylic acid derivatives exhibit anti-inflamatory and antidepressant activities, and also liquid crystal properties [3]. Various thiazole derivatives have shown herbicidal, anti-inflamatory, antimicrobial, or antiparasitic activity [4]. However, the syntheses and physiochemical properties of 1,1,3-trisubstituted cyclobutane thiazoles and their carbamate derivatives have not been reported so far. These compounds seem to be suitable candidates for further chemical modifications and may be pharmacologically active and useful ligands in coordination chemistry.

Thiazole and its derivatives have biological significance, e.g., they are found in the vitamin B_1 molecule and in coenzyme cocarboxylase [5]. The penicillin molecule also contains a thiazolidine ring. 2-Aminothiazoles are known mainly as biologically active compounds with a broad range of activity and as intermediates in the synthesis of antibiotics and dyes [6].

The ligands used in this work (Fig. 1) have three different and important functionalities: cyclobutane,

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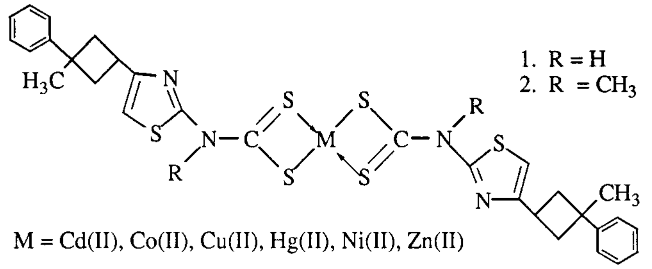


FIGURE 1 Suggested structure of tetrahedral and square-planar complexes of the ligands.

thiazole, and carbamate. The extensive synthetic possibilities of these compounds due to the presence of several reaction sites hold promise for the preparation of useful new thiazole derivatives.

Since these ligands are not reported in the literature, our paper deals with the preparation, characterization, and antibacterial activity studies of the ligands, as well as their complexes with cadmium(II), cobalt(II), copper(II), mercury(II), nickel(II), and zinc(II).

EXPERIMENTAL

Isobutylene, acrolein, $KMnO_4$, *N*-methylthiourea, thiourea, and metal salts, purchased from E. Merck, were used as received. Benzene was purchased from E. Merck and purified by standard procedures. 1-Phenyl-1-methyl-3-(2-chloro-1-oxoethyl)cyclobutane has been synthesized according to literature published previously [7]. All solvents were of analytical grade and, where appropriate, were purified by standard procedures.

Physical Measurements

Elemental analyses (C, H, N, S) were performed on a LECO-932 CHNSO elemental analyses apparatus. The IR spectra were recorded, using KBr discs (4000–400 cm^{-1}), on a Mattson 1000 S FT-IR spectrophotometer. Electronic spectra in the 200- to 900-nm range were obtained on a CECIL CE 5502 UV–Vis spectrophotometer. Magnetic susceptibilities were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant on a Sherwood Scientific magnetic susceptibility balance (Model MK 1) at room temperature (20°C), diamagnetic corrections being calculated from Pascal's constants. ^{13}C and ^{1}H NMR spectra were recorded on a Brucker GmbH Dpx-400 MHz High Performance Digital FT-NMR or JEOL FX-90Q spectrometer. Melting points were determined on a Gallenkamp melting point apparatus and checked by a differential scanning calorimeter (DSC) and are uncorrected. Thermogravimetric curves were recorded on a Schimadzu TG-50 thermobalance using ~5 mg samples. Thermogravimetric curves were obtained at a heating range of 10°C/min; in all cases a 20–850°C temperature range was studied and a dry nitrogen atmosphere was utilized. Metal contents of the complexes were determined by use of an Ati Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposing the compounds in concentrated HCl and subsequent dilution with 0.01 M HCl being used.

*Synthesis of 4-(1-Phenyl-1-methylcyclobutane-3-yl)-2-(N-methyl)aminothiazole (**2**)*

To a solution of 0.902 g (10 mmol) of *N*-methylthiourea in 50 ml of absolute ethanol, a solution of 2.225 g (10 mmol) of 1-phenyl-1-methyl-3-(2-chloro-1-oxoethyl)cyclobutane in 20 ml of absolute ethanol was added dropwise at 60–70°C, with continuous stirring and monitoring of the course of the reaction by IR spectroscopy. Monitoring of the carbonyl group of 1-phenyl-1-methyl-3-(2-chloro-1-oxoethyl)-cyclobutane is easily done and thus it is very easy to determine the completion of the reaction. After completed reaction, the solution was made alkaline with an aqueous solution of NH_3 (5%) causing separation of a pale yellow solid substance, 4-(1-phenyl-1-methylcyclobutane-3-yl)-2-(*N*-methyl)aminothiazole (**2**). The precipitate was filtered off, washed with aqueous ammonia solution and water several times, dried in air, and crystallized from aqueous ethanol (1:3). The compound was found to be soluble in methanol, ethanol, $CHCl_3$, acetone, THF, DMSO, or DMF. Characteristic ^{1}H NMR peaks ($CDCl_3$, TMS, δ ppm): 1.56 (s, 3H, CH_3), 2.50 (d, 4H, $-CH_2-$ in cyclobutane ring), 2.89 (s, 3H, CH_3), 3.65 (quint., 1H, $>CH-$ in cyclobutane ring), 5.99 (broad singlet, 1H, $-NH-$), 6.08 ($=CH-$ in thiazole ring), 7.13–7.35 (m, 5H, aromatic). Characteristic ^{13}C NMR peaks ($CDCl_3$, TMS, δ ppm): 34.14 (C_1), 173.50 (C_2), 101.10 (C_3), 159.11 (C_4), 33.03 (C_5), 40.85 (C_6), 42.29 (C_7), 32.10 (C_8), 154.38 (C_9), 127.28 (C_{10}), 130.21 (C_{11}), 126.79 (C_{12}).

*Synthesis of Dithiocarbamate Ligands (**3**,**4**)*

To a solution of 2.44 g (10 mmol) of 4-(1-methyl-1-phenylcyclobutyl-3-yl)-2-aminothiazole **1**, [or in the case of **2**, 2.58 g] in 10 ml of dimethylformamide solvent, 0.56 g (10 mmol) of potassium hydroxide and 0.76 g (10 mmol) of carbon disulfide were added. The mixture was stirred for 1 h at 25–30°C. After cooling to 15°C, the solution was added dropwise to a mixture of 10 ml of ethyl acetate and 100 ml of anhydrous diethyl ether. The solid which separated was collected by filtration, washed with cold ether, and crystallized from tetrahydrofuran–petroleum ether (1:3) to give pale yellow crystals. Yield, color, melting point, elemental analysis results, and characteristic IR bands (NaCl cell, cm^{-1}) are tabulated in Tables 1 and 2. The compounds were found to be highly soluble in DMF, DMSO, and THF, but sparingly soluble in common solvents such as methanol, ethanol, acetone, and $CHCl_3$.

Preparation of Metal Complexes

A quantity of 0.1793 g (0.5 mmol) of the ligand **1** [in the case of ligand **2**, 0.1863 g (0.5 mmol)] was dissolved in 10 ml of water. A solution of 0.25 mmol of each metal salt [$CdCl_2 \cdot H_2O$ (0.0503 g), $CoCl_2 \cdot 6H_2O$ (0.0595 g), $CuCl_2 \cdot 2H_2O$ (0.0426 g), $HgCl_2 \cdot$ (0.0679 g) $NiCl_2 \cdot 6H_2O$ (0.0594 g), or $ZnCl_2$ (0.0341 g)] in 5 ml of water was added dropwise under continuous stirring. In the case of the cobalt complex, nitrogen gas was passed into the reaction vessel. The complexes precipitated immediately, which were filtered off, and washed with water several times and dried in vacuo at 60°C. Yield, color, melting point, elemental analysis results, and characteristic IR bands (NaCl cell, cm^{-1}) are given in Tables 1 and 2.

Preparation of Microbial Cultures

Microorganisms have been provided from the culture collection of the Microbiology Laboratory of Biological Sciences of Science and Art Faculty, Fırat University, Turkey. In this work, *Bacillus subtitis* IMG 22, *Micrococcus luteus* LA 2971, *Escherichia coli* DM, *Staphylococcus aureus* COWAN I bacterias, and *Saccharamyces cerevisiae* UGA 102 and *Candida albicans* CCM 314 yeasts have been used to investigate the bacterological and antifungal activites of ligands and their transition metal complexes.

Bacteria strains have been nourished in Nutrient Broth (Difco) and yeast in Malt Extract Broth (Difco) and incubated for 24 and 48 h, respectively. According to the Disc Diffusion Method, bacterias have been inoculated on Mueller Hinton Agar (oxoid) and yeasts on Saburoud Dextrose Agar. Ligands and their complexes have been dissolved in absolute ethanol in the amount of 50 ppm each and absorbed on the sterile paper antibiotic discs that were placed by pressing gently into petri dishes which were previously inoculated. Prepared samples were left for 1 h at 4°C; bacteria samples were incubated at 32°C for 18–24 h; and yeast samples were incubated at 25°C for 72 h. Ethyl alcohol absorbed discs were used for the control only. The resulting inhibition zones on the plates were measured in millimeters. The data reported in Table 5 are the average data of three experiments.

RESULTS AND DISCUSSION

The synthetic process for the preparation of the cyclobutane-substituted 2-(*N*-R)aminothiazoles and their thiocarbamate derivatives are shown in Scheme 1.

Thus, treatment of 1-phenyl-1-methyl-3-(2-chloro-1-oxoethyl)cyclobutane, which was prepared according to the literature procedure published previously [7], with thiourea, using ethyl alcohol as the solvent, followed by precipitation brought about by addition of an aqueous solution of NH_3 (5%), yields the pale yellow, ethyl alcohol soluble

TABLE 1 Analytical and Physical Data of the Compounds

				Elemental Analyses (%)[a]			
Compound	*Color*	*mp (°C)*	*Yield (%)*	*C*	*H*	*N*	*S*
$L^1K \cdot H_2O$ (3)	Dark yellow	92	65	47.84 (48.10)	4.55 (4.19)	7.44 (7.49)	25.54 (25.76)
$Cd(L^1)_2$	Light brown	140	77	47.96 (48.09)	4.03 (3.83)	7.46 (7.11)	25.60 (25.13)
$Co(L^1)_2$	Dark brown	199	90	51.63 (51.14)	4.33 (3.84)	8.03 (7.82)	27.57 (28.04)
$Cu(L^1)_2$	Dark brown	145	85	51.29 (51.57)	4.30 (3.92)	7.98 (7.77)	27.39 (22.98)
$Hg(L^1)_2$	Black	189[d]	95	42.92 (42.55)	3.60 (3.58)	6.67 (7.01)	22.91 (22.97)
$Ni(L^1)_2$	Dark brown	165	82	51.65 (51.44)	4.33 (4.18)	8.03 (8.13)	27.58 (27.37)
$Zn(L^1)_2$	Dark yellow	158	92	51.16 (51.54)	4.29 (3.95)	7.95 (8.07)	27.31 (27.66)
$L^2K \cdot H_2O$ (4)	Orange	96	83	49.20 (49.39)	4.90 (4.76)	7.17 (7.07)	24.62 (24.42)
$Cd(L^2)_2$	Amber	126	95	49.31 (49.09)	4.40 (4.31)	7.19 (7.39)	24.68 (24.23)
$Co(L^2)_2$	Dark brown	152	90	52.94 (52.64)	4.72 (4.84)	7.72 (7.94)	26.50 (26.44)
$Cu(L^2)_2$	Dark brown	192	93	52.61 (52.57)	4.69 (4.82)	7.67 (8.11)	26.33 (26.68)
$Hg(L^2)_2$	Orange	85	88	44.30 (44.25)	3.95 (3.68)	6.46 (6.07)	22.17 (21.97)
$Ni(L^2)_2$	Dark brown	214	91	52.96 (53.07)	4.72 (4.58)	7.72 (8.15)	26.51 (26.37)
$Zn(L^2)_2$	Amber	98	81	52.48 (52.24)	4.68 (4.95)	7.65 (7.76)	26.26 (26.66)

[a] Values indicate calculated and found (in parentheses) values respectively.

TABLE 2 Infrared Spectral Data of the Ligands and Their Complexes

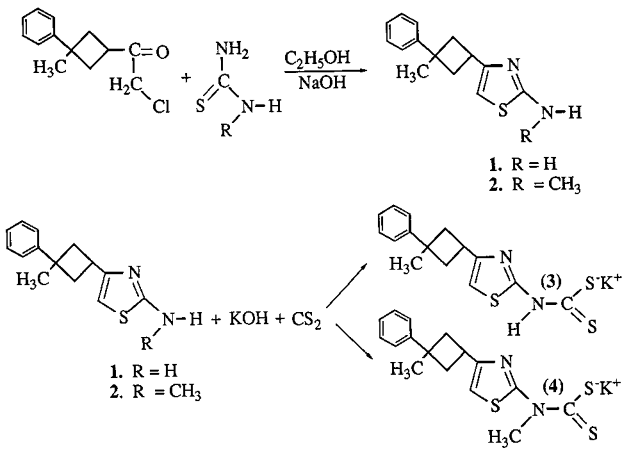
Compound	$\upsilon(H_2O)$	υ(N—H)	υ(C$\overset{\cdots}{-}$N)	υ(C═N)	υ(C—S—C)	υ(C$\overset{\cdots}{-}$S)
L^{1}K · H$_2$O (3)	3464 b	3106 s	–	1625	655 s	987 s
Cd(L^1)$_2$		–	1446 vs	1625	655 s	1000 s
Co(L^1)$_2$		–	1446 vs	1625	655 s	1004 s
Cu(L^1)$_2$			1446 vs	1625	655 s	1010 s
Hg(L^1)$_2$		–	1446 vs	1625	655 s	1010 s
Ni(L^1)$_2$		–	1446 vs	1625	655 s	1004 s
Zn(L^1)$_2$		–	1446 vs	1625	655 s	1008 s
L^{2}K · H$_2$O (4)	3412 b	–	–	1600	685 s	961 s
Cd(L^2)$_2$	–	–	1344 vs	1600	685 s	990 s
Co(L^2)$_2$	–	–	1370 vs	1600	685 s	995 s
Cu(L^2)$_2$	–	–	1370 vs	1600	685 s	995 s
Hg(L^2)$_2$	–		1344 vs	1600	685 s	978 s
Ni(L^2)$_2$	–	–	1370 vs	1600	685 s	985 s
Zn(L^2)$_2$	–	–	1344 vs	1600	685 s	985 s

s: strong; vs: very strong; b: broad.

compound 4-(1-methyl-1-phenylcyclobutyl-3-yl)-2-aminothiazole **1**. For the preparation of 4-(1-phenyl-1-methylcyclobutane-3-yl)-2-(*N*-methyl)aminothiazole **2**, 1-phenyl-1-methyl-3-(2-chloro-1-oxoethyl)-cyclobutane was reacted with *N*-methylthiourea in the same way.

Recently we have described the synthesis and structure elucidation of **1** [8]. For the structural characterization of **2**, ligands **3** and **4**, and the complexes of these ligands, IR,^{1}H, and ^{13}C NMR spectroscopies were used and analytical data of the related compounds are given in the experimental section. Other analytical data are tabulated in Tables 1–4.

The most important infrared spectral bands of the ligands **3** and **4** and their complexes are provided in Table 2. In the spectrum of **3**, the most characteristic absorptions are at 3106 cm^{-1} [υ(—NH—)], 1625 cm^{-1} [υ(C═N) in thiazola ring], 655 cm^{-1} [υ(C—S—C) in thiazole ring], 987 cm^{-1} [υ(C$\overset{\cdots}{-}$S) stretching]. Especially, the band observed at 987 cm^{-1} is characteristic for the (C$\overset{\cdots}{-}$S) bonds of dithiocarbamates [9]. IR absorptions of aromatic and aliphatic groups of **3** appear at 3055 cm^{-1} and 2978–2927 cm^{-1}, respectively, and the positions of these groups were not changed in the case of complexes. The IR spectra of **4** exhibited close comparison with those of ligand **3**, except for —NH— stretching. There is no —NH— absorption in the IR spectra of **4** as expected for the formula given in Scheme 1. Characteristic IR bands of **4** are at 1600 cm^{-1} [υ(C═N) in thiazole ring], 685 cm^{-1} [υ(C—S—C) in thiazole ring], 961 cm^{-1} [υ(C$\overset{\cdots}{-}$S) stretching]. These facts confirm the formation of the expected compounds **3** and **4**, which are also in agreement with their elemental analyses.



SCHEME 1

The ligands L^{1}K and L^{2}K on reaction with Cd(II), Co(II), Cu(II), Hg(II), Ni(II), and Zn(II) salts yielded complexes corresponding to the general formula ML$_2$. The analytical data of all these complexes are presented in Tables 1–4. The metal-to-ligand ratio of all the complexes synthesized was found to be 1:2. The infrared bands observed at 987 and 961 cm^{-1} for each of the ligands, respectively, can be attributed to the υ(C$\overset{\cdots}{-}$S) group vibration. In the complexes, these bands are shifted to higher frequencies (see Table 2), indicating that the C$\overset{\cdots}{-}$S groups take part in complexation [10]. In the spectra of all the complexes, there is a sharp and intensive band, not seen in the free ligands, that is due to υ(C$\overset{\cdots}{-}$N) bonding [11]. This very strong band is seen at 1446 cm^{-1} for L^{1}K ligand complexes and seen in different frequencies (1344–1370 cm^{-1}) for L^{2}K ligand complexes. The band seen at 3106 cm^{-1} for the L^{1}K ligand and assigned to the υ(N—H) vibration disappeared on complexation. In

TABLE 3 Characteristic UV–Vis Bands of the Ligands and Complexes

Compound	*Solvent*	λ_{max} *(nm)*	μ_{eff} *(B.M.)*
$L^1K \cdot H_2O$ (3)	$CHCl_3$	245, 300	–
$Cd(L^1)_2$	$CHCl_3$	217, 300, 355[a], 450[a]	dia[b]
$Co(L^1)_2$	$CHCl_3$	244, 300[a], 331, 385, 510[a], 650	2.47
$Cu(L^1)_2$	$CHCl_3$	248, 301, 360, 425[a], 500[a]	1.80
$Hg(L^1)_2$	$CHCl_3$	245, 300, 355, 500[a]	dia
$Ni(L^1)_2$	$CHCl_3$	245, 260[a], 345, 458	dia
$Zn(L^1)_2$	$CHCl_3$	250, 304, 340[a], 380[a], 490[a]	dia
$L^2K \cdot H_2O$ (4)	$CHCl_3$	245[a], 270, 335[a], 430	–
$Cd(L^2)_2$	$CHCl_3$	247, 270[a], 314, 330[a], 427, 500	dia
$Co(L^2)_2$	$CHCl_3$	245, 300[a], 332, 386, 50[a], 630	2.42
$Cu(L^2)_2$	$CHCl_3$	245, 270[a], 320, 335[a], 453, 650[a]	1.77
$Hg(L^2)_2$	$CHCl_3$	245, 295, 330, 436, 500[a]	dia
$Ni(L^2)_2$	$CHCl_3$	243, 260, 300[a], 337, 449, 505[a]	dia
$Zn(L^2)_2$	$CHCl_3$	245[a], 265, 345, 370[a], 435	dia

[a] Shoulder.
[b] dia: diamagnetic complexes.

general, when investigations of the IR spectra of the complexes are carried out, some IR bands of the ligands either shift to different frequencies or disappear or lose their intensities after complexation. Despite their presence in the ligand and the possibility of complexation by the C═N group and sulfur atoms in the thiazole ring, the unchanged band positions for these groups in the IR spectra of the complexes indicates that the thiazole ring does not complex to the metal.

In order to identify the solution structures of the carbamate ligands, the ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$. The ^{1}H NMR spectral data of L^1K were similar to those of **1** except for the —NH_2 resonance. ^{13}C NMR spectra of the ligand L^1K shows an extra C resonance at 194.6 ppm, supporting the authenticity of the ligand L^1K. Signals due to —NH_2 in **1** and —NH— in L^1K protons disappear in D_2O solution. The ^{1}H NMR spectra of L^2K has the same resonances as those of **2**, which is its starting substance, except for the —NH— resonance. In the ^{1}H NMR spectra of L^2K, the —NH— resonance is not seen. This ligand has also an extra C resonance in its ^{13}C NMR spectra at 195.3 ppm. All these data are also in agreement with the given molecular structure shown in Scheme 1. The ^{1}H NMR spectral data of all the diamagnetic complexes exhibited the same resonances with those of their free ligands.

The electronic spectral bands of all complexes, as well as the spectra of the ligands, are given in Table 3. In the complexes, the low inensity bands in the 650- to 500-nm range are consistent with $d \rightarrow d$ transitions of the metal ions and intraligand $n \rightarrow \pi^*$ transitions [12]. The more intense bands at 450–350 nm in the complexes may be due to the coincidence of charge transfer, $d \rightarrow \pi^*$, $L \rightarrow M$ [13].

TABLE 4 Antimicrobial Effects of the Ligands and Complexes

Compound	*B. subtilis*	*M. luteus*	*S. cerevisiae*	*E. coli*	*St. aureus*	*C. albicans*
$L^1K \cdot H_2O$ (3)	10	9	10	11	10	9
$Cd(L^1)_2$	–	–	8	–	10	–
$Co(L^1)_2$	–	–	–	–	–	–
$Cu(L^1)_2$	–	–	–	–	–	–
$Hg(L^1)_2$	–	–	–	–	–	–
$Ni(L^1)_2$	19	10	10	10	10	9
$Zn(L^1)_2$	14	13	12	14	13	11
$L^2K \cdot H_2O$ (4)	–	–	–	–	–	–
$Cd(L^2)_2$	10	10	12	8	10	14
$Co(L^2)_2$	–	–	–	–	–	–
$Cu(L^2)_2$	–	–	–	–	–	–
$Hg(L^2)_2$	12	–	–	–	–	–
$Ni(L^2)_2$	–	–	–	–	–	–
$Zn(L^2)_2$	–	8	8	–	8	8

The magnetic moments of all of the complexes (Table 3) were measured at room temperature. The Co(II) and Cu(II) complexes are paramagnetic and their magnetic susceptibility values are 2.47 and 1.80 B.M., respectively, which indicate one unpaired electron for each of the ions, Co(II) and Cu(II). These values suggest a square-planar complex geometry for Co(II) and a tetrahedral structure geometry for Cu(II) complexes for L^1K [14]. The Co(II) and Cu(II) complexes of L^2K are also paramagnetic and their magnetic susceptibility values are 2.42 and 1.77 B.M., respectively. These results imply that the Cu(II) complex is of a tetrahedral nature and the Co(II) complex is square-planar [14]. The other complexes of the ligands synthesized are all diamagnetic.

The ligands L^1K and L^2K potasium salts, after loss of their 1 mol. of water of crystallization between 76 and 178°C and 73 and 212°C, respectively, exhibit in the range of 178–429°C and 121–441°C a polysulfide K_2S_3 type, which then undergo oxidation to K_2SO_4 and K_2O in each case. The TGA curves of all complexes show that thermal decomposition of the anhydrous products takes place in several steps. As a result, the observed weight losses for all complexes are in good agreement with the calculated values.

From the above observations, the structure of the complexes are proposed as shown in Fig. 1.

Both ligands and their complexes mentioned above, were screened against six different bacterias and yeasts as described in the experimental section. Results of the testing (Table 4) showed some compounds to be very effective on some of the microorganisms studied. The Co(II), Cu(II), and Hg(II) complexes of L^1K and the L^2K ligand itself and its Co(II), Cu(II), and Ni(II) complexes exhibit no inhibition towards all the microorganisms under the test conditions. However, other complexes of the ligands exhibit inhibition against some microorganisms. The detailed biological activity data are given in Table 4.

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