Bimetallic Complexes of Schiff Base Bis-[4-hydroxycuomarin-3-yl]-[1]N,[5]N-thiocarbohydrazone as a Potentially Dibasic Pentadentate Ligand. Synthesis, Spectral, and Antimicrobial Properties

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The Schiff base bis-[4-hydroxycuomarin-3-yl]-[1]N,[5]N-thiocarbohydrazone, H_2L, was prepared by the reaction of 4-hydroxycoumarine-3-carbaldehyde with thiocabohydrazide in 2:1 molar ratio. The ligand and its binuclear complexes with Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Fe(III) and Cr(III) ions were characterized *via* elemental analysis, ^{1}H NMR, mass spectrometry, infrared, and electronic spectra, as well as room temperature magnetic susceptibilities. Furthermore, the thermal stabilities of two representative complexes were also investigated. The Schiff base and its metal complexes were screened for their antifungal and antibacterial activities against different species of pathogenic fungi and bacteria and their biopotency have been discussed.

INTRODUCTION

Thiosemicarbazones are well established as an important class of sulfur donor Schiff base ligands particularly for transition metal ions [1-3]. This is due to the remarkable biological activities observed for these compounds, which has been shown to be related to their metal complexing ability. Thiosemicarbazones Schiff bases are a class of important compounds in medicinal and pharmaceutical field. They show biological activities including antibacterial [4-10], antifungal [11-14], anticancer [10-19], and herbicidal [12] activities. Furthermore, Schiff bases are utilized as starting materials in the synthesis of industrial [15-20] and biological compounds [14-25].

The chelating behavior, spectral properties and coordination modes of thiosemicarbazones having pyrazolone
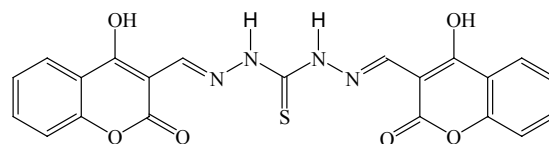

Fig. 1. Structure of the Schiff base, H_2L.

ring as a NNS donor in their structures have already been examined [26,27]. It is known that chelation of metal ions with organic ligands acts synergistically to increase their biological activities [28]. In the present work, we report the synthesis, and binuclear metal complexes of N,N'-thiocarbohydrazone bis(4-hydroxycoumarine) (H_2L, Fig. 1) with the object of gaining more information about their nature of coordination and related structural and spectral properties as well as their antimicrobial properties.

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EXPERIMENTAL

Materials

The chlorides salts of Cu(II), Ni(II), Zn(II), Co(II), Zn(II), Cr(III) and Fe(III) were obtained from BDH. Hydrazine hydrate, carbon disulphide, carbon tetrachloride, DMF, acetic acid and hydrochloric acid were either from BDH or Merck. Chromone-3-carbamide was synthesized as described elsewhere [29].

Synthesis of H$_2$L

Synthesis of 4-hydroxycoumarin-3-carbaldehyde (I). The preparation was carried out according to a previously reported method [30]. Chromon-3-carbamide (6.4 g, 20 mmol) was added gradually to a solution of KOH (200 ml, 1 M). The mixture was stirred for 15 min then acidified with concentrated HCl until complete precipitation. The precipitated solid was filtered off, washed with 10 ml distilled water, 5 ml ethanol and finally with diethyl ether and then recrystallized from petroleum ether, 100-120 (yield 84% and m.p.: 137 ^{o}C).

Synthesis of thiocarbohydrazide (TCH) (II). Carbon disulphide (5 ml) was added gradually to 20 ml hydrazine hydrate (80%). The reaction mixture was refluxed for 30 min. The reaction mixture was cooled in a water bath for further 30 min and the yellow precipitate formed was filtered off and washed several times with ethanol followed by diethyl ether. The white crystals were then recrystallized from the least amount of water and dried over anhydrous CaCl$_2$ and collected (yield 80%, m.p.: 171 ^{o}C).

Synthesis of H$_2$L. The ligand was prepared by the following general method. A hot solution of (**I**) (1.9 g, 10 mmol) dissolved in 20 ml ethanol was added to thiocarbohydrazide (TCH) (**II**) (5.3 g, 5 mmol) dissolved in the least amount of ethanol-water mixture (10/5 v/v). The reaction mixture was left under stirring while it is hot for 30 min and then allowed to cool. The deep yellow crystals formed were filtered off, washed several times with hot ethanol and finally dried over anhydrous CaCl$_2$ for 24 h. (yield 65%, m.p.: 280 ^{o}C). The proposed chemical structure of the thiocarbazone ligand was found to be in good agreement with the ratios concluded from analytical data (Table 1).

Synthesis of Metal Complexes

A general method has been used for the preparation of the binuclear complexes by the reaction of the metal salts and the Schiff base ligand at a metal-to-ligand molar ratio of 2:1 (10 mmol dissolved in 10 ml ethanol). The mixture was heated on a water bath to ensure complete dissolution of the metal salt. To this solution, the ligand (2.2 g, 5 mmol dissolved in 10 ml ethanol) was added gradually. The reaction mixture was refluxed for 3 h with constant stirring. The precipitated colored solid complexes were filtered off, washed several times with 50% (v/v) ethanol-water mixture to remove any traces of the unreacted starting materials, then washed with diethyl ether and dried in vacuum over CaCl$_2$. The structural features and properties of the resulting solid metal complexes are shown in Table 1.

Physical Measurements and Analyses

Reflectance spectra of the ligand and its metal complexes were recorded as BaSO$_4$ discs using a model 1601 Shimadzu UV-Vis spectrophotometer in the range 190-1100 nm. The solution of the ligand, in ethanol was recorded on a Jasco V-550 UV-Vis spectrometer in the range 200-900 nm. The IR spectra were recorded as CsI discs using a FT-IR 4000 Perkin Elmer Spectrometer. The ^{1}H NMR spectra were carried out in DMSO-d$_6$ at room temperature using TMS as internal standard on a Brucker 250 MHz spectrometer. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a model MK1 Johnson Matthey. Alpha products magnetic susceptibility balance. The effective magnetic moments were calculated using the relation:

$$\mu_{eff} = 2.828 \, (\chi_m \, T)^{\frac{1}{2}} \text{ B.M.}$$

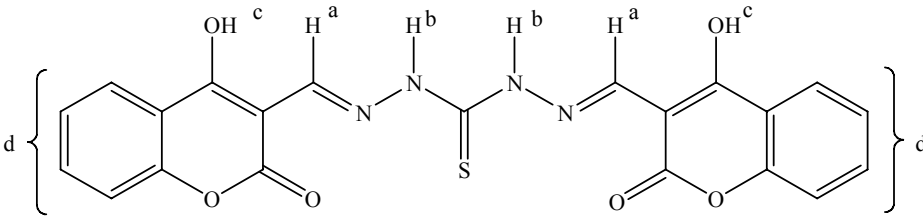where χ_m is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds.

The TG-DTA measurements were carried out on a Shimadzu thermogravimetric analyzer in dry nitrogen atmosphere and a heating rate of 10 ^{o}C min^{-1} using the TA-50 WS1 program. Mass spectra were recorded at 70 eV and 300 ^{o}C on an MS 5988 Hewlett-Packard mass spectrometer. Conductivities were measured in DMF solutions of the complexes (10^{-3} M) using a model LBR, WTWD-812 Wilhelm

Table 1. Elemental Analyses, Color, Yield, Melting Points and Molar Conductance of H_2L and its Metal Complexes

Compound	F.W.	Color	Yield (%)	M.p. (°C)	Elemental analysis, Found/(Calcd) %						EC^a
					C	H	N	Cl	S	M	
H_2L $C_{21}H_{14}N_4O_6S$	450	Deep orange	65	280	56.47 (56.00)	3.44 (3.11)	12.64 (12.44)	-	7.41 (7.11)	-	-
(**1**)$[(L)Cu_2Cl_2].H_2O$ $C_{21}H_{14}N_4O_7Cl_2SCu_2$	666	Green	53	247 (decomp)^b	38.10 (37.84)	2.45 (2.10)	8.81 (8.41)	11.01 (10.66)	5.10 (4.80)	19.73 (19.37)	10.22
(**2**)$[(L)Ni_2Cl_2(OH_2)_2].H_2O$ $C_{21}H_{22}N_4O_{11}Cl_2SNi_2$	655	Pale Green	45	220 (decomp)	38.81 (38.45)	3.81 (3.36)	8.86 (8.54)	11.12 (10.83)	4.47 (4.88)	18.21 (17.91)	7.44
(**3**)$[(L)Zn_2Cl_2(OH_2)_2].H_2O$ $C_{21}H_{22}N_4O_{11}Cl_2SZn_2$	669	Yellow	50	254 (decomp)	(38.12) (37.68)	3.82 (3.29)	8.83 (8.37)	11.05 (10.62)	4.39 (4.78)	19.76 (19.44)	6.24
(**4**)$[(L)Co_2Cl_2(OH_2)_2].H_2O$ $C_{21}H_{22}N_4O_{11}Cl_2SCo2$	656	Yellowish Green	47	250 (decomp)	38.85 (38.41)	3.63 (3.35)	9.01 (8.54)	11.20 (10.82)	5.02 (4.88)	18.30 (17.99)	9.24
(**5**)$[(L)Mn_2Cl_2(OH_2)_2].H_2O$ $C_{21}H_{22}N_4O_{11}Cl_2SMn_2$	648	Deep brown	44	260 (decomp)	39.12 (38.89)	3.60 (3.40)	8.43 (8.64)	11.20 (10.96)	5.23 (4.94)	16.58 (16.98)	9.34
(**6**)$[(L)Fe_2Cl_4(OH_2)_2].H_2O$ $C_{21}H_{18}N_4O_9Cl_4SFe_2$	756	Reddish brown	46	264 (decomp)	33.73 (33.33)	3.10 (2.38)	7.21 (7.41)	19.21 (18.78)	4.53 (4.23)	15.23 (14.81)	8.54
(**7**)$[(L)Cr_2Cl_4(OH_2)_2].2H_2O$ $C_{21}H_{20}N_4O_{10}Cl_4SCr_2$	766	Green	48	275 (decomp)	32.53 (32.90)	3.10 (2.61)	7.21 (7.31)	18.21 (18.54)	4.53 (4.18)	14.04 (13.58)	8.44

^{a}EC = Electrical Conductance, 10^{-3} M solution in DMF, Ohm^{-1} cm^2 mol^{-1}. ^{b}(decomp.) = decomposed.

Table 2. ^{1}H NMR Data of the Ligand in DMSO-d_6

Chemical shift, δ_{TMS} (ppm)	Assignment
6.50	s, 2H (a)
11.29	s, 2H (b)
15.17	s, 2H (c)
7.20-7.72	m, 8H (d) couramine

S = singlet, m = multiplet.

Conductivity meter fitted with a model LTA100 cell. Analyses of the metal content of the complexes were carried out after their decomposition in concentrated nitric acid. The resulting solutions were diluted with distilled water and filtered to remove the precipitated ligand. The solutions were then neutralized with aqueous ammonia solution and the metal ions were titrated with EDTA. Microanalyses of carbon, hydrogen, nitrogen and chlorine were carried out in the Micro analytical Center, Cairo University, Giza, Egypt.

Screening of Antibacterial and Antifungal Activities

The *in vitro* evaluation of antimicrobial activity was performed according to the diffusion technique [31-33]. The bacteria including *Staphylococcus aureus* and *Escherichia coli* were grown in nutrient broth at 37 ºC for 24 h. *Candida albicans* and *Fusarium solani* were grown in malt broth at 28 ºC for 48 h. The ligand and its complexes were tested using the diffusion technique on solid media [31-33]. Sterile (5 mm) diameter sensitivity discs were impregnated with different concentrations of the compounds in DMF (50 μg or 100 μg ml^{-1}). Discs of each tested compound were laid onto nutrient agar for bacteria or potato dextrose agar for fungi. Plates were surface spread with 0.2 ml of logarithmic phase bacteria or fungi cultures. A 0.5 ml spore suspension (10^8 spores ml^{-1}) for bacteria or for filamentous fungi was also spread onto potato dextrose agar plates. The plates were then incubated for 24 h at 37 ºC for bacteria and 28 ºC for 48 h for fungi. Additionally

antibiotic discs for Cephalosporin and/or Streptomycin were tested as positive control. The results were recorded by measuring the zones of growth inhibition surrounding the discs.

RESULS AND DISCUSSION

The Schiff base ligand H_2L is expected to act as a pentadentate ligand, the possible coordination sites being coumarin-carbonyl, thione, azomethine-nitrogen, imine-nitrogen and the phenolic-oxygen. A study and comparison of the IR spectra of the ligand and its metal complexes imply that the Schiff base behaves as a dibasic pentadentate ligand with two phenolic-oxygens, two azomethine-nitrogens, and a thione group, as a $(ON)_2S$ ligand. The present thiocarbazone ligand exists in its thione form, since it has a -NH-C=S thio amide group; although, in many instances, the thiol form or a equilibrium mixture of both forms has been observed in thiosemicarbazones.

The ^{1}H NMR data of the ligand are collected in Table 2. The spectra showed two signals at chemical shifts 15.17 and 11.29 ppm for the protons of the phenolic OH and the NH groups, respectively [34,35]. A signal is also observed at 6.50 ppm corresponding to the hydrazide CH. The protons of the coumarine moiety observed in the range of 7.20-7.72 ppm [34,35]. Addition of D_2O results in diminishing the signals due to the protons of phenolic OH and HN-N groups. The signal

Table 3. Characteristic IR Bands (cm^{-1}) of the H_2L and its Metal Complexes

Compound	ν(C=N)	ν(N-H)	ν(N-N)	ν(C=S)	ν(C=O)	ν(OH), H_2O	ν(M-O)	ν(M-N)	ν(M-S)	Other bands
H_2L $C_{21}H_{14}N_4O_6S$	1600 s	3270 m	1120 s	876	1740	3332 (phenolic)	-	-	-	δ(COH)ip 1345
(**1**)[(L)Cu$_2$Cl$_2$].H$_2$O $C_{21}H_{14}N_4O_7Cl_2SCu_2$	1610 s	3265 m	1136 s	829	1735	3450 m, br coordinated water	560 m	420 w	395 m	-
(**2**)[(L)Ni$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SNi_2$	1625 m	3268 m	1137 w	820	1740	3450 m, br coordinated water	540 m	425 w	375 m	-
(**3**)[(L)Zn$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SZn_2$	1635 m	3270 s	1140 w	829	1739	3455 m, br coordinated water	545 m	430 w	390 m	-
(**4**)[(L)Co$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SCo2$	11610 m	3269 s	1125 w	839	1738	3436 m, br coordinated water	555 m	410 w	385 m	-
(**5**)[(L)Mn$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SMn_2$	1615 m	3268 s	1136 s	850	1740	3438 m, br coordinated water	560 w	445 w	395 m	-
(**6**)[(L)Fe$_2$Cl$_4$(OH$_2$)$_2$].H$_2$O $C_{21}H_{18}N_4O_9Cl_4SFe_2$	1620 m	3270 s	1140 w	820	1735	3430 m, br coordinated water	555 w	445 w	375 m	-
(**7**)[(L)Cr$_2$Cl$_4$(OH$_2$)$_2$].2H$_2$O $C_{21}H_{20}N_4O_{10}Cl_4SCr_2$	1625 m	3269 s	1140 w	820	1738	3435 m, br coordinated water	557 w	446 w	377 m	-

S = strong, w = weak, m = medium, br. = broad.

Table 4. Magnetic Moment, Electronic Spectral Data (nm) for H_2L and its Metal Complexes

Compound	$\mu_{eff.}$[a] B.M.	μ_{compl}[b] B.M.	Charge transfer (nm)	d → d (nm)
H_2L $C_{21}H_{14}N_4O_6S$	-	-	279, 300, 353, 364, 382, 309	-
(**1**)[(L)Cu$_2$Cl$_2$].H$_2$O $C_{21}H_{14}N_4O_7Cl_2SCu_2$	1.83	2.82 (3.66)	240, 311, 325, 348	665
(**2**)[(L)Ni$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SNi_2$	2.88	4.44 (5.71)	240, 315, 327, 348, 355	737, 659
(**3**)[(L)Zn$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SZn_2$	-	-	269, 310, 353, 364, 385, 309	-
(**4**)[(L)Co$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SCo2$	5.2	7.52 1(10.4)	239, 315, 327, 350, 359	656, 675, 414, 477
(**5**)[(L)Mn$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SMn_2$	5.9	7.39 (11.80)	245, 315, 330, 352, 365	469-853
(**6**)[(L)Fe$_2$Cl$_4$(OH$_2$)$_2$].H$_2$O $C_{21}H_{18}N_4O_9Cl_4SFe_2$	5.9	7.49 (11.80)	233, 315, 327, 350, 355, 396	722
(**7**)[(L)Cr$_2$Cl$_4$(OH$_2$)$_2$].2H$_2$O $C_{21}H_{20}N_4O_{10}Cl_4SCr_2$	3.8	4.85 (7.60)	233, 315, 327, 350, 355, 396	592, 396

[a] $\mu_{eff.}$ is the magnetic moment of only one cationic species in the complex. [b] $\mu_{compl.}$ is the magnetic moment of the complex. In parentheses are given the expected values calculated by adding known susceptibilities of the metal cations present in the suggested structures of the complexes.

due to the S-H (thiol) is not observed in the expected range of 2-3 ppm [34,35] indicating that the ligand exists in its thione form.

As summarized in Table 4, the UV-Vis spectrum recorded for an ethanolic solution of ligand showed absorption bands at 279, 300 nm assigned for π-π* transitions within the coumarine and hydrazide CH. The bands observed at 353 and 364 nm are attributed to the n-π* transition of the azomethine C=N and coumarine C=O, respectively. The absorption bands at 382 and 390 nm assigned for the CT transitions which encroaches on the visible region and impact the ligand's color [34,35]. The mass spectrum of the ligand showed its molecular ion at m/e of 450 (15%) which coincide with formula weight. The base peak observed at m/e of 198 corresponded to the $[C_{10}H_7NO_3]^+$ ion. Metastable ion(s) is/are not observed [34].

All the complexes have shown good solubility in all common organic solvents but were found insoluble in ether, water, acetone and benzene. All the complexes are amorphous powders, stable at room temperature and do not show any

decomposition on standing for several months. The molar conductance values of the complexes in DMF are presented in Table 1. The values are too low to account for any dissociation; therefore, the complexes are considered to be nonelectrolytes [36].

Elemental Analyses and Infrared Spectra

The elemental analysis data of the metal complexes obtained (Table 1) are in agreement with the formula given. The binding mode of the ligand to metal ions was further elucidated by analysis of the IR spectra of ligand and its metal complexes. A study and comparison of infrared spectra of the free ligand and its metal complexes (Tables 3) imply that this Schiff base behaves as a dibasic pentadentate ligand and each metal ion is coordinated through the deprotonated oxygen atoms of the phenolic group, the nitrogen atoms of azomethines and the sulfur atom of thio-keto group.

The IR spectra of metal complexes revealed that the absorption bands associated with the v(O-H) stretching of the

phenolic groups (observed at 3332 cm^{-1} in the free ligand) disappeared in all spectra, indicating the loss of phenolic protons on complexation and thus forming a metal-oxygen bond. The δ(COH)ip mode, which appeared at 1345 cm^{-1} in the spectrum of the ligand, was not observed in the spectra of the complexes and thus supported the suggestion that the ligand coordinates to the metal ion through its deprotonated form. The presence of coordinated water was suggested by the very broad absorption centered around 3450 cm^{-1} in the infrared spectra. Bands at 930 and 770 cm^{-1} may attributed to rocking and wagging modes of the coordinated water [37].

Furthermore, the strong bands observed at 3270 and at 1740 cm^{-1} region in the free ligand are assigned to ν(NH) and ν(C=O)$_{coumarine}$ vibrations, respectively. Practically no effect on these frequencies after complexation was observed, indicating the noninvolvement of these groups in coordination with the metal ion. The most notable change in the ligand spectral features when coordinated to metal ion is the observed C=N red shift. The ν(C=N) band at 1660 cm^{-1} [38,39] in the ligand spectrum exhibited a red shift of 50-40 cm^{-1} in the spectra of the complexes. This finding may be taken as an evidence for the participation of C=N group in coordination to the metal ions.

A medium band at 1120 cm^{-1}, which is assigned to ν(N-N) in ligand, is shifted to a higher frequency in the spectra of all complexes. This kind of shift on hydrazinic nitrogen describes the presence of electron withdrawing groups [40]. A strong band at 876 cm^{-1} in ligand is mainly due to the (C=S) stretching vibration which shifted towards lower frequencies and occurred at 850-820 cm^{-1} in metal complexes, indicating the coordination of thione sulfur to metal atom [40]. This also describes a considerable change in bond order and a metal-sulfur bond.

The possibility of thione (H-N-C=S)-thiol (C=N.SH) tautomerism in this ligand has been ruled out from the fact that no band is observed around 2700-2500 cm^{-1}, which are characteristic of thiol group in the infrared absorption [41,42]. The new bands observed at 560-375 cm^{-1} are tentatively assigned to ν(M-O), ν(M-N) and ν(M-S) (metal-ligand) stretching bands [43-45]. In conclusion, the infrared spectral studies suggested the dibasic pentadentate nature of the ligand with (ON)$_2$S coordination sites. This was accounted for as the ligand contains two phenolic, two azomethine and one thione groups.

^{1}H NMR and Mass Spectra of Zn(II)-Complex

The ^{1}H NMR spectrum of diamagnetic binuclear Zn(II) complex showed the disappearance of the signal due to the phenolic proton, which is attributed to its involvement in coordination with the zinc ion. The signal due to the NH proton is remaining and appeared at 6.5 ppm, indicating the noninvolvement of the nitrogen atom of this group in coordination. The signals due to the protons of the hydrazide C=H and cuomarine groups remained unchanged as observed in the parent ligand. Also, the spectrum showed an additional signal at 3.9 ppm due to the coordinated water molecule.

Moreover, the mass spectrum of binuclear Zn(II) complex, (3), which was chosen as a representative example of this type of complexes, show a peak at m/e of 651 (8.5%) corresponding to the $[(L)Zn_2Cl_2(OH_2)_2]^+$ ion. The molecular ion (m/e = 669) does not appeared, may be due the loss of a lattice molecule water in the ionization chamber, in accordance with the results obtained from the thermal analysis. Also, the spectrum exhibited fragments at m/e of 616 (20%) and 480 (66%) corresponding to the $[(L)Zn_2Cl_2]^+$ and $[C_{20}H_{20}N_4O_{11}Zn_2]^+$ ions, respectively. The base peak fragment observed at m/e of 288 corresponds to the $[C_{10}H_8N_2O_5Zn]^+$ ion, in agreement with the results of thermal analysis.

Magnetic Moments and Electronic Spectral Data of the Metal Complexes

Electronic spectra and magnetic moments data of the metal complexes are listed in Table 4. Generally, in all spectra of the metal complexes, the π-π* and n-π* absorption bands of the free ligand have shifted to lower frequencies upon the coordination of ligand with metal ions.

The spectrum of the Cu(II) complex (Table 4) showed absorption bands at 240, 311, 325 and 665 nm. The first four bands are due to the ligand absorption, which are shifted from those of the parent ligand upon complex formation. The band at 665 nm is due to $^2A_{1g} \rightarrow {}^2B_{1g}$ d-d transition which characterizes the Cu(II) ion in a square-planar geometry [46-48]. The shift of the $d \rightarrow d$ absorption band to a lower energy than that expected for a square-planar geometry (e.g., 550 nm for square-planar N,N'-ethylene-bis(salicylideneimine) copper(II)) [49] may be due to the distortion of the square-

planar geometry towards tetrahedral [46-48]. The observed magnetic moment of this complex (Table 1) is 2.82 BM. This value is lower than the expected value for the two Cu(II) ions involved, most possibly because of antiferromagnetic interactions between the adjacent Cu(II) ions in the complex. The square-planar geometry is achieved by the coordination of the two Cu(II) ions with a single ligand molecule, each through $(ON)_2S$ coordination sites, and the chloride ions [46-48].

The reflectance spectrum of the binuclear Ni(II) complex showed a diffuse band at 659-837 nm, indicating the fact that each Ni(II) ion is coordinated to the ligand through $(ON)_2S$ sites in an octahedral geometry [46-48]. Each Ni(II) ion completes its six-coordination sphere by two water molecules and chloride ions. The magnetic moment of this complex is 4.44, which is smaller than the calculated value for two Ni(II) ions in a octahedral geometry, indicating the possible antiferromagnetic interactions between adjacent Ni(II) ions in the complex [46-48].

The octahedral, tetrahedral and square-planar cobalt(II) complexes are reported to have magnetic moments between 4.9-5.2, 4.2-4.8 and 2.2-2.9 B.M., respectively [46-48]. The $\mu_{eff.}$ values for the present Co(II) complex is 7.52 B.M., which is smaller than the calculated value for two Co(II) ions in an octahedral geometry, indicating the possible antiferromagnetic interactions between adjacent Co(II) ions in the complex. The reflectance spectra of complex showed the $^4T_{1g}(F) \rightarrow \,^4A_{2g}(F)$ d-d transition at 656 and 675 nm, respectively. The two shoulders observed at 414 and 477 nm may be due to $^4T_{1g}(F) \rightarrow \,^4A_{2g}(P)$ transition indicating that the Co(II) ion possesses an octahedral geometry. Here, each Co(II) ion completes its six-coordination sphere by two water molecules and chloride ions.

The spectrum of binuclear Mn(II) complex showed a series of weak bands in the range 469-853 nm. These bands are both Laporte and spin-forbidden. Such weak bands sometimes appear due to the instantaneous distortion of octahedral structures around the metal cations [46-49]. The magnetic moment of the complex is 7.39 B.M., indicating the antiferromagnetic interaction between the adjacent metal cations.

On the other hand, the electronic spectrum of Fe(III) complex showed broad bands 577 and 722 nm. The former band may be due to the spin forbidden $^6A_{1g} \rightarrow \,^4T_{2g}(G)$ transition, which may gain intensity as a result of the vibronic mechanism in the octahedral field around ferric ion. The second bands may be attributed to $^6A_1 \rightarrow \,^4T_1(G)$ transitions [50]. In addition, a third absorption band with a high intensity observed at 396 nm assigned for charge transfer transition. The magnetic moment of complex is 7.49 B.M., which is quite low compared to the calculated magnetic moment value for a binuclear ion complex [49-52].

The reflectance spectrum of the binuclear Cr(III) complex showed two broad bands at 592 and 396 nm, besides the bands due to the ligand adsorptions. The observed bands at 592 and 396 nm may be due to $^4A_{2g} \rightarrow \,^4T_{2g}$ and $^4A_{2g} \rightarrow \,^4T_{1g}$ electronic transitions, respectively [51-53]. The $^4A_{2g} \rightarrow \,^4T_{1g}(P)$ transition would be in the UV region and overlapped by ligand transitions. The magnetic moment of the complex is 4.85 B.M., where the expected value for $\mu_{eff.}$ of a single Cr(III) ion in its octahedral complexes is 3.80 B.M. Thus, it seems that there is an antiferromagnetic exchange between the two Cr(III) ions in the complex.

The spectra of the diamagnetic Zn(II) complexes are dominated only by the ligand bands [45]. The magnetic moment values of all complexes are lower than the values excepted for metal complexes containing two metal cations [48]. This can be explained on the bases of antiferromagnetic interactions [48,51,52]. An anti-ferromagnetic interaction acts to anti-align neighboring spins. If the energy is expressed as the sum of all pairs of the two metal ions, M_i and M_j over an interaction term $J(M_i,M_j)$, times the spin of atom M_i times the spin of atom M_j, $J < 0$ is a ferromagnetic interaction and $J > 0$ is an antiferromagnetic interaction. The combination of both can lead to spin-glass behavior [48]. Unlike ferromagnetism, the anti-ferromagnetic interactions can lead to multiple optimal states (ground states-states of minimal energy) between the adjacent metal atoms which results in lower overall magnetic moments of the binuclear complexes [48,51,52].

Thermal Analyses

Generally, there is less known about the thermal properties of transition metal complexes of thiocarbazones [3,54-58]. In the present work, we report the thermal decomposition data for two representative complexes (**1**) and (**3**) and the results are presented in Table 5. The thermogravimetric results suggested

Table 5. Thermal Decomposition Data for $[(L)Cu_2Cl_2].H_2O$, (1), and $(L)Zn_2Cl_2(OH_2)_2].H_2O$, (3) Complexes

Complex	Stage of decomp.	Reaction	Peak Temp. in DTG (^oC)	Temp. range in DTG (^oC)	Peak Temp. in DTA (^oC)
(1) $[(L)Cu_2Cl_2].H_2O$ $C_{21}H_{14}N_4O_7Cl_2SCu_2$	I	$[(L)Cu_2Cl_2].H_2O \rightarrow [(L)Cu_2Cl_2] + H_2O$	125	95-150	120 (endo)
	II	$[(L)Cu_2Cl_2] \rightarrow H_2CS + Cl_2 + (C_{20}H_{12}N_4O_7Cu_2)$	350	320-420	550 (exo)
	III	$(C_{20}H_{12}N_4O_7Cu_2) \rightarrow 2CuO$	730	680-770	740 (exo)
(3) $[(L)Zn_2Cl_2(H_2O)_2].H_2O$ $C_{21}H_{22}N_4O_{11}Cl_2SZn_2$	I	$[(L)Zn_2Cl_2(H_2O)_2].H_2O \rightarrow [(L)Zn_2Cl_2(H_2O)_2] + H_2O$	135	95-150	125 (endo)
	II	$[(L)Zn_2Cl_2(H_2O)_2] \rightarrow [(L)Zn_2Cl_2] + 2H_2O$	150	125-220	180 (endo)
	III	$[(L)Zn_2Cl_2] \rightarrow H_2CS + Cl_2 + (C_{20}H_{20}N_4O_{11}Cu_2)$	420	390-560	550 (exo)
	IV	$(C_{20}H_{20}N_4O_{11}Zn_2) \rightarrow 2ZnO$	730	680-770	740 (exo)
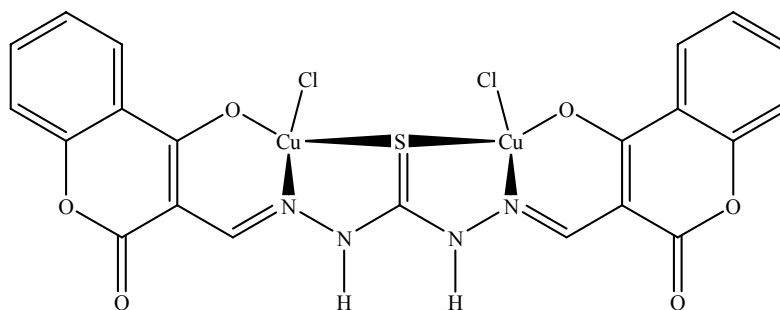
Square-planar Cu(II)-complex (**1**)
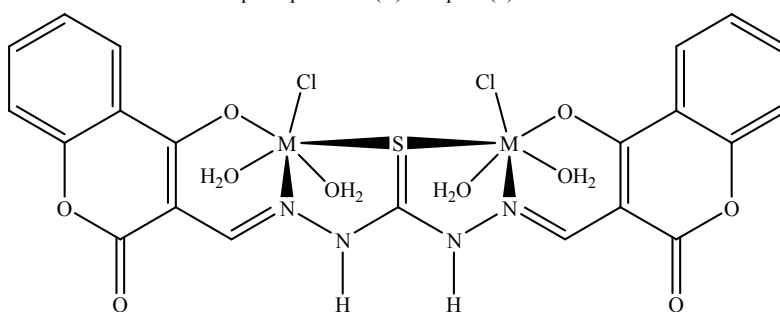
Octahedral complexes (**2-5**)
(M = Ni(II), Zn(II), Mn(II), or Co(II))
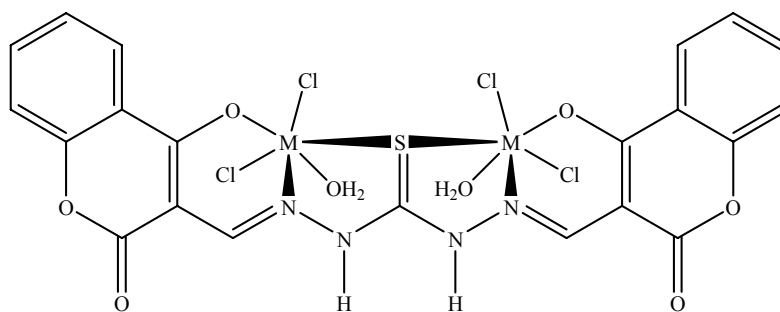
Octahedral complexes (**6,7**)
(M = Fe(III) or Cr(III))

Fig. 2. Suggested structures of the metal complexes.

that both complexes contain one lattice water molecule, which is evident by a weight loss at ~120 ºC. Complex (**3**) showed a second decomposition step at 180 ºC where the complex losses 2 coordinated water molecules. After that, both complexes loss one H_2S molecule and on Cl_2 molecule in a single step at ~250 ºC. There is no change between 250~400 ºC and, after that, the rest of the organic ligand began to decompose at ~550 ºC. Finally, at ~760 ºC, metal oxides are formed [56-58]. Based on the above results, the structures in

Fig. 2 are suggested for the metal complexes.

Antimicrobial Activities

The Schiff base and its metal complexes were evaluated for antimicrobial activity against one strain Gram positive bacteria (*Staphylococcus aureus*) (**a**), Gram negative bacteria (*Escherichia coli*) (**b**), fungus (*Candida albicans*) (**c**) and fungus *Fusarium solani* (**d**) and the results are summarized in Table 6. The Schiff base ligand was found to be biologically

Table 6. Antimicrobial Activity of the Schiff base Ligand and its Metal Complexes

Compound	Microbial species			
	(a)	**(b)**	**(c)**	**(d)**
HL $C_{16}H_{12}N_3Cl$	+++	++	+++	+++
(**1**)[(L)Cu$_2$Cl$_2$].H$_2$O $C_{21}H_{14}N_4O_7Cl_2SCu_2$	+++	+++	++	+++
(**2**)[(L)Ni$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SNi_2$	++++	+++	++	++
(**3**)[(L)Zn$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SZn_2$	+++	++	+++	+++
(**4**)[(L)Co$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SCo2$	++++	+++	++++	+++
(**5**)[(L)Mn$_2$Cl$_2$(OH$_2$)$_2$].H$_2$O $C_{21}H_{22}N_4O_{11}Cl_2SMn_2$	++++	+++	+++++	++++
(**6**)[(L)Fe$_2$Cl$_4$(OH$_2$)$_2$].H$_2$O $C_{21}H_{18}N_4O_9Cl_4SFe_2$	+++	+++	++	++
(**7**)[(L)Cr$_2$Cl$_4$(OH$_2$)$_2$].2H$_2$O $C_{21}H_{20}N_4O_{10}Cl_4SCr_2$	++++	++++	+++	++++
Cephalosporin[e]	++++	+++	+++	++++
Streptomycin[f]	++++	+++	+++	++

(**a**) *S. aureus*. (**b**) *E. coli*. (**c**) *Candida. Albicans*. (**d**) *Fusarium solani*. [e]Standard antifungal and [f]antibacterial agents. Inhibition zone diameter in nm (%inhabitation): (+) 8-10 (36-45%); (++) 10-16 (45-73%); (+++) 16-19 (73-86); (++++) 19-22 (86-100%). Percent inhabitation values are relative to inhabitation zone (22 mm) with 100% inhabitation.

active and their metal complexes enhanced antimicrobial activity against one or more strain. Remarkable result is that the complexes (**4**), (**5**) and (**7**) showed 100% inhibition against *Staphylococcus aureus* (**a**), *Candida albicans* (**c**) and *Fusarium solani* (**d**), respectively. It is known that chelation tends to make the ligand a more powerful and potent bactericidal agent. A possible explanation for the observed increased activity upon chelation is that the positive charge of the metal in chelated complex is partially shared with the ligand's donor atoms so that there is an electron delocalization over the whole chelate ring. This, in turn, will increase the lipophilic character of the metal chelate and favors its permeation through the lipoid layers of the bacterial membranes. Generally, it is suggested that the chelated complexes deactivate various cellular enzymes, which play a

vital role in various metabolic pathways of these microorganisms. Other factors such as solubility, conductivity and dipole moment which affected by the presence of metal ions, may also be possible reasons for increasing the biological activity of the metal complexes as compared to the corresponding ligand [33].

CONCLUSIONS

The results of this study clearly indicated that thiocarbazone is coordinated to metal ions as a dibasic pentadentate (ON)$_2$S ligand. The magnetic and electronic spectral studies suggested a square-planar geometry for the Cu(II) complex and octahedral configurations for the other metal complexes, namely, Ni(II), Zn(II), Co(II), Mn(II),

Cr(III) and Fe(III) ions. The resulting metal complexes enhanced the antimicrobial activity of the free ligand.

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