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Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis, Characterization and Antifungal Activity of Metal Complexes of 2-(5-((2-Chlorophenyl)Diazenyl)-2-Hydroxybenzylidene) Hydrazinecarbothioamide

Abdou S. El-Tabl^a, Mohamad M. E. Shakdofa^{bc}, Ahmed M. A. El-Seidy^{bd} & Ahmed N. Al-Hakimi^e

^a Department of Chemistry, Faculty of Science , Menoufia University , Shebin El-Kom , Egypt

^b Inorganic Chemistry Department, National Research Center, Cairo, Egypt

 $^{\rm c}$ Department of Chemistry, Faculty of Science and Arts, Khulais , King Abdulaziz University , Saudi Arabia

^d Chemistry Department, Faculty of Science , The Imam Muhammad bin Saud Islamic University , Riyadh , Saudi Arabia

 $^{\rm e}$ Department of Chemistry, Faculty of Science , Ibb University , Ibb , Yemen

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SYNTHESIS, CHARACTERIZATION AND ANTIFUNGAL ACTIVITY OF METAL COMPLEXES OF 2-(5-((2-CHLOROPHENYL)DIAZENYL)-2-HYDROXYBENZYLIDENE) HYDRAZINECARBOTHIOAMIDE

Abdou S. El-Tabl,¹ Mohamad M. E. Shakdofa,^{2,3} Ahmed M. A. El-Seidy,^{2,4} and Ahmed N. Al-Hakimi⁵

 ¹Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt
 ²Inorganic Chemistry Department, National Research Center, Cairo, Egypt
 ³Department of Chemistry, Faculty of Science and Arts, Khulais, King Abdulaziz University, Saudi Arabia
 ⁴Chemistry Department, Faculty of Science, The Imam Muhammad bin Saud Islamic University, Riyadh Saudi Arabia
 ⁵Department of Chemistry, Faculty of Science, Ibb University, Ibb, Yemen

GRAPHICAL ABSTRACT



Abstract New metal complexes of Co(II), Cu(II), Ni(II), Zn(II), Mn(II), Fe(III), Ru(III), $UO_2(II)$, and VO(II) with the Schiff base, 2-(5-((2-chlorophenyl)diazenyl)-2-hydroxybenzylidene) hydrazine-carbothioamide (H_2L) have been prepared and characterized by elemental and thermal analyses, FT-IR, UV–Vis, mass spectra, ¹H-NMR, and ESR as well as conductivity and magnetic moments measurements. The IR spectra showed that the ligand acts as neutral tridentate, neutral bidentate or monobasic tridentate ligand.

Address correspondence to Abdou S. El-Tabl, Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt. E-mail: asaeltabl@yahoo.com

The geometries of metal complexes were either octahedral or square pyramidal. The ESR spectra of the solid copper(II) complexes indicated an axial symmetry type of a $d_{(x^2,y^2)}$ ground state with considerably ionic or covalent environment. The effect of the presence of an azo group on the biological activity of the ligand was investigated. The ligand and its complexes are biologically inactive due to the presence of azo group.

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the related elements to view the free supplemental file.

Keywords Thiosemicabazone; azo-dye; complexes; spectroscopic studies; Schiff base; synthesis

INTRODUCTION

Many Schiff base transition metal complexes are reported to have anticancer and antimicrobial activities.^{1–3} It was reported that some drugs have greater activity when administered as metal complexes than that as free organic compounds.⁴ Hence, Schiff base transition metal complexes may be an untapped reservoir for drugs.^{5,6} Recently, complexes of transition and nontransition metals with Schiff base ligands are promising materials for electronic applications due to their outstanding photo and electroluminescent (PL and EL) properties, and the ease of synthesis that readily allows structural modification for optimization of material properties.^{7–10} Zinc complexes of Schiff base became attractive for their interesting fluorescent properties, in particular, the salicylideneamine–zinc(II) complexes exhibit photo luminescence as well as electroluminescence.^{7,9} In view of the above facts, this article aimed to the synthesis, identification and antimicrobial investigation metal complexes of the Schiff base ligand, 2-(5-(2-chlorophenyl)diazenyl)-2-hydroxy benzylidene)hydrazinecarbothioamide. The coordination behavior of this Schiff base toward transition metals was investigated via the elemental and thermal analyses, IR, UV–Vis, mass spectra, ¹H-NMR and ESR as well as conductivity and magnetic moments measurements.

RESULTS AND DISCUSSION

The analytical (Table 1) and spectroscopic data (Tables 2 and 3) are compatible with the formation of the ligand (Figure 1) and the suggested structures (Figure 2). The complexes are colored, stable in air, and insoluble in H_2O , ethanol, and nonpolar solvents such as benzene. However, they are soluble in polar solvents such as DMF and DMSO. All the complexes except complex (13) are nonelectrolytes.

Infrared Spectra (IR)

The mode of coordination of the ligand can be obtained by comparing the infrared spectra of the complexes with that of the free ligand.^{11,12} Important spectral bands are presented in Table 2. The infrared spectrum of the ligand (**H**₂**L**) showed two medium bands appeared at 3265 and 3158 cm⁻¹ which may be assigned to the $v(NH_2)$ and v(NH) groups, respectively.¹³ The very strong band at 1610 was assigned to the v(C=N) of the azomethine group,¹⁴ while the bands at 3440 and 855 cm⁻¹ was assigned to the hydroxyl¹² and C=S groups, respectively.¹⁵

In all complexes the bands of the azomethine and thio-ketone were shifted to lower wave number $(9-15 \text{ cm}^{-1} \text{ and } 20-27 \text{ cm}^{-1}$, respectively) with decreasing their intensities which indicates their coordination to the central metal ion.^{11,16} In all complexes

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	Ligands/			M				Anal./four	id (calc.) (%)			Molar conductance Am
No.	Complexes	Color	FW	point	Yield%	С	Н	z	s	a	Μ	$(\Omega^{-1} \mathrm{cm}^2 \mathrm{mol}^{-1})$
-	H ₂ L C ₁₄ H ₁₂ CIN ₅ OS	Red	333.80	190	74	50.09(50.38)	3.94(3.62)	21.32(20.98)	9.39(9.61)	10.91(10.62)		
6	$H_2LCu(OC(O)CH_3)_2(H_2O)$	Brown	533.45	>300	75	40.11(40.53)	4.07(3.78)	13.25(13.13)	6.20(6.01)	6.41(6.65)	11.45(11.91)	10.1
	C ₁₈ H ₂₀ CICuN ₅ O ₆ S											
e	$H_2LCuCl_2(H_2O)$	Dark brown	486.26	>300	79	34.09(34.58)	3.12(2.90)	14.78(14.40)	6.22(6.59)	21.55(21.87)	12.84(13.07)	16.1
	$C_{14}H_{14}Cl_3CuN_5O_2S$											
4	$HLCu(ONO_2)(H_2O)_2$	Dark brown	494.37	>300	70	33.99(34.01)	3.30(3.06)	17.09(17.00)	6.89(6.49)	7.25(7.17)	12.99(12.85)	20.2
	C ₁₄ H ₁₅ ClCuN ₆ O ₆ S											
ŝ	$H_2LCu(OOSO_2)(H_2O)$	Dark brown	511.42	>300	69	32.65(32.88)	3.00(2.76)	13.99(13.69)	12.41(12.54)	7.12(6.93)	12.11(12.43)	16.5
	$C_{14}H_{14}CICuN_5O_6S_2$											
9	$H_2LNi(OC(O)CH_3)_2(H_2O)$	Brown	528.59	>300	76	40.79(40.90)	4.01(3.81)	13.45(13.25)	5.99(6.07)	7.08(6.71)	11.44(11.10)	10.4
	C ₁₈ H ₂₀ CIN ₅ NiO ₆ S											
2	$H_2LCo(OC(O)CH_3)_2$	Brown	510.82	>300	81	42.09(42.32)	3.21(3.55)	14.00(13.71)	6.03(6.28)	7.10(6.94)	11.09(11.54)	12.2
	$C_{18}H_{18}CIC_0N_5O_5S$											
×	$H_2LZn(OC(O)CH_3)_2(H_2O)$	Red	535.28	>300	75	40.85(40.39)	3.66(3.77)	12.88(13.08)	6.15(5.99)	7.06(6.62)	11.98(12.21)	11.3
	$C_{18}H_{20}CIN_5O_6SZn$											
6	$H_2LMn(OC(O)CH_3)_2(H_2O)$	Brown	524.84	>300	80	41.02(41.19)	3.99(3.84)	13.24(13.34)	5.98(6.11)	7.00(6.76)	10.85(10.47)	13.1
	C ₁₈ H ₂₀ ClMnN ₅ O ₆ S											
10	$H_2LUO_2(OC(0)CH_3)_2$	Brown	721.91	>300	74	29.82(29.95)	2.56(2.51)	9.98(9.70)	4.55(4.44)	5.04(4.91)	32.60(32.97)	9.6
	C ₁₈ H ₁₈ CIN ₅ O ₇ SU											
11	H ₂ LFeCl ₃ C ₁₄ H ₁₂ Cl ₄ FeN ₅ OS	Dark brown	496.00	>300	74	33.54(33.90)	2.78(2.44)	14.32(14.12)	6.12(6.46)	28.68(28.59)	11.45(11.26)	19.6
12	$H_2LRuCl_3(H_2O)$	Dark brown	559.24	>300	69	30.32(30.07)	2.89(2.52)	12.58(12.52)	6.00(5.73)	25.44(25.36)	17.87(18.07)	13.2
	$C_{14}H_{14}Cl_4N_5O_2RuS$											
13	$[H_2LV(H_2O)]SO_4$	Brown	514.82	>300	72	32.48(32.66)	3.05(2.74)	14.03(13.60)	6.44(6.89)	7.12(6.89)	9.66(9.90)	110.7
	$C_{14}H_{14}CIN_5O_7S_2V$											

No.	Ligands/ Complexes	ν(OH)	ν (NH/NH ₂)	v(C=N)	ν(C-0)	v(C=S)	$ u_{\rm s}({\rm CO}_2)/ u_{\rm as}({\rm CO}_2), $ $(\Delta_{\rm COO})$ or NO ₃ or SO ₄
-	H ₂ L	3440s	3265m, 3158m	1615v.s	1220m	855s	
7	$H_2LCu(OC(O)CH_3)_2(H_2O)$	3417w	3267, 3155 sh	1606s	1232m	830w	1542/1333 (209)
3	$H_2LCuCl_2(H_2O)$	3425w	3266, 3152	1604s	1238m	828w	Ι
4	$HLCu(ONO_2)(H_2O)_2$		3270, 3149	1603s	1240m	830w	1479, 1300
S	$H_2LCu(OOSO_2)(H_2O)$	3421m	3264, 3159	1608s	1237m	833w	1213, 1031, 964
6	$H_2LNi(OC(O)CH_3)_2(H_2O)$	3404m	3275m, 3155m	1602s	1235m	829w	1526/1323 (203)
7	$H_2LC_0(OC(O)CH_3)_2$	3410w	3270, 3150	1600s	1229m	829w	1523/1321 (202)
8	$H_2LZn(OC(O)CH_3)_2(H_2O)$	3423s	3271	1605s	1234m	832m	1550/1319 (231)
6	$H_2LMn(OC(O)CH_3)_2(H_2O)$	3425w	3269, 3148	1598s	1230m	831m	1533/1310 (223)
10	$H_2LUO_2(OC(O)CH_3)_2$	3441m	3266, 3149	1605s	1222m	829m	1530/1326 (204)
11	$H_2 LFeCl_3$	$3410 \mathrm{m}$	3271, 3143	1601s	1235m	832m	
12	$H_2 LRuCl_3(H_2O)$	3440s	3280m, 3154m	1604s	1221m	832m	
13	$[H_2LV(H_2O)]SO_4$	3409m	3272, 3148	1604s	1236m	835m	1161, 1021, 617

 Table 2 IR spectral data for the ligand and its metal complexes and their assignments

No.	Ligands/Complexes	$\pi - \pi^*$, n $-\pi^*$ and CT bands	d–d bands	μ_{eff} in BM
1	H ₂ L	235, 265, 315, 335, 435, 500	I	
2	$H_2LCu(OC(0)CH_3)_2(H_2O)$	240, 280, 320, 340, 440, 498	615	1.72
3	$H_2LCuCl_2(H_2O)$	230, 270, 330, 350, 443, 495	630	1.85
4	$HLCu(ONO_2)(H_2O)_2$	240, 275, 325, 345, 441, 490	620	1.69
S	$H_2LCu(OOSO_2)(H_2O)$	230, 270, 315, 360, 445, 495	680	1.73
6	$H_2LNi(OC(O)CH_3)_2(H_2O)$	230, 280, 310, 350, 435, 505	680	3.31
7	$H_2LCo(OC(0)CH_3)_2$	235, 290, 325, 350, 430, 485	590, 645	4.96
8	$H_2LZn(OC(O)CH_3)_2(H_2O)$	235, 280, 315, 340, 425, 500		Diamagnetic
6	$H_2LMn(OC(0)CH_3)_2(H_2O)$	225, 270, 310, 335, 433, 490	550, 645	5.45
10	$H_2LUO_2(OC(O)CH_3)_2$	230, 285, 305, 325, 442, 495	540, 630	Diamagnetic
11	H_2LFeCl_3	230, 285, 325, 345, 415, 485	540, 660, 870	5.89
12	H ₂ LRuCl ₃ (H ₂ O)	240, 260, 305, 340, 380, 492	520	1.76
13	$[H_2LV(H_2O)]SO_4$	240, 265, 310, 335, 405, 495	520, 780	1.73

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except (4), (10), and (12), the band due to hydroxyl group were shifted to lower frequency $(13-36 \text{ cm}^{-1})$ together with a lower intensity, which indicates the coordination of the hydroxyl oxygen.¹² In case of complex (4) this band disappeared indicating the subsequent deprotonation of the phenolic proton prior to coordination,¹² while in case of complexes except (10) and (12) the hydroxyl signal almost found at its original place with the same intensity which indicates that it is not involved in coordination. In all complexes except (10) and (12) the band due to the phenolic ν (C–O) were shifted to higher wave number which further support its involvement in coordination.¹² In all complexes except (10) and (12) new bands appeared in the 505-545, 345-384, and 450-467 cm⁻¹ regions due to the v(M-N), v(M-S) and v(M-O) vibrations, respectively.^{11,12,16,17} Complexes (10) and (12) showed new bands in the 510–540 and 340–380 cm^{-1} regions due to the v(M-N) and v(M-S) vibrations, respectively.^{11, 12, 17} The chloro complexes (3), (11), and (12) showed new band in the 298–400 cm^{-1} range due to the presence of v(M–Cl).¹⁷ The appearance of two characteristic bands in the ranges 1523–1550 cm⁻¹ and 1310–1333 cm⁻¹ in case of complexes (2) and (6)–(10) were attributed to v_{asym} (COO⁻) and $v_{\rm sym}$ (COO⁻), respectively, indicating the participation of the carboxylate oxygen in the complexes formation.^{16,17} The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the v_{asym} (COO⁻) and $v_{\rm svm.}(\rm COO^{-})$. The separation value (Δ) between $v_{\rm asvm}(\rm COO^{-})$ and $v_{\rm svm.}(\rm COO^{-})$ in this complex was more than 200 cm⁻¹ (202 cm⁻¹) suggesting the coordination of carboxylate group in a monodentate fashion.^{17,18} The vanadyl complex (**13**), showed signals at 1161, 1021, and 617 cm⁻¹characteristic for the uncoordinated sulfate group which was further confirmed from conductance value.^{17,19} The IR spectrum of the VO(II) complex display a band at 980 cm⁻¹ assigned to the stretching frequency of the v(V=O).²⁰ In the case of sulfate complex (5), new bands appeared at 1213, 1031, and 964 cm⁻¹. These bands indicate that sulfate ion is coordinated to the metal ion in a chelating unidentate fashion.²¹ Complex (4) showed two bands at 1479 and 1300 cm^{-1} indicating that the nitrate ion is coordinated to the copper(II) ion as a monodentate ligand.²² The broad bands in the 3508-3480 cm⁻¹ region are due to coordinated water or water of crystallization. The bands for water of crystallization are different from those of coordinated water; the latter has bands in the 970-930 cm⁻¹ and 660-600 cm⁻¹ regions. The presence of water molecules within the coordination sphere in the hydrated complexes were supported by the presence of bands at $3508-3480 \text{ cm}^{-1}$, $1580-1595 \text{ cm}^{-1}$, $920-940 \text{ cm}^{-1}$, and $610-640 \text{ cm}^{-1}$ due to OH stretching, HOH deformation, H₂O rocking, and H₂O wagging, respectively.^{23,24}

Molar Conductivity

The molar-conductance 1×10^{-3} M solution of the metal complexes in DMF at room temperature are in the 9.6–20.2 Ω^{-1} cm² mol⁻¹ range, indicating their nonelectrolytic nature of these complexes except complex (**13**). These confirmed that the anion is coordinated to metal ion. The considerably high values of some complexes may be due to the partial solvolysis by DMF.²⁵

Electronic Spectra

The structure of the ligand reveals that the two lone pairs of electrons of azo group are not the only interacting nonbonding electrons. Since Schiff base part of the ligand contains



Figure 1 Preparation of 2-(5-((2-chlorophenyl)diazenyl)-2-hydroxybenzylidene) hydrazinecarbothioamide (H₂L).

nitrogen and sulphur atoms which also may be extra sources of lone pair of electrons. Thus other $n \rightarrow \pi^*$ transition is expected to take place from these nonbonding orbital to different π^* molecular orbital extending over such a large molecules. The electronic spectral data of the ligand and its complexes in dimethylformamide (DMF) are given in Table 3. The data reveal that the ligand comprises three sets of bands in the UV and visible regions.²⁶ The first set of the shortest wave length at 235 ($\varepsilon = 0.1 \times 10^{-4} \text{ mol}^{-1} \text{cm}^2$) and 265 nm ($\varepsilon = 2.9 \times 10^{-4} \text{mol}^{-1} \text{cm}^2$) may be assigned to the $\pi \rightarrow \pi^*$ transition in the benzenoid moiety and intra ligand $\pi \rightarrow \pi^*$ transition.^{27–29} The second set appears at 315, and 335 may be assigned to $n \rightarrow \pi^*$ of the azomethine and C = S groups.^{16,27} The third set located at 400 nm which maybe corresponds to $\pi \rightarrow \pi^*$ transition involving the π electron of the azo group.^{26,29} The band located in the visible region at 500 nm can be assigned to $\pi \rightarrow \pi^*$ transition involving the whole electronic system of the compounds with a considerable charge transfer character arising mainly from the phenolic moiety.^{26,29} Compared to the free ligand, the n- π^* transitions of the complexes was shifted to some extent, probably due to imino-nitrogen coordination to the metal ion. Copper(II) complexes (2-5) showed bands in the range 615–680 nm assignable to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ transition. This



Figure 2 Suggested structural representations of metal complexes.

suggests that these complexes have tetragonal distorted octahedral geometry³⁰ (Figure 2). These complexes exhibit magnetic moment due to its spin-only value in the 1.69–1.85 B.M. The nickel complex ($\mathbf{6}$) showed magnetic moment value of 3.31 B.M., which is in the normal range observed for a high spin octahedral Ni(II) complex. Its electronic spectrum displays a band at 680 nm which can be assigned to ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ transition, consistent with its octahedral stereochemistry³¹ (Figure 2). The cobalt(II) complex (7) showed to signals at 590 and 645 assignable to ${}^{4}A_{1g} \rightarrow {}^{4}E_{g}$ and ${}^{4}A_{1g} \rightarrow {}^{4}B_{1g}$, respectively, with a magnetic moment value of 4.96 B.M., in a high spin square pyramidal geometry³² (Figure 2). The electronic absorption spectrum of manganese(II) complex (9) displays weak absorption bands at 645 and 550 nm. These band may be assigned to ${}^{6}A_{1}g \rightarrow {}^{4}T_{1}g$ (${}^{4}G$) and ${}^{6}A_{1}g \rightarrow {}^{4}Eg$ (⁴G), transitions, respectively. These transitions are characteristic to manganese(II) ion in octahedral geometry³³ (Figure 2). This complex shows magnetic moment value equal 5.45 B.M., which are corresponding to five unpaired electrons and close to high spin manganese(II) (d⁵). The high spin octahedral ferric complex (11) showed three bands at 540, 660, 870 assignable to ${}^{6}A_{1g} \rightarrow {}^{4}A_{1g}(G)$, ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}(G)$, and ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(G)$, respectively, with a magnetic moment value of 5.89 BM (Figure 2).^{34,35} The ground state of ruthenium(III) in an octahedral environment is ${}^{2}T_{2g}$, arising from the t_{2g}^{5} configuration, and the first excited doublet levels in the order of increasing energy are ${}^{2}A_{2g}$ and ${}^{2}T_{1g}$, arising from the $t_{2g}^4e_{1g}$ configuration. The ruthenium(III) complex (12) showed one band at 520 nm corresponding to the transition ${}^2T_{2g} \rightarrow {}^2T_{1g} {}^{34,35}$ (Figure 2). The electronic spectrum of the vanadyl complex (13) has two bands in the visible region at 780 and 520 nm, which are assigned to ${}^{2}B_{2} \rightarrow {}^{3}E$ and ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ transitions, respectively, as expected for a square pyramidal geometry (Figure 2).²⁵ This complex exhibits magnetic moment due to its spinonly value of 1.73 B.M.

Electron Spin Resonance of Copper(II) Complexes

The X-band ESR spectra of the complexes provide further insight into the environment around the metal centers. The ESR spectra of the solid copper(II) complexes (2) and (3) at room temperature show nonaxial type symmetry with three g-values $g_x = 2.241$, g_y = 2.105, and $g_z = 2.059$ and $g_x = 2.249$, $g_y = 2.093$ and $g_z = 2.044$ for the two complexes respectively $(g_2 - g_3)/(g_1 - g_2) < 1$ (= 0.344 and 0.314), indicating a $d_{(x^2 - y^2)}$ ground state with covalent bond character.³⁶⁻³⁸ The ESR spectra of solid copper(II) complexes (4) and (5) at room temperature are characteristic to d⁹ configuration and having an axial symmetry type of a $d_{(x2-y2)}$ ground state which is the most common for copper(II) complexes.^{29,37,38} The g values are $g_{\parallel} = 2.48, 2.227; g_{\perp} = 2.074, 2.044$ with $g_{iso} = 2.21, 2.105$, respectively, suggest elongated tetragonal octahedral geometry.^{30,37,38} The trend of g-values show $g_{II} < g_{\perp} < g_{e(2.0023)}$ confirmed the tetragonal distortion around the copper(II) ion corresponding to elongation the four fold symmetry axis $z^{37,39}$ In addition, exchange coupling interactions between the copper(II) ion is explained by Hathaway expression $G = (g_{\downarrow}((-2))/(g_{\downarrow}(-2))$. If the value of G < 4.0 a considerable exchange coupling is present in the solid complex. If G < 4.0 the exchange interactions is negligible which is typically as in the case of our complexes (4) and (5) (G = 6.49, 5.19) confirmed tetragonal octahedral structures.^{39–41} Kivelson and Neiman showed that for ionic environment g_{\parallel} is \geq 2.3 but for covalent environment g_{\parallel} < 2.3. The g_{\parallel} -values for complexes (4) and (5) are 2.48 and 2.227, respectively; consequentially the environment for 4 is considerably ionic but for 5 it is covalent.^{40,41}

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No.	Temp. range ^o C	Loss in weight Found (calc.)	Assignment	Composition of the residue
4	130-180	7.33 (7.29)	Loss of two molecule of coordinated water	[HLCu(ONO ₂)]
	275-335	12.68 (12.54)	Loss of two nitrate ion (2HNO ₃)	[HLCu]
	350-650	66.98 (67.32)	Decomposition of the complex forming	[CuO]
6	115-175	3.51 (3.41)	Loss of one molecule of coordinated water	$[H_2LNi(OC(O)CH_3)_2]$
	245-360	22.27 (22.34)	Loss of one sulphate ion (H_2SO_4)	[H ₂ LNi]
	370-630	62.48 (63.15)	Decomposition of the complex forming NiO	NiO
11	195-225	3.53 (3.63)	Loss of one molecule of coordinated water	[H ₂ LFeCl ₃]
	255-345	22.38 (21.44)	Loss of Three chloride ions (3HCl)	[H ₂ LFe]
	360-580	58.14 (55.58)	Decomposition of the complex forming	Fe ₂ O ₃
12	195-230	3.18 (3.22)	Loss of two molecule of coordinated water	[H ₂ LRuCl ₃]
	250-300	18.055 (19.02)	Loss of three chloride ion (3HCl)	[H ₂ LRu]
	330-680	58.97 (59.68)	Decomposition of the complex forming	Ru_2O_3
13	120-155	3.60 (3.49)	Loss of one molecule of coordinated water	$[H_2LV(O)].SO_4$
	320-380	18.16 (18.65)	Loss of sulphate group	$[H_2LV(O)]$
	400-490	65.97 (64.85)	Decomposition of the complex forming	V ₂ O ₃

Table 4 The thermal analysis (TG) of some complexes

Thermal Analysis of Some Complexes

The thermo-gravimetric analysis (TG) was measured in the temperature 20–800 °C range and the results are shown in Table 4. The results show a good agreement in weight loss between calculated and found formula. The results show that the complexes (4), (6), (11), (12), and (13) generally decomposed in several steps. The first step is the elimination of water of coordination, in the temperature 115–230 °C range. The second step is the loss of anions in the 245–380 °C temperature range. The third step is the complete decomposition of the complexes through degradation of the ligand in 350–680 °C temperature range leaving the metal oxide.

Antibacterial and Antifungal Screening

The microbial activities' results of the ligand and its metal complexes showed that all compounds are inactive toward gram-positive bacterium (*Bacillus subtilis*) and gram-negative bacterium (*Escherichia Coli*), fungus (*Aspergillusniger*), and Yeast (*Saccharomyces cerevisie*). The most interesting point of biological measurement is that the ligand and its complexes are biologically inactive while other types of thiosemicarbazide Schiff base metal complexes such as benzyloxybenzaldehyde-4-phenyl-3-thiosemicarbazone⁴² derivatives, 2-3-dimethyl-1-phenyl-3-pyrazolin-5-thiosemicarbazone, ⁴³ 2-acetylpyridine-N(4)-cyclohexyl thiosemicarbazone,⁴⁴ and thiosemicarbazones, semicarbazones, dithiocarbazates, and hydrazide/hydrazones compounds⁴⁵ are biologically active. So, we can say that the biological activity of these compounds against both bacteria and fungi inhibited due to the presence of azo group.

CONCLUSION

The synthesis of the new Schiff base H_2L has been reported. Its metal complexes with transition metals have been characterized and all the data collected are in agreement with the proposed structures. The spectral data indicate that the ligand can behave as

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neutral bidentate, neutral tridentate, and monobasic tridentate, and coordinates through the C=N, C=S, and C-S and/or deprotonated or protonated phenolic hydroxyl oxygen atom. The study revealed octahedral geometry around Ni(II), Cu(II), Mn(II), Ru(III), and Fe(III) complexes. However, square pyramidal geometry is suggested for cobalt(II) and vanadyl(II) complexes. The biological results show that the ligand and its complexes are biologically inactive against Gram positive bacterium (*Bacillus subtilis*), Gram negative bacterium (*Escherichia coli*), Fungus (*Aspergillus niger*), and Yeast (*Saccharomyces cerevisie*). The effect of substitution on the biological activity of the parent ligand may be positive or negative. In this case, the effect was very negative and by comparing the previous results of thiosemicabazonederivatives we can say that the azo group inhibits the activity of the compound.

EXPERIMENTAL

Materials

All the reagents employed for the preparation of the ligand and its complexes were of the best grade available and used without further purification.

Physical Measurements

The ligand and its metal complexes were analyzed for C, H, N, Cl, and S at the Microanalytical Laboratory, Cairo University, Egypt. 4-((4-chlorophenyl)diazenyl)-2-hydroxy benzaldehyde was prepared by a published method.⁴⁶ Standard analytical methods were used to determine the metal ion content.⁴⁷⁻⁵⁰ IR spectra of the ligand and its metal complexes was measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400-4000 cm⁻¹ and in the 500-100 cm⁻¹ region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. Electronic spectra in the 200-900 nm regions were recorded on a Perkin-Elmer 550 spectrophotometer. The thermal analysis (TG) was carried out on a Shimadzu DT-30 thermal analyzer from room temperature to 800 °C at a heating rate of 10 °C/min. Magnetic susceptibilities were measured at 25 °C by the Gouy method using mercuric tetrathiocyanatocobaltate(II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal's constant.⁵¹ The magnetic moments were calculated from the equation: $\mu_{eff.} = 2.84 \sqrt{\chi_M^{corr} T}$. Molar conductances were measured on a Tacussel type CD₆NG conductivity bridge using 10⁻³M DMF solutions. ¹H NMR spectrum was obtained on Brucker Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. ESR measurements of solid complexes at room temperature were made using a Varian E-109 spectrophotometer, with DPPH as a standard material. TLC is used to confirm the purity of the compounds.

Synthesis of Ligand

The ligand 2-(5-(2-chlorophenyl)diazenyl)-2-hydroxy benzylidene)hydrazinecarbothioamide (H₂L) was prepared by adding equimolar amounts of hydrazinecarbothioamide (91 mg, 1.0 mmol) in ethanol (20 mL) to 4-((4-chlorophenyl)diazenyl)-2-hydroxy benzaldehyde (261 mg, 1.0 mmol.) in ethanol 20 mL (Figure 1). The mixture was refluxed while stirring for 4 h. The solid product was filtered off, washed with cold ethanol, followed by crystallization from ethanol and, finally, dried under vacuum over anhydrous CaCl₂. ¹H NMR (300 MHz, DMSO): $\delta = 11.65$ and 11.05 [s, OH and NH], 10.49 and 10.35 [s, NH₂], 8.94 [s, 1H, HC = N], and $\delta = 6.50-8.67$ [m, (8H) aromatic proton].

Synthesis of Metal Complexes

All metal complexes, except complex **13**, were prepared by refluxing a hot ethanol/water (7: 3) solution of the metal salts with a suitable amount of a hot ethanol solution of the ligand using a 1:1 ligand:metal molar ratio. In the case of complex **13**, a water solution of VOSO₄.H₂O was used. The reaction mixtures were refluxed for 3h accompanied by stirring. The products, which precipitated (except in complex **4**), were filtered off, washed with ethanol then by diethyl ether and dried in vacuum desiccators over P_4O_{10} . For complex 4, no precipitation occured until 3 mL of diethyl amine was added to the reaction mixture. The analytical data are given in Table 1.

In-vitro Antibacterial and Antifungal Activities

The antifungal and antibacterial activities of the newly synthesized Schiff base ligand, its metal complexes, and metal salts were carried out in the Botany Department, Laboratory of Microbiology, Faculty of Science, El-Menoufia University. They have been studied for their antifungal and antibacterial activities by disc diffusion method.^{52,53}

REFERENCES

- Bekhit, A. A.; El-Sayed, O. A.; Al-Allaf, T. A. K.; Aboul-Enein, H. Y.; Kunhi, M.; Pulicat, S. M.; Al-Hussain, K.; Al-Khodairy, F.; Arif, J. *Eur. J. Med. Chem.* **2004**, 39, 499-505.
- 2. Golcu, A.; Tumer, M.; Demirelli, H.; Wheatley, R. A. Inorg. Chim. Acta, 2005, 358, 1785-1797.
- 3. Singh, K.; Barwa, M. S.; Tyagi, P. Eur. J. Med. Chem. 2006, 41, 147-153.
- 4. Chakraborty, J.; Patel, R. N. J. Indian Chem. Soc. 1996, 73, 191-195.
- Charo, J.; Lindencrona, J. A.; Carlson, L. M.; Hinkula, J.; Kiessling, R. J. Virol. 2004, 78, 11321-11326.
- 6. Gulerman, N. N.; Rollas, S.; Erdeniz, H.; Kiraj, M. J. Pharm. Sci. 2001, 26, 1-5.
- 7. Kunkely, H.; Vogler, A. Inorg. Chim. Acta, 2001, 321, 171-174.
- Shen, Y. Z.; Gu, H. W.; Pan, Y.; Dong, G.; Wu, T.; Jin, X. P.; Huang, X. Y.; Hu, H. W. J. Organomet. Chem. 2000, 605, 234-238.
- 9. Qiao, J.; Wang, L. D.; Duan, L.; Li, Y.; Zhang, D. Q.; Qiu, Y. Inorg. Chem. 2004, 43, 5096-6102.
- Chang, K.-H.; Huang, C.-C.; Liu, Y.-H.; Hu, Y.-H.; Chou, P.-T.; Lin, Y.-C. Dalton Trans. 2004, 1731-1738.
- Youssef, N. S.; El-Zahany, E.; El-Seidy, A. M. A. *Phosphorus, Sulfur Silicon Relat. Elem.* 2010, 185, 785-789.
- Youssef, N. S.; El-Zahany, E.; Barsoom, B. N.; El-Seidy, A. M. A. Trans. Met. Chem. 2009, 34, 905-914.
- 13. Sallam, S. A. Trans. Met. Chem. 2005, 30, 341-351.
- 14. Mandal, S.; Rout, A. K.; Pilet, G.; Bandyopadhyay, D. Trans. Met. Chem. 2009, 34, 719-724.
- 15. El-Tabl, A. S.; El-Saied, F. A.; Al-Hakimi, A. N. Trans. Met. Chem. 2007, 32, 689-701.
- Pouralimardan, O.; Chamayou, A.–C.; Janiak, C.; Hosseini-Monfared, H. Inorg. Chim. Acta, 2007, 360, 1599-1608.
- Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., Wiley & Sons: New York, 1977, pp. 244-247.

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- 18. Murukan, B.; Mohanan, K. Trans. Met. Chem. 2006, 31, 441-446.
- 19. Gupta, L. K.; Bansal, U.; Chandra, S. Spectrochim. Acta Part A, 2007, 66, 972-975.
- Katsoulakou, E.; Bekiari, V.; Raptopoulou, C. P.; Terzis, A.; Lianos, P.; M.–Zoupa, E.; Perlepes, S. P. Spectrochim. Acta Part A, 2005, 61, 1627-1638.
- 21. Emara, A. A. A.; Saleh, A. A.; Adly, O. M. I. Spectrochim. Acta Part A, 2007, 68, 592-604.
- 22. Chandra, S.; Gupta, L. K. Spectrochim. Acta Part A, 2005, 61, 1181-1188.
- 23. Teotia, M. P.; Gurtu, J. N.; Rana, V. B. J. inorg. nucl. Chem. 1980, 42, 821-831.
- 24. El-Dissouky, A.; Fahmy, A.; Amer, A. Inorg. Chim. Acta, 1987, 133, 311-316.
- Ali, M. A.; Mirza, A. H.; Bujang, F. H.; Hamid, M. H. S. A.; Bernhardt, P. V. Polyhedron, 2006, 25, 3245-3252.
- 26. Geaey, W. J. Coord. Chem. Rev. 1971, 7, 81-122.
- 27. Rageh, N. M.; Abdel Mawgoud, A. M.; Mostafa, H. M. Chem. Papers, 1999, 53, 107-113.
- 28. Gup, R.; Kirkan, B. Spectrochim. Acta. Part A, 2005, 62, 1188-1195.
- Fouda, M. F. R.; Abd-Elzaher, M. M.; Shakdofa, M. M.; El-Saied, F. A.; Ayad, M. I.; El-Tabl, A. S. J. Coord. Chem. 2008, 61, 1983-1996.
- 30. Gup, R.; Giziroglu, E.; Kirkan, B. Dyes Pigments, 2007, 73, 40-46.
- 31. Chandra, S.; Sangeetika, ?? Spectrochim. Acta Part A, 2004, 60, 2153-2163.
- Tascioglu, S.; Yalcin, B.; Nasrullayeva, T. M.; Andac, O.; Buyukgungor, O.; Aydin, A.; Medjidov, A. A. Polyhedron, 2006, 25, 1279-1286.
- 33. Mohamed, G. G. Spectrochim. Acta Part A, 2006, 64, 188-195.
- 34. Kumar, K. G.; John, K. S. React. Funct. Polym. 2006, 66, 1427-1433.
- 35. Mohamed, G. G.; Omar, M. M.; Hindy, A. M. M. Spectrochim. Acta Part A, 2005, 62, 1140-1150.
- El-Tabl, A. S.; El-Saied, F. A.; Plass, W.; Al-Hakimi, A. N. Spetrochim. Acta Part A, 2008, 71, 90-99.
- 37. Hathaway, B. J.; Billing, D. E. Coord. Chem. Rev. 1970, 5, 143-207.
- 38. El-Tabl, A. S. Trans. Met. Chem. 1998, 23, 63-65.
- 39. El-Tabl, A. S. Trans. Met. Chem. 2002, 27, 166-170.
- 40. Ray, R. K.; Kauffman, G. B. Inorg. Chim. Acta, 1990, 174, 237-244.
- 41. Ray, R. K.; Kauffman, G. B. Inorg. Chim. Acta, 1990, 174, 257-262.
- Prathima, B.; Rao, Y. S.; Reddy, S. A.; Reddy, Y. P.; Reddy, A. V. Spectrochim. Acta Part A, 2010, 77, 248-252.
- 43. Raman, N.; Selvan, A.; Manisankar, P. Spectrochim. Acta Part A, 2010, 76, 161-173.
- 44. Li, M.-X.; Zhang, D.; Zhang, L.-Z.; Niu, J.-Y.; Ji, B.-S. Inorg. Chem. Comm. 2010, 13, 1572-1575.
- Pavan, F. R.; da, P. I.; Maia, S.; Leite, S. R. A.; Deflon, V. M.; Batista, A. A.; Sato, D. N.; Franzblau, S. G.; Leite, C. Q. F. *Eur. J. Med. Chem.* **2010**, 45, 1898-1905.
- 46. Liu, J.-N.; Wu, B.-W.; Zhang, B.; Liu, Y. Turk. J. Chem. 2006, 30, 41-48.
- Svehla, G. Vogel's Textbook of Macro and Semi Micro Quantitative Inorganic Analysis, 5th ed., Longman New York, 1979.
- 48. Welcher, F. J. The Analytical Use of EDTA, D. Van Nostrand Company, Inc.: New York, 1958.
- Vogel, A. I. Text Book of Quantitative Inorganic Analysis, 4th ed., Longmans: London, UK, 1978.
- Holzbecher, Z.; Divis, L.; Kral, M.; Sucha, L.; Vracil, F. Handbook of Organic Reagents in Inorganic Analysis, Wiley: Chichester, UK, 1976.
- 51. Lewis, L.; Wilkins, R. G. Modern Coordination Chemistry, Interscience, New York, 1960.
- 52. Offiong, E. O.; Martelli, S. Il Farmaco, 1994, 49, 513-518.
- Collee, J. G.; Duguid, J. P.; Farser, A. G.; Marmion, B. D. *Practical Medical Microbiology*, Churchill Livingstone: New York, 1989.