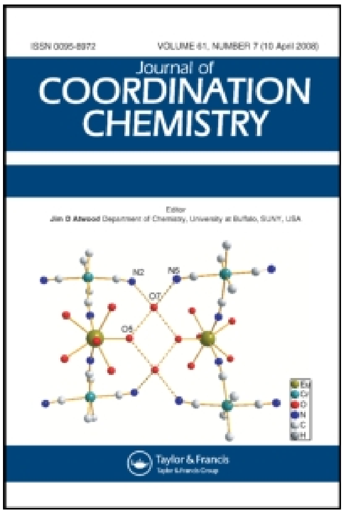

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Metal complexes of some thiocarbohydrazone ligands: synthesis and structure

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METAL COMPLEXES OF SOME THIOCARBOHYDRAZONE LIGANDS: SYNTHESIS AND STRUCTURE

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The synthesis, structure, physico-chemical investigation and biological studies of some metal complexes of thiocarbohydrazone ligands are described. The ligands were obtained by condensation of *N*,*N*′-thiocarbohydrazide with carbonyl compounds such as 2-hydroxyacetophenone or 5-chlorosalicylaldehyde. A variety of binuclear or mononuclear complexes were obtained with the ligands in mono-, bi- and/or tri-deprotonated forms. The bonding sites are the azomethine nitrogen atom, phenolic oxygen atom and thiol sulfur atom. The metal complexes exhibit either tetrahedral or octahedral structures. Preliminary antimicrobial screening showed that the ligands and their metal complexes possess antimicrobial activity towards bacteria and fungi.

Keywords: Thiocarbohydrazones metal complexes; Infrared; UV-visible; Magnetic moment; Molar conductivity; Antimicrobial activities

INTRODUCTION

Although ligands having oxygen and nitrogen as donor atoms are by far the most extensively studied, interest in sulfur donor chelating agents has grown over the years and the number of chemical studies in this area has increased considerably [1]. Interest in complexes of these ligand systems now covers several areas ranging from general considerations of the effect of sulfur and electron delocalization in transition metal complexes to potential biological activity and practical application [2–4].

Thiosemicarbazones and their transition metal complexes have been studied for their antimicrobial and antifungal properties [5]. However, little is known about the biological properties of thiocarbohydrazones. Some have been tested as fungicides for textile fabrics [6], and more recently a series of 2-acetylpyridine thiocarbohydrazones were synthesized and tested as inactivators of HSV-1 ribonucleotide reductase [7], with better results than the analogous 2-acetylpyridine thiosemicarbazone derivatives.

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As a rule, coordination of a metal cation to bis(thiocarbohydrazones) of the thiocarbohydrazide, N^1H_2–N^2H–C(=S)–N^3H–N^4H_2, shows that even under condensation with aldehyde or ketones, it has two nitrogen donor atoms that are the two terminal N^1 and N^4 nitrogens and in most cases the sulfur donor atom [8,9].

The aim of the present work is to synthesize new bis(thiocarbohydrazone) ligands, and study two series of their transition metal complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions. *N*,*N*′-Thiocarbohydrazide condenses easily with two molecules of carbonyl compounds (2-hydroxyacetophenone and 5-chlorosalicylaldehyde) on the N^1H_2 and N^4H_2 hydrazine amino groups to produce the two desired ligands H_4L_a and H_4L_b. Figure 1 shows representative structures of the two ligands, H_4L_a and H_4L_b, and their possible tautomeric forms.

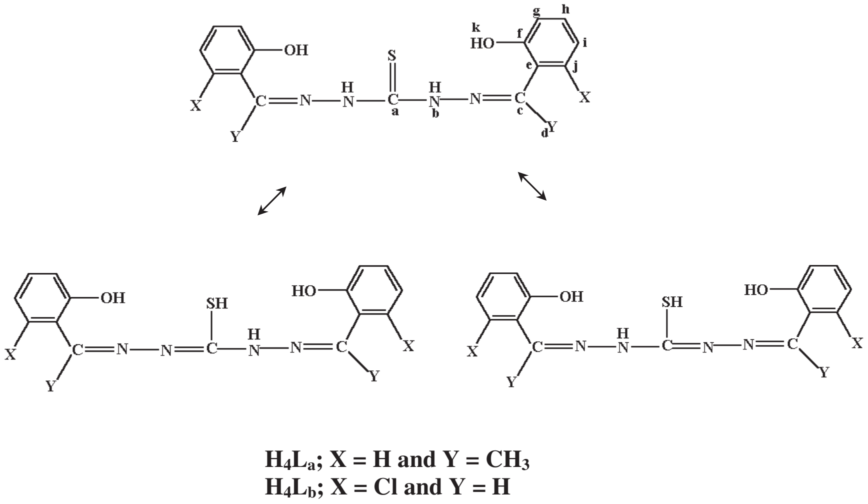


FIGURE 1 Structure of 2-hydroxyacetophenone thiocarbohydrazone (H_4L_a) and 5-chlorosalicyldehyde thiocarbohydrazone (H_4L_b) ligands, and their possible tautomeric forms.

The tautomerism of these ligands and also the well-known tendency of oxygen and sulfur donors to act as bridging ligands [10,11] allow various structural possibilities for the corresponding metal complexes. The antimicrobial studies towards bacteria and fungus are also of considerable interest.

EXPERIMENTAL

Materials

All chemicals used were of Merck or BDH commercial grade. Metal nitrates of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were used. The *N*,*N*′-thiocarbohydrazide was prepared as described in the literature [12].

Preparation of *N*,*N*′-Thiocarbohydrazone Bis(2-hydroxyacetophenoneiminate) (H_4L_a)

N,*N*′-Thiocarbohydrazone bis(2-hydroxyacetophenoneiminate), H_4L_a, was prepared by dropwise addition of a hot solution of *N*,*N*′-thiocarbohydrazide (1.06 g, 10.0 mmol dissolved in 60 mL ethanol) to a solution of 2-hydroxyacetophenone (2.8 g, 20.6 mmol in 40 mL ethanol). The mixture was stirred continually for 4 h. A creamy product precipitated out and was washed several times with small amounts of ethanol, filtered off and dried over anhydrous $CaCl_2$ in a desiccator. The yield was 2.87 g (74.4%) and the melting point >250°C.

Preparation of *N,N′*-Thiocarbohydrazone Bis(5-chlorosalicylideneiminate) (H_4L_b)

N,N′-Thiocarbohydrazone bis(5-chlorosalicylideneiminate), H_4L_b, was prepared by a similar procedure as H_4L_a. 5-Chlorosalicylaldehyde (3.2 g, 20.5 mmol in 40 mL ethanol) was used instead of 2-hydroxyacetophenone. The yield was 3.47 g (81.4%) and the melting point >250°C.

Preparation of the Transition Metal Complexes of the Thiocarbohydrazones

Complexes of the thiocarbohydrazone ligands were prepared by reaction of the thiocarbohydrazones, H_4L_a and H_4L_b, with the transition metal salts in the appropriate molar ratios. Metal nitrates of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were used. In a representative preparation, the complex was prepared by the dropwise addition of 1.920 g (5.01 mmol) of H_4L_b, in 50 mL ethanol, with constant stirring to the corresponding amount of the transition metal nitrate in the molar ratio 1 : 1 [1.487 g, 5.00 mmol of Zn(II) nitrate hexahydrate]. The mixture was heated to reflux for 1 h. The product was filtered off, washed several times with ethanol and dried over anhydrous $CaCl_2$ in a desiccator.

Analysis and Physical Measurements

Carbon, hydrogen, nitrogen, chlorine and sulfur were analyzed by standard microanalysis methods at the Microanalysis Center, Cairo University, Giza, Egypt. Analysis of the metal ions followed the dissolution of the solid complex in hot concentrated HCl, then diluting the resulting solution with water. The solution was then neutralized with ammonia solution and the metal ions were estimated by EDTA titration using Eriochrome Black T, Murexide or ammonium thiocyanate as indicators. The infrared spectra were recorded as KBr disks using a Perkin Elmer spectrophotometer model 1430, in the range 400–4000 cm^{-1}. Electronic absorption measurements were performed using a Shimadzu W250 nm spectrophotometer. The spectra were recorded in DMF. Thermal gravimetric analysis (TGA) data were measured at room temperature up to 800°C at a heating rate of 20°C/min. The data were obtained using a Shimadzu TGA-50H instrument. The percentage of H_2O in the compounds was determined from the weight loss obtained by heating 0.2000 g of the complex within the range 120–240°C to a constant weight. Mass spectrometric analysis was performed by a Shimadzu-GC-MS-QL mass spectrometer model 1000EX using a direct inlet system, at the Microanalysis Center, Faculty of Science, Ain-Shams University. Fragmentation was carried out at 205–260°C and 70 eV. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alfa Product, Model No. MKI magnetic susceptibility balance. Effective magnetic moments were calculated from the expression $\mu_{eff} = 2.828(\chi_M T)^{1/2}$ BM, where χ_M is the molar susceptibility [13]. Diamagnetic corrections were calculated from Pascal's constants for all atoms in the compounds [13]. ^{1}H and ^{13}C NMR spectra of the *N*,*N′*-thiocarbohydrazide and the thiocarbohydrazone ligands H_4L_a and H_4L_b in DMSO, with and without D_2O, were recorded on a Bruker WP 200 SY spectrometer at room temperature using TMS as an external standard. Molar conductivity measurements were carried out on a YST model 35 conductance meter (made in the UK).

Antibacterial and Antifungal Activity

Thiocarbohydrazones and their transition metal complexes are generally screened for antibacterial and antifungal activity using the bacteria *Azotobacter* and *Rhizobium* and the fungus *Fusarium oxysporium* [14]. Two media were prepared for the bacteria while Czabek's medium was prepared for the fungus. The media and growth of the bacteria and fungi and the method of studying the effect of the complexes on bacteria and fungus are cited elsewhere [15,16].

RESULTS AND DISCUSSION

The ligands were obtained from the condensation of the carbonyl compounds and thiocarbohydrazide in a 2 : 1 molar ratio. Absence of the NH_2 group was confirmed by IR [$\nu(NH_2) \approx 3280\,\mathrm{cm}^{-1}$] and ^{1}H NMR (a broad peak between $\delta \approx 4.5$ and 5.0 ppm) spectroscopies.

TABLE I ^{1}H and ^{13}C NMR chemical shifts (ppm) and coupling constants (Hz) for the H_4L_a and H_4L_b ligands

	H_4L_a			H_4L_b		
	Chemical shifts		*Coupling constants*	*Chemical shifts*		*Coupling constants*
	$\delta(^{1}H)$	$\delta(^{13}C)$		$\delta(^{1}H)$	$\delta(^{13}C)$	
(a)		177.6 (s)			174.7 (s)	
(b)	11.44 (s)			11.73 (s)		
(c)		129.8 (d)	$^{1}J(^{13}C–^{1}H)$ 165.5		130.9 (d)	$^{1}J(^{13}C–^{1}H)$ 166.3
(d)	2.82 (s)	21.4 (s)		7.66 (s)		
(e)		156.7 (s)			155.8 (s)	
(f)		119.8 (s)			120.0 (s)	
(g)	8.32 (d)	145.7 (d)	$^{1}J(^{13}C–^{1}H)$ 172.5 $^{3}J(^{1}H–^{1}H)$ 5.9	8.52 (d)	147.7 (d)	$^{1}J(^{13}C–^{1}H)$ 173.9 $^{3}J(^{1}H–^{1}H)$ 6.3
(h)	7.07 (d of d)	130.1 (d)	$^{1}J(^{13}C–^{1}H)$ 171.4 $^{3}J(^{1}H–^{1}H)$ 5.7 $^{3}J(^{1}H–^{1}H)$ 5.5	7.37 (d)	129.0 (d)	$^{1}J(^{13}C–^{1}H)$ 170.0 $^{3}J(^{1}H–^{1}H)$ 5.0 $^{3}J(^{1}H–^{1}H)$ 6.4
(i)	6.85 (d)	138.2 (d)	$^{1}J(^{13}C–^{1}H)$ 170.2 $^{3}J(^{1}H–^{1}H)$ 5.3	7.00 (d)	139.6 (d)	$^{1}J(^{13}C–^{1}H)$ 170.1 $^{3}J(^{1}H–^{1}H)$ 5.9
(j)	7.37 (d of d)	117.7 (s)	$^{3}J(^{1}H–^{1}H)$ 5.3 $^{3}J(^{1}H–^{1}H)$ 4.5		116.4 (s)	
(k)	9.54 (s)			10.44 (s)		

s, singlet; d, doublet; d of d, doublet of doublets.
The labeling of the ^{1}H and ^{13}C signals for the ligand molecules are as described in Fig. 1.
Samples were measured in DMSO solvent and referenced externally at 24°C with respect to neat liquid TMS for both ^{1}H and ^{13}C.
$J(^{13}C\text{-}^{1}H)$ were measured from ^{13}C NMR spectra for the coupling and decoupling processes.
^{13}C NMR spectrum of the thiocarbohydrazide in DMSO showed only one signal at 181.4 ppm.

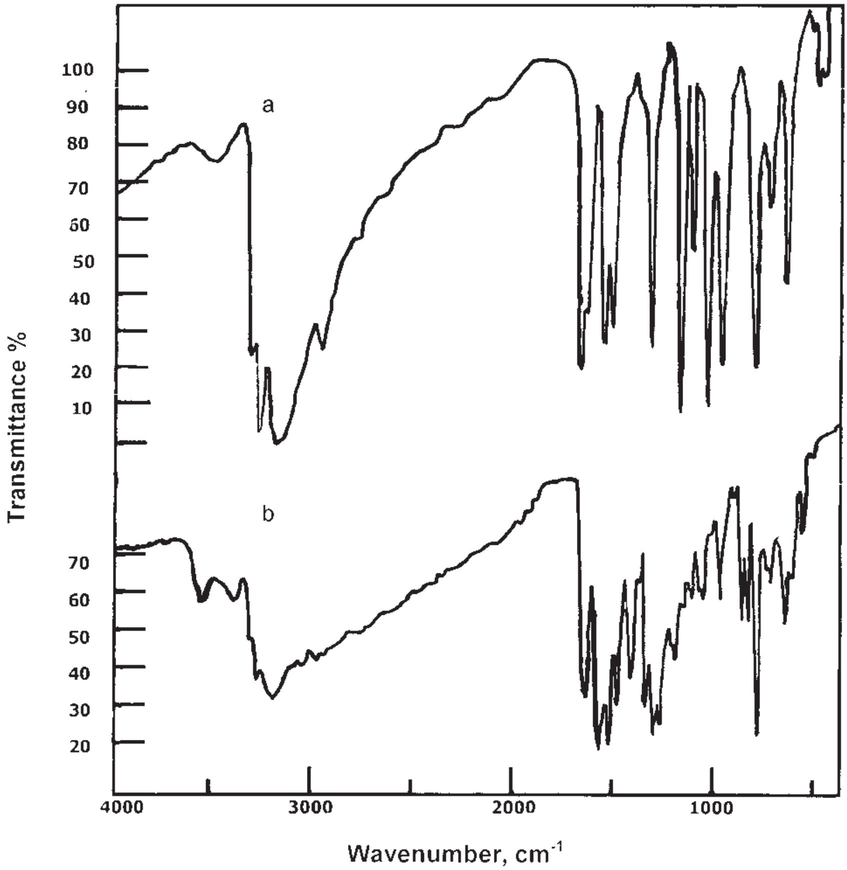
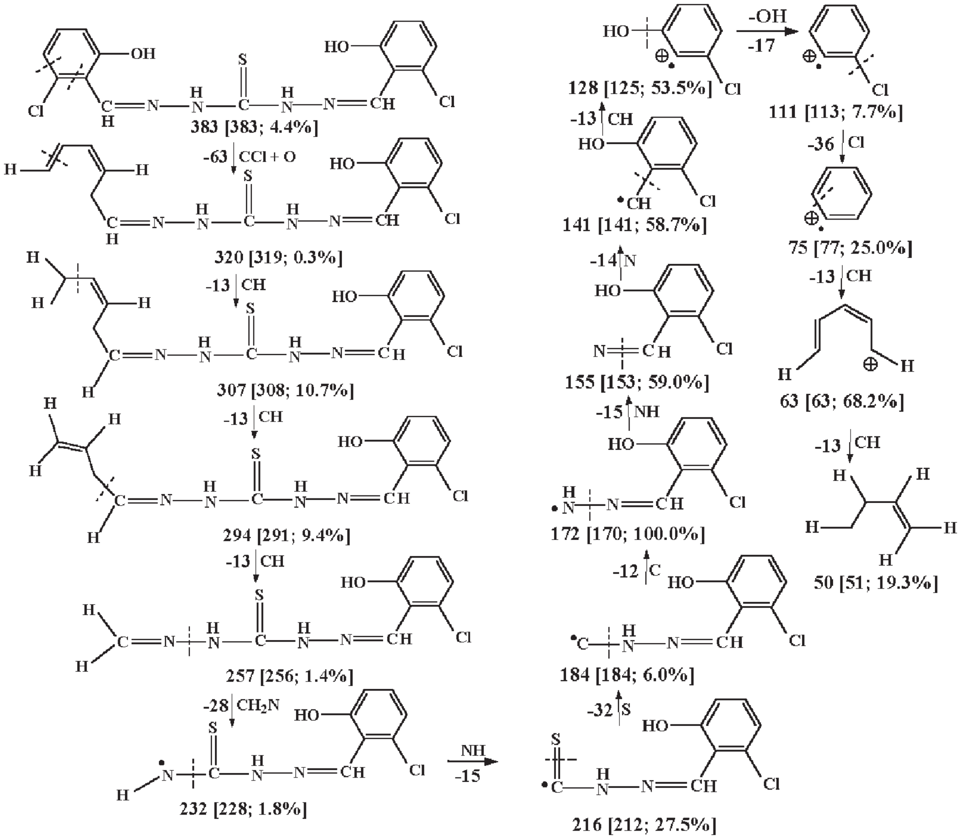


FIGURE 2 Infrared spectra of the (a) thiocarbohydrazide and (b) thiocarbohydrazone (H_4L_a) ligand.

^{1}H and ^{13}C NMR spectra were obtained for the ligands. ^{1}H NMR spectra of the ligands show signals at δ 2.82 ppm for the protons of the methyl signal in H_4L_a and δ 7.66 ppm for the azomethine proton in H_4L_b, phenolic OH protons at δ 9.54 and 10.44 ppm, and amino NH protons at $\delta \approx 11.44$ and 11.73 ppm for H_4L_a and H_4L_b, respectively. The protons of the phenyl signals were assigned at $\delta \approx 6.85$–8.52 ppm. Table I lists the ^{1}H and ^{13}C NMR parameters for the H_4L_a and H_4L_b ligands. Figure 2 shows the change in the IR spectra of the thiocarbohydrazide and its thiocarbohydrazone ligand H_4L_a. Fragmentations of the mass spectra of the H_4L_b ligand are depicted in Scheme 1. These observations along with the elemental analyses suggest that these ligands exist as shown in Fig. 1.

A great variety of binuclear or mononuclear metal complexes are obtained with the ligands in mono-, bi- and/or tri-deprotonated form. IR spectra of the ligands and their transition metal complexes show that the binding sites are the azomethine nitrogen atom, phenolic oxygen atom and thiol sulfur atom. Coordinating properties of the ligands have been studied with regard to Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions. Molecular formulas of the ligands and complexes, and the percentage yields, colors, melting points and the elemental analyses, molar conductivities and magnetic moments are listed in Table II.



SCHEME 1 Fragmentations of the mass spectrum of the H_4L_b ligand. *Calcd./[Found, % intensity]. Differences between calculated and found values are due to abstraction or addition of free H radicals.

IR spectra of these complexes were recorded to confirm their structure. Vibration frequencies and their tentative assignments for the thiocarbohydrazone ligands H_4L_a and H_4L_b and their transition metal complexes are listed in Table III. The assignments were aided by comparison with the vibration frequencies of the free ligands and their related thiocarbohydrazone [8,9] and thiosemicarbazone [17–21] compounds.

The broad band that appeared in the spectra of the ligands and their metal complexes in the range 3306–3565 cm^{-1} is assigned to the stretching vibration of ν(N–H) and ν(OH) for the uncoordinated phenolic oxygen (the OH group). The band assigned to the stretching vibration of the azomethine groups of the ligands (*ca.* 1646–1687 cm^{-1}) is shifted to lower frequency (1602–1629 cm^{-1}) in the metal complexes, suggesting that one of the coordination sites of the ligand to the central metal atom is through a nitrogen atom of the azomethine groups [22].

The band corresponding to the stretching vibration of the C=S group appears at 1200–1194 cm^{-1} for the ligands [18]. The absence of this band in the IR spectra in the metal complexes can be explained by the tautomerism of the C=S group with one of the imino groups to form the C–SH in the molecules of both ligands (see Fig. 1). The band that appears in the range 705–715 cm^{-1} is thus assigned to the stretching vibration of ν(C–S) in the IR spectra of the metal complexes.

TABLE II Physical and analytical data for the thiocarbohydrazone ligands (H_4L_a and H_4L_b) and their metal complexes

Ligands/Complexes	*Molecular formula*	*MW Yield* (%)	*Color*	*Mp* (°C)	*Elemental analyses: Found (Calcd.)* (%)						*Conductance*	μ_{eff} (BM)
					C	*H*	*N*	*Cl*	*S*	*M*		
(1) H_4L_a	$C_{17}H_{18}N_4O_2S$	342.424	Creamy	>250	59.57	5.27	16.24		9.42	–	3	–
		74.4			(59.62)	(5.30)	(16.35)		(9.36)			
(2) H_4L_b	$C_{15}H_{12}N_4O_2Cl_2S$	383.259	Creamy	>250	46.97	3.21	14.44	18.57	8.42	–	9	–
		81.4			(47.01)	(3.16)	(14.62)	(18.50)	(8.37)			
(3) $[Cr(HL_a)(H_2L_a)] \cdot 3H_2O$	$C_{34}H_{39}N_8O_7S_2Cr$	787.863	Green	>250	51.66	4.58	14.11	–	8.07	6.26	6	3.77
		75.6			(51.83)	(4.99)	(14.22)		(8.14)	(6.60)		
(4) $[Mn(H_2L_a)(H_2O)_3]$	$C_{17}H_{22}N_4O_5SMn$	449.391	Black	>250	45.40	4.76	12.63	–	7.58	11.92	20	5. 18
		46.4			(45.44)	(4.94)	(12.47)		(7.14)	(12.22)		
(5) $[Fe(HL_a)(H_2L_a)] \cdot 3H_2O$	$C_{34}H_{39}N_8O_7S_2Fe$	791.714	Black	>250	51.30	4.97	14.04	–	8.33	7.44	22	5.34
		57.2			(51.58)	(4.97)	(14.15)		(8.10)	(7.05)		
(6) $[Co_2(HL_a)(H_2O)_2]NO_3.EtOH$	$C_{19}H_{25}N_5O_8SCo_2$	601.370	Brownish blue	>250	37.81	4.16	11.41	–	4.94	19.32	61	4.73
		65.4			(37.95)	(4.16)	(11.65)		(5.33)	(19.60)		
(7) $[Ni_2(HL_a)(H_2O)_2]NO_3$	$C_{17}H_{19}N_5O_7SNi_2$	554.817	Dark green	>250	36.86	3.70	12.85	–	5.91	20.70	86	3.43
		76.5			(36.80)	(3.45)	(12.62)		(5.78)	(21.16)		
(8) $[Cu_2(HL_a)(H_2O)_2]NO_3.EtOH$	$C_{19}H_{25}N_5O_8SCu_2$	610.596	Dark green	>250	37.31	4.71	11.06	–	5.47	20.61	65	2.10
		61.6			(37.38)	(4.13)	(11.47)		(5.25)	(20.81)		
(9) $[Zn(H_2L_a)(H_2O)]$	$C_{17}H_{18}N_4O_3SZn$	423.799	Yellow	>250	48.22	4.07	12.96	–	7.83	14.80	6	–
		60.8			(48.18)	(4.28)	(13.22)		(7.57)	(15.43)		
(10) $[Cr(HL_b)(H_2L_b)] \cdot 3H_2O$	$C_{30}H_{27}N_8O_7Cl_4S_2Cr$	869.530	Green	>250	41.40	2.74	12.80	16.63	7.78	5.98	20	3.80
		57.9			(41.44)	(3.13)	(12.89)	(16.31)	(7.38)	(5.98)		
(11) $[Mn(H_2L_b)(EtOH)(H_2O)_2]$	$C_{17}H_{20}N_4O_5Cl_2SMn$	518.281	Black	>250	39.15	3.81	11.02	13.56	6.47	10.59	19	5.81
		66.2			(39.40)	(3.89)	(10.81)	(13.68)	(6.19)	(10.60)		
(12) $[Fe(HL_b)(H_2L_b)] \cdot 3H_2O$	$C_{30}H_{27}N_8O_7Cl_4S_2Fe$	873.379	Black	>250	40.93	3.25	12.95	16.44	7.71	6.56	15	5.64
		58.6			(41.26)	(3.12)	(12.83)	(16.24)	(7.34)	(6.39)		
(13) $[Co_2(HL_b)(H_2O)_2]NO_3$	$C_{15}H_{13}N_5O_7Cl_2SCo_2$	596.135	Brownish blue	>250	30.39	1.92	11.88	12.26	5.50	19.54	68	4.80
		68.6			(30.22)	(2.20)	(11.75)	(11.89)	(5.38)	(19.77)		
(14) $[Ni_2(HL_b)(H_2O)_2]NO_3$	$C_{15}H_{13}N_5O_7Cl_2SNi_2$	595.650	Green	>250	29.97	1.82	11.87	12.11	5.35	19.89	82	3.34
		72.5			(30.25)	(2.20)	(11.76)	(11.90)	(5.38)	(19.71)		
(15) $[Cu_2(HL_b)(H_2O)_2]NO_3$	$C_{15}H_{13}N_5O_7Cl_2SCu_2$	605.362	Pale green	>250	29.87	2.57	11.49	11.14	5.39	21.30	91	2.01
		79.1			(29.76)	(2.17)	(11.57)	(11.71)	(5.30)	(20.99)		
(16) $[Zn(H_2L_b)(EtOH)]$	$C_{17}H_{16}N_4O_3Cl_2SZn$	492.690	Yellow	>250	41.61	3.20	11.32	14.62	6.26	12.93	7	–
		48.7			(41.44)	(3.27)	(11.37)	(14.39)	(6.51)	(13.27)		

Molar conductance ($ohm^{-1} cm^2 mol^{-1}$) was measured in DMF solvent. Magnetic moment values, μ_{eff}, were calculated for one metal ion in the complex.

TABLE III Infrared frequencies (cm^{-1}) of the thiocarbohydrazone ligands (H_4L_a) and (H_4L_b) and their transition metal complexes[a]

		$\nu(O–H)$, $\nu(N–H)$	$\nu(=C–H)$	$\nu(CH_3)$	$\nu(C=N)$	$\nu(C–O)$	$\nu(C–N)$	$\nu(C–S)$[b]	$\nu(C–Cl)$	$\nu(M–O)$	$\nu(M–N)$
(1)	H_4L_a	3565 m 3391 s	–	3009 m 2938 w	1687 vs, br	1265 m	1319 vs		–	–	–
(2)	H_4L_b	3493 m 3323 s	–		1646 vs	1269 m	1319 vs		835 m	–	–
(3)	$[Cr(HL_a)(H_2L_a)] \cdot 3H_2O$	3389 s, br 3332 s	–	2987 m 2935 w	1614 s	1252 s	1344 m 1305 m	705 m	–	480 w	352 w
(4)	$[Mn(H_2L_a)(H_2O)_3]$	3435 s 3391 s	–	2995 m 2940 w	1629 s 1685 vs	1237 s 1260 m	1341 m 1325 m	705 m	–	429 m	360 w
(5)	$[Fe(HL_a)(H_2L_a)] \cdot 3H_2O$	3380 s, br 3327 s	–	2983 m 2930 m	1614 s	1244 s	1345 s 1306 s	709 m	–	448 w	350 w
(6)	$[Co_2(HL_a)(H_2O)_2]NO_3 \cdot EtOH$	3410 s, br 3326 s, br	–	2993 m 2938 m	1604 vs	1253 s	1320 s	708 m	–	490 m	372 w
(7)	$[Ni_2(HL_a)(H_2O)_2]NO_3$	3422 s, br	–	2982 m 2932 w	1602 vs	1248 m	1361 s 1318 m	709 m	–	448 m	380 w
(8)	$[Cu_2(HL_a)(H_2O)_2]NO_3 \cdot EtOH$	3410 m, br	–	2987 m 2932 w	1617 s 1612 s	1253 sh 1242 m	1354 s 1322 s	711 m 700 m	–	460 m	356 w
(9)	$[Zn(H_2L_a)(H_2O)]$	3362 s, br 3395 s	–	2995 m 2935 w	1616 s 1680 s	1237 m 1265 m	1345 m 1306 m	705 m	–	435 m	366 w
(10)	$[Cr(HL_b)(H_2L_b)] \cdot 3H_2O$	3400 s, br 3321 s	3070 m 3090 m	–	1618 s	1255 sh 1231 s	1344 m 1305 m	712 m 700 m	834 m	479 w	342 w
(11)	$[Mn(H_2L_b)(EtOH)(H_2O)_2]$	3490 s 3389 s	3095 m, br	–	1645 s 1620 s	1267 s 1213 sh	1341 m 1325 m	702 m	837 m	425 m	–
(12)	$[Fe(HL_b)(H_2L_b)] \cdot 3H_2O$	3400 s, br 3325 s	3090 m	–	1610 vs	1257 sh 1231 s	1345 s 1306 s	708 m	834 m	445 w	350 w
(13)	$[Co_2(HL_b)(H_2O)_2]NO_3$	3434 s, br 3306 s, br	3079 s, br	–	1614 vs	1250 s 1240 s	1320 s	715 m	832 m	488 m	–
(14)	$[Ni_2(HL_b)(H_2O)_2]NO_3$	3446 s, br	3071 s, br	–	1624 s	1238 m	1361 s 1318 m	704 m	836 s	440 m	389 w
(15)	$[Cu_2(HL_b)(H_2O)_2]NO_3$	3527 m, br	3088 m, br	–	1632 s	1234 m	1354 s 1322 s	708 m	835 s	465 m	348 w
(16)	$[Zn(H_2L_b)(EtOH)]$	3466 s, br 3385 s	3080 s	–	1650 v 1624 s	1232 m 1267 m	1345 m 1306 m	700 m	834 s	437 m	360 w

s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

The ligands showed the stretching frequencies of $\nu(C=S)$ at 1200 s and 1194 s for H_4L_a and H_4L_b, respectively.

In the IR spectra of the ligands, the band at 1265–1269 cm^{-1} is ascribed to the stretching vibration of the phenolic ν(C–O) [22]. This band is shifted to lower frequency (1231–1257 cm^{-1}) in IR spectra of the metal complexes indicating that the metal ions are coordinated through the oxygen atom(s) of the phenolic group(s) after deprotonation. In the IR spectrum of the H_4L_b ligand, the band corresponding to the stretching frequency of the C–Cl bond appears at the same position (832–837 cm^{-1}) in its transition metal complexes. The new bands in all complexes in the frequency ranges at 342–389 and 425–490 cm^{-1} can be assigned to the stretching frequencies ν(M–N) and ν(M–O), respectively, which are absent in the IR spectra of the free ligands [10]. The presence of the bands at 2878 cm^{-1} is due to the ν(H-bonded OH).

Electronic spectral data of the H_4L_a and H_4L_b ligands and their transition metal complexes were recorded in DMF solutions and are listed in Table IV. In the electronic spectra of both ligands, five absorption bands at 220, 315, 240, 350 and 390 nm for the former ligand, and 210, 240, 300, 365 and 390 nm for the latter ligand, were characterized. The first and third bands correspond to $^1L_a \rightarrow {}^1A_1$ and $^1L_b \rightarrow {}^1A_1$ transitions of the phenyl ring, the second band corresponds to the $\pi \rightarrow \pi^*$ transition of the C=S group [23]. The fourth band corresponds to the $\pi \rightarrow \pi^*$ transition of the azomethine group, and the fifth band corresponds to the $n \rightarrow \pi^*$ transitions from the phenyl ring to the azomethine group [24].

The absorption bands of the azomethine group (C=N) at 350 and 365 nm for the ligands appear at lower wavenumbers (345–360 nm) in the spectra of the complexes due to the coordination of the nitrogen atoms of the ligands to the metal ions.

TABLE IV Electronic absorption bands (nm) of the thiocarbohydrazone ligands (H_4L_a and H_4L_b) and their transition metal complexes[a] and their assignments

Ligand[b]	$^1L_a \rightarrow {}^1A$ *Phenyl ring*	$\pi \rightarrow \pi^*$ *C=S*	$^1L_b \rightarrow {}^1A$ *Phenyl ring*	$\pi \rightarrow \pi^*$ *C=N*	$n \rightarrow \pi^*$	
(1)	210 (1.30)	240 (0.56)	300 (1.00)	365 (0.07)	390 (0.05)	
(2)	210 (1.30)	240 (0.56)	300 (1.00)	365 (0.07)	390 (0.05)	
Complexes[b]	$^1L_a \rightarrow {}^1A_1$ *Phenyl ring*	$\pi \rightarrow \pi^*$ *C=S*	$^1L_b \rightarrow {}^1A$ *Phenyl ring*	$\pi \rightarrow \pi^*$ *C=N*	*L → M and M → L (CT)*	*d–d transition*
(3)		245 (0.31)		345 (0.10)	420 (0.06)	580 (0.03)
(4)			310 (0.64)	350 (0.50)	400 (0.72)	500 (0.02)
(5)		247 (0.64)		360 (0.45)	420 (0.04)	670 (0.02)
(6)		250 (0.32)		350 (0.07)	404 (0.05)	641 (0.02)
(7)		245 (0.61)		360 (0.30)	420 (0.05)	813 (0.05)
						707 (0.03)
						657 (0.03)
(8)		250 (0.77)		360 (0.55)	430 (0.06)	645 (0.02)
(9)		250 (0.68)		350 (0.41)	430 (0.03)	–
(10)		245 (0.31)		345 (0.10)	420 (0.06)	585 (0.03)
(11)			310 (0.64)	350 (0.50)	400 (0.72)	503 (0.02)
(12)		247 (0.64)		360 (0.45)	420 (0.04)	670 (0.02)
(13)		250 (0.32)		350 (0.07)	404 (0.05)	650 (0.02)
(14)		245 (0.61)		360 (0.30)	420 (0.05)	781 (0.05)
						712 (0.03)
						689 (0.03)
(15)		250 (0.77)		360 (0.55)	430 (0.06)	650 (0.02)
(16)		250 (0.68)		350 (0.41)	430 (0.03)	–

[a] Values of $\varepsilon_{\max}$ are in parentheses and multiplied by 10^{-4} ($\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$).

[b] See Table II for characterization of the compounds.

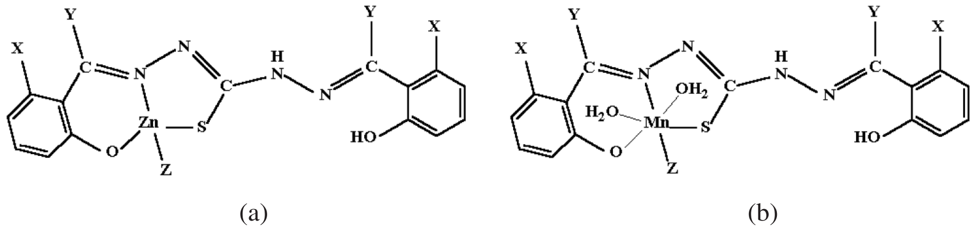
TABLE V Thermal gravimetric analysis (TGA) data of the thiocarbohydrazone (H_4L_a and H_4L_b) metal complexes

Metal complex		*MW*	*Weight* (%)/*Temp.* (°C)				*Residue*	
			A	*B*	*C*	*D*	%	*MW*
(3)	$[Cr(HL_a)(H_2L_a)] \cdot 3H_2O$	787.863	7.32 (25–200)	14.23 (192–289)	61.25 (289–663)	–	17.20	92.90
(4)	$[Mn(H_2L_a)(H_2O)_3]$	449.391	–	3.88 (107–209)	15.76 (209–480)	65.41 (480–790)	14.95	78.50
(5)	$[Fe(HL_a)(H_2L_a)] \cdot 3H_2O$	791.714	10.00 (25–200)	54.55 (200–435)	21.62 (435–600)	–	13.83	69.02
(6)	$[Co_2(HL_a)(H_2O)_2]NO_3 \cdot EtOH$	601.370	3.92 (25–95)	25.48 (95–290)	18.30 (290–468)	40.25 (472–797)	12.05	55.21
(7)	$[Ni_2(HL_a)(H_2O)_2]NO_3$	554.817	8.30 (25–105)	47.62 (105–309)	27.48 (309–570)	–	16.60	79.01
(8)	$[Cu_2(HL_a)(H_2O)_2]NO_3 \cdot EtOH$	610.596	4.23 (25–100)	36.09 (100–420)	42.33 (420–650)	–	17.35	80.29
(9)	$[Zn(H_2L_a)(H_2O)]$	423.799	–	8.32 (100–236)	55.40 (236–470)	18.40 (470–770)	17.9	86.39
(10)	$[Cr(HL_b)(H_2L_b)] \cdot 3H_2O$	869.530	7.32 (25–200)	14.23 (192–289)	61.25 (289–663)	–	17.20	92.90
(11)	$[Mn(H_2L_b)(EtOH)(H_2O)_2]$	518.281	–	3.88 (95–240)	15.76 (240–480)	65.41 (480–780)	14.95	78.50
(12)	$[Fe(HL_b)(H_2L_b)] \cdot 3H_2O$	873.379	10.00 (25–200)	54.55 (200–435)	21.62 (435–600)	–	13.83	69.02
(13)	$[Co_2(HL_b)(H_2O)_2]NO_3$	596.135	3.92 (25–95)	25.48 (95–290)	18.30 (290–468)	40.25 (472–797)	12.05	55.21
(14)	$[Ni_2(HL_b)(H_2O)_2]NO_3$	595.650	8.30 (25–105)	47.62 (105–309)	27.48 (309–570)	–	16.60	79.01
(15)	$[Cu_2(HL_b)(H_2O)_2]NO_3$	605.362	4.23 (25–100)	36.09 (100–420)	42.33 (420–650)	–	17.35	80.29
(16)	$[Zn(H_2L_b)(EtOH)]$	492.690	–	8.32 (100–236)	55.40 (236–470)	18.40 (470–770)	17.90	86.39

Thermogravimetric analysis (TGA) data for the thiocarbohydrazone complexes are presented in Table V. One of the features in the TGA data concerning the associated water molecules within the complexes supports the elemental analyses [25]. Water of crystallization was lost within the temperature range 95–120°C, whereas the coordinated water molecules were lost within the temperature range 140–200°C.

From the elemental analyses, molar conductivity, UV-visible spectral data, magnetic measurements, IR spectral data and TGA, it is possible to determine the type of coordination of the thiocarbohydrazones in their metal complexes. The ligands act either as dinegative tridentates in coordinating Zn(II) and Mn(II) ions to form mononuclear complexes, or as trinegative hexadentates in coordinating Cu(II), Ni(II) and Co(II) ions to form binuclear complexes. On the other hand, in the case of Fe(III) and Cr(III) ions, when two ligand molecules were coordinated to the metal cation, one of them acts as a dinegative tridentate and the other acts as a mononegative tridentate ligand. Bonding sites are the phenolic oxygen atom, N^1 or N^4 nitrogen atoms and the thiol sulfur atom of the ligands.

The zinc(II) and manganese(II) complexes are monometallic, even if the starting metal : ligand molar ratio is 2 : 1, probably due to their low solubility so that they precipitate immediately in the reaction medium. The great flexibility of the ligands and the presence of numerous donor sites make it difficult to establish the coordination type in the monometallic complexes, even when it is clear that at least one oxygen from the



(a) (b)

H_4L_a; X = H, Y = CH_3 and Z = H_2O

H_4L_b; X = Cl, Y = H and Z = EtOH

FIGURE 3 Suggested structures of (a) Zn(II) and (b) Mn(II) complexes of the mononuclear tridentate thiocarbohydrazone (H_4L_a and H_4L_b) ligands.

phenolic site and its imine nitrogen are involved in the coordination, as well as the thiol sulfur atom. In all the monometallic complexes of related ligand complexes characterized by X-ray diffraction analysis, the ligand is in the *syn* form. However, the structure of the different metal complexes of the related bis(phenyl-2-pyridyl ketone) thiocarbohydrazone ligand suggests that the ligand behaves as a tridentate [26]. In addition, in $[Co(HL)]_4(CH_3COO)_4 \cdot H_2O$ (H_2L = tetra(2-pyridyl)thiocarbazone) [27], where the ligand is pentadentate, a cobalt-based cationic molecular square is obtained by self-assembly. Figure 3 shows the suggested structure of mononuclear Zn(II) and Mn(II) tridentate thiocarbohydrazone complexes in a *syn* form.

The stretching frequencies of both the uncoordinated protonated phenolic oxygen (OH group) and the amino (NH group) together with ν(OH) of the coordinated H_2O or EtOH molecules persist in the IR spectra of the Zn(II) and Mn(II) complexes, in the range 3362–3490 cm^{-1}, and thus the IR spectra do not offer significant proof of the correct structure. On the other hand, two bands were observed for the stretching frequencies of the azomethine groups that could be assigned to the coordinated and uncoordinated azomethine group at 1616–1629 and 1645–1685 cm^{-1}, respectively. The IR spectra of the Zn(II) and Mn(II) complexes show two bands for the stretching frequencies of the coordinated and uncoordinated phenolic oxygen, ν(CO), at 1232–1237 and 1260–1267 cm^{-1}, respectively.

ONS coordination around the metal, completed by solvent molecule(s), is likely in these complexes. Molar conductance values of the mononuclear Zn(II) and Mn(II) complexes in DMF solution lie in the range 6–20 $ohm^{-1} cm^2 mol^{-1}$, indicating their nonelectrolytic nature [28]. From the absence of any counterion, charge balance and coordination number, it can be concluded that one molecule of the ligand is deprotonated two times in the case of divalent Zn(II) and Mn(II) cations.

Although manganese(II) is a d^5 system and the absorption bands are very weak, the spectrum exhibits one additional band at 500 and 503 nm for the complexes of the H_4L_a and H_4L_b ligands, respectively. The band position suggests the formation of an octahedral structure [29]. This complex is paramagnetic with magnetic moment 5.71 BM [30].

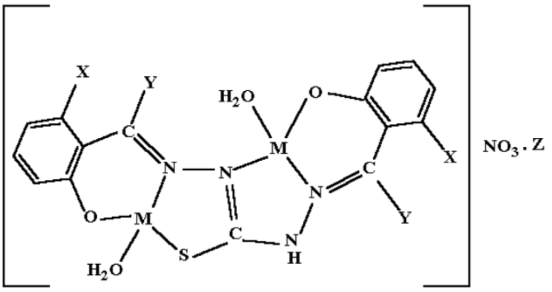
Zinc(II) ions favor formation of tetrahedral complexes with a variety of oxygen donor ligands, and more stable ones with nitrogen-donor ligands such as NH_3. However, in some cases Zn(II) ions have the ability to increase the coordination number above four; among these is $[Zn(S_2CNEt_2)_2]_2$, which achieves five-coordination by dimerizing [31].

From the TGA data (Table V), the coordinated water and ethanol molecules were lost within the temperature range 95–240°C, supporting the structure of the Zn(II) and Mn(II) complexes.

Electronic spectra of the Co(II) complexes with H_4L_a and H_4L_b ligands show mainly one absorption band at 641 or 650 nm, respectively, which is attributed to the $^2A_2 \rightarrow {}^4T_1(P)$ transitions, typical for complexes having a tetrahedral structure. The magnetic moment values, $\mu_{eff} = 4.73$ and 4.80 BM, respectively, confirm the formation of tetrahedral complexes [29,30]. Electronic spectra of the Ni(II) complexes show absorption bands at 813, 707 and 657 nm for H_4L_a, and 781, 712 and 688 nm for H_4L_b. These bands are assigned to the $^3T_1 \rightarrow {}^3T_1(P)$ transition. The complexes show paramagnetic behavior with magnetic moments $\mu_{eff} = 3.43$ and 3.34 BM, respectively, suggesting the formation of tetrahedral structures [29,30]. Copper(II) is a d^9 system and has an asymmetric band at 645 and 656 nm for its complexes with H_4L_a and H_4L_b, respectively, assigned to the $^2E_g \rightarrow {}^2T_{2g}(G)$ transition. This transition may be made up of overlapping symmetrical bands due to the splitting of the e_g and t_{2g} levels, which results from the tetragonal distortion of Cu(II) complexes. The measured values of the magnetic moments for the Cu(II) complexes, 2.10 and 2.01 BM, respectively, confirm their tetrahedral structure [29,30].

The molar conductance measurements of the Co(II), Ni(II) and Cu(II) complexes in DMF solution lie in the range 41–91 $ohm^{-1}\,cm^2\,mol^{-1}$, indicating that the complexes fall in the expected range of 1 : 1 electrolytes [28] due to the presence of an uncoordinated nitrate ion.

IR spectra of the NO_3^- ion are not sufficiently well resolved to indicate free nitrate ion or its coordination as a mono- or bidentate nitrate, which could be shown by splitting of $\nu_3(NO_3)$ to double bands where the interference is in the region *ca* 1400–974 cm^{-1} [22]. Figure 4 shows the suggested structure of the binuclear Co(II), Ni(II) and Cu(II) thiocarbohydrazone (H_4L_a and H_4L_b) complexes.



M = Co(II), Ni(II) and Cu(II)

H_4L_a; X = H, Y = CH_3 and Z = EtOH (in Co(II) and Cu(II) only)

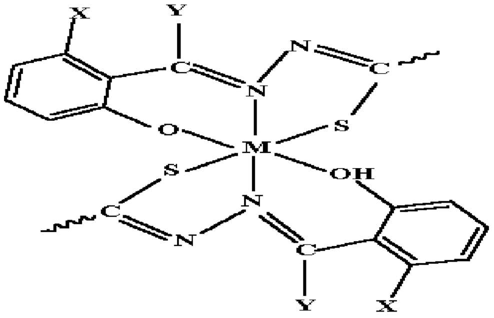
H_4L_b; X = Cl, Y = H and Z = none

FIGURE 4 Suggested structures of the binuclear Cu(II), Ni(II) and Co(II) thiocarbohydrazone (H_4L_a and H_4L_b) complexes.

The reaction of iron(III) and chromium(III) nitrate nonahydrates with each of the ligands H_4L_a and H_4L_b in ethanol afforded the corresponding monomeric complexes. Both Fe(III) and Cr(III) gave complexes of the same molecular formula $[M(HL)(H_2L)]$ with three lattice water molecules. IR spectra of Fe(III) and Cr(III) complexes show a significant band assigned to the stretching frequencies of the phenolic OH group, ν(OH), at 3321–3332 cm^{-1}. The formulations are in accord with elemental analyses, physical and spectroscopic measurements. The complexes are soluble in either dimethylformamide or dimethylsulfoxide. Molar conductance values of the Cr(III) and Fe(III) complexes were determined at concentrations of *ca* 1×10^{-3} M in DMF and lie in the range 6–22 $ohm^{-1} cm^2 mol^{-1}$, indicating that the complexes are nonelectrolytes [28]. The effective magnetic moments ($\mu_{eff} = 3.77–3.80$ BM for Cr(III) and $\mu_{eff} = 5.34–5.64$ BM for Fe(III) complexes) are close to the spin-only value ($\mu_{eff} =$ 3.87 BM for the three unpaired electrons of the Cr(III) complexes and $\mu_{eff} = 5.82$ BM for the five unpaired electrons of the Fe(III) complexes), confirming their suggested structure. The geometry of $FeO_2N_2S_2$ is octahedral or distorted octahedral. Figure 5 shows the suggested structures of the mononuclear Fe(III) and Cr(III) thiocarbohydrazone complexes.

The visible spectrum of the Fe(III) cation was obscured by a charge transfer band tailing into the visible region at 670 nm resulting in its dark color. Cr(III) showed mainly one peak in its visible spectrum at 580 or 585 nm due to $^4A_{2g} \rightarrow {}^4T_{2g}$ and the two transitions due to the $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and the $^2A_{2g} \rightarrow {}^4T_{1g}(P)$ did not appear and may be obscured by the ligand bands. These results indicate octahedral arrangements of the ligands in these complexes [29,30].

The thiocarbohydrazone ligands H_4L_a and H_4L_b and their transition metal complexes were screened for antimicrobial activity by a reported method [16]. Table VI shows that the ligands have lower activity against either *Azotobacter* and *Rhizobium* bacteria or *Fusarium oxysporium* fungus. The activity of both $[Fe(HL_b)(H_2L_b)] \cdot 3H_2O$ and $[Co_2(HL_b)(H_2O)_2]NO_3$ complexes was less towards *Azotobacter* than *Rhizobium* bacteria. The values of the percentage of inhibition of bacteria or



M = Fe(III) and Cr(III)

H_4L_a; X = H and Y = CH_3 H_4L_b; X = Cl and Y = H

FIGURE 5 Suggested structures of the mononuclear Fe(III) and Cr(III) thiocarbohydrazone (H_4L_a and H_4L_b) complexes.

TABLE VI Values of the percentage of the zone of inhibition of bacteria or fungus for the thiocarbohydrazone ligands (H_4L_a and H_4L_b) and their transition metal complexes[a]

Ligand/ Complex	*Percentage of zone of inhibition of bacteria or fungus*		
	Fusarium oxysporium	*Azotobacter*	*Rhizobium*
(**1**)	13.6	13.2	19.7
(**2**)	12.2	14.4	16.7
(**3**)	38.6	58.7	56.2
(**4**)	30.7	44.4	37.2
(**5**)	31.4	38.5	45.8
(**6**)	39.2	16.7	41.6
(**7**)	48.1	37.7	47.6
(**8**)	45.3	39.2	19.8
(**9**)	39.4	21.9	22.1
(**10**)	35.5	57.8	51.1
(**11**)	26.7	37.8	35.6
(**12**)	27.8	15.6	46.7
(**13**)	35.6	17.8	37.8
(**14**)	44.4	34.4	45.6
(**15**)	42.2	28.9	16.7
(**16**)	37.8	26.4	24.4

[a] See Table II for characterization of the compounds.

fungal growth also show that all the complexes are more active than their thiocarbohydrazone ligands (Table VI).

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