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Synthesis, magnetic, spectral and biological studies of copper(II) complexes of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-substituted thiosemicarbazones

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Abstract: The synthesis and characterization of copper(II) complexes with 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one thiosemicarbazone and N(4)-substituted thiosemicarbazones are reported. Elemental analysis, molar conductivities, magnetic measurements and spectral (i.r., electronic, e.s.r., and n.m.r.) studies have been used to characterize the complexes. The i.r. spectra show that the thiosemicarbazones behave as bidentate ligands, either in the thione or thiolato form. Stereochemistries are proposed for the complexes on the basis of spectral and magnetic studies. Both the thiosemicarbazones and their complexes show either modest or no growth inhibitory activity against Aspergillus niger and Paecilomyces variotii.

Keywords: Synthesis, Thiosemicarbazones, Characterization, Complexes, Stereochemistries, Antifungal

1. Introduction

Transition metal ion complexes of thiosemicarbazones have been the subject of many articles [1- 4]. These compounds possess a range of biological applications that include antitumor [5], antifungal [6], antiviral [7], antibacterial [8] and antimalarial [9] activities. There have been an increasing number of studies featuring complexes of heterocyclic thiosemicarbazones, particularly thiosemicarbazones prepared from commercially available thiosemicarbazide [10, 11]. In addition, reports concerning iron(III), cobalt(II, III) [12], nickel(II), zinc(II) [13], and copper(II) [14] complexes of 4-formylantipyrine N(4)-methyl-, N(4)-dimethyl- and piperidylthiosemicarbazones. We describe here the preparation and characterization of copper(II) complexes with 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one thiosemicarbazone, N(4)-methyl-, N(4)-dimethyl- and 3-piperidylthiosemicarbazones (HBATP4DH, HBATP4M, HBATP4DM and HBATPpip, respectively),

2. Experimental

2.1. Materials

4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one, thiosemicarbazide, N(4)-methyl thiosemicarbazide and copper salts were purchased from Aldrich and used without further purification.

2.2. Synthesis of Ligands

N(4)-Dimethyl thiosemicarbazide and 3-piperidylthiosemicarbazide were prepared following the method of Scovill [15]. Thiosemicarbazones were prepared by mixing equimolar amounts of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and the desired thiosemicarbazide in anhydrous EtOH and stirring for 2 hrs.

2.3. Synthesis of Metal Complexes

All the metal complexes were prepared by adding a solution of the copper(II) salt (0.002 mol) in EtOH (40 cm^3) was mixed with a solution of the desired thiosemicarbazone

(0.002 mol) in EtOH (40 cm^3), and the resulting mixture was stirred under reflux for 3 hrs. The resulting solids were filtered off and placed on a warm plate at 35 ^oC until required for characterization.

2.4. Instruments

IR spectra of the solid ligands and there complexes were recorded on Perkin-Elmer infrared spectrometer 681 or Perkin-Elmer 1430 using KBr disc. The ^1H NMR spectra were recorded with a JEOL EX-270 MHz or JEOL ECA-500 MHz FT-NMR spectrometer in d_6-DMSO as solvent, where the chemical shifts were determined relative to the solvent peaks. The molar conductivity of the metal complexes in DMF at 10^{-3} M concentration was measured using a dip cell and a Bibby conductimeter MC1 at room temperature. The resistance measured in ohms whereas the molar conductivities were calculated according to the equation: $\Lambda=V\times K\times Mw/g\times\Omega$, where: Λ= molar conductivity ($ohm^{-1}cm^2mol^{-1}$), V = volume of the complex solution, K = cell constant 0.92 cm^{-1}, Mw = molecular weight of the complex, g = weight of the complex, Ω = resistance measured in ohms. Electronic absorption spectra (Near infrared / Visible / Ultraviolet) were recorded on a Perkin Elmer 550 spectrometer using cm^{-1} quartz cells taking DMSO as solvent. The nujol mull electronic absorption spectra were recorded using whatman filter paper No.1 and referenced against another similar filter paper saturated with paraffin oil. The magnetic susceptibilities of the polycrystalline complexes were measured in a borosilicate tube with a Johnson Matthey Magnetic susceptibility Balance at room temperature using the modified Gouy method. The solid ESR spectra of the complexes recorded with ELEXSYS E500 Bruker spectrometer in 3-mm Pyrex Tubes at 298 ^oK. Diphenylpicrylhydrazide (DPPH) was used as a g-marker for the calibration of the spectra. The elemental analysis (CHN) was performed in the Microanalytical Unit within Cairo University (Egypt) by the usual methods of analysis. All the thiosemicarbazones and their copper(II) chloride and copper(II) bromide complexes were examined for biological activity by testing them against two pathogenic human fungi, Aspergillus niger and Paecilomyces variiotti. Testing was done using an agar diffusion method. Sabourad Dextrose Agar (25 ml) was poured into petri dishes and after solidification, a 0.5 ml portion of a spore suspension containing the desired fungi was added. The 6 mm assay disks were saturated with a dimethylsulfoxide solution containing either a thiosemicarbazone or a metal ion complex. Five concentrations were tested: 200, 400, 600, 1000 and 1600 µg/ml. The antifungal activity was determined by measuring the diameter of the inhibition zones. An average value for each solution was obtained by discarding the high and low values and averaging the remaining six. These values were compared to nystatin, a commercially available antifungal agent.

3. Results and Discussion

The prepared ligands were investigated by elemental analyses (Table 1) and (^{1}HNMR and infrared) spectroscopy (Table 2).

Table 1. *Colors, partial elemental analyses, molar conductivities and magnetic susceptibilities of the copper(II) complexes of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-Substituted Thiosemicarbazones*

No.	Compound	Color, Fw.	Found (Calc)%				Λ-[a]$_M$	[n]eff (B.M.)[a]
			C	H	N	Cl		
	HBATP4DH	White	61.87	5.02	19.88	-	-	
	$C_{18}H_{17}N_5OS$	337.49	(61.52)	(4.88)	(19.93)			
1	[Cu(HBATP4DH)Cl_2].2H_2O	Green	40.96	4.24	13.92	13.97	24.5	1.83
	$C_{18}H_{21}Cl_2CuN_5O_3S$	521.91	(41.42)	(4.06)	(13.42)	13.59		
2	[Cu(HBATP4DH)Br_2]. H_2O	Green	36.96	3.34	11.92		18.7	1.78
	$C_{18}H_{19}Br_2CuN_5O_2S$	592.80	(36.47)	(3.23)	(11.81)			
3	[Cu(BATP4DH)(OAc)]$_2$.H_2O	Green	51.90	5.04	13.82		11.9	0.93
	$C_{44}H_{51}Cu_2N_{10}O_7S_2$	1023.16	(51.65)	(5.02)	(13.69)			
4	[Cu (HBATP4DH)$_2$].(BF_4)$_2$	Green	47.40	3.40	14.87		133.5	1.74
	$C_{36}H_{34}B_2CuF_8N_{10}O_2S_2$	940.00	(46.00)	(3.65)	(14.90)			
	HBATP4M	Pale yellow	61.50	5.21	19.22	-	-	
	$C_{19}H_{19}N_5OS$	365.45	(62.45)	(5.24)	(19.16)			
5	[Cu(HBATP4M)Cl_2]. H_2O	Blue	44.10	4.44	13.70	13.89	28.5	1.92
	$C_{19}H_{21}Cl_2CuN_5O_2S$	517.92	(44.06)	(4.09)	(13.52)	13.69		
6	[Cu(HBATP4M)Br_2]	Blue	38.70	3.20	11.70		30.2	1.71
	$C_{19}H_{19}Br_2CuN_5OS$	588.81	(38.76)	(3.25)	(11.89)			
7	[Cu(BATP4M)(OAc)]$_2$	Brown	53.19	5.80	13.24	-	10.7	0.96
	$C_{46}H_{53}Cu_2N_{10}O_6S_2$	1033.20	(53.48)	(5.17)	(13.56)			
8	[Cu (HBATP4M)$_2$].(BF_4)$_2$].H_2O	Buff	43.40	4.93	9.60	-	126.3	1.58
	$C_{38}H_{40}B_2CuF_8N_{10}O_3S_2$	986.07	(46.29)	(4.09)	(9.36)			
	HBATP4DM	yellow	63.40	5.93	18.60			
	$C_{20}H_{21}N_5OS$	379.48	(63.30)	(5.58)	(18.46)			
9	[Cu(HBATP4DM)Cl_2]. H_2O	Brown	45.61	4.20	13.80	13.90	19.50	1.74
	$C_{20}H_{23}Cl_2CuN_5O_2S$	531.95	(45.16)	(4.36)	(13.17)	(13.33)		
10	[Cu(HBATP4DM)Br_2].2H_2O	Brown	37.61	4.20	10.80		17.7	1.63
	$C_{20}H_{25}Br_2CuN_5O_3S$	638.86	(37.60)	(3.94)	(10.96)			
11	[Cu(BATP4DM)(OAc)]$_2$.H_2O	Brown	53.61	5.21	13.80		11.3	0.86

No.	Compound	Color, Fw.	Found (Calc)%				Λ-[a]$_M$	[a]eff (B.M.)[a]
			C	H	N	Cl		
12	$C_{47}H_{56}Cu_2N_{10}O_7S_2$ [Cu (HBATP4DM)$_2$].(BF$_4$)$_2$ $C_{39}H_{39}B_2CuF_8N_{10}O_3S_2$	1064.24 Brown 981.08	(53.04) 47.61 (47.75)	(5.30) 4.21 (4.01)	(13.16) 14.80 (14.28)		119.7	1.57
13	HBATPpip $C_{23}H_{25}N_5OS$ [Cu(HBATPpip)Cl$_2$] $C_{20}H_{23}Cl_2CuN_5O_2S$	Yellow 419.54 Brown 554.00	65.61 (65.85) 49.61 (49.87)	6.21 (6.01) 4.20 (4.55)	16.84 (16.69) 12.75 (12.64)	12.92 (12.80)	16.3	1.84
14	[Cu(HBATPpip)Br$_2$].H$_2$O $C_{23}H_{27}Br_2CuN_5O_2S$	Brown 660.91	41.74 (41.80)	4.30 (4.12)	10.79 (10.60)		10.6	1.74
15	[Cu(BATPpip) (OAc)].H$_2$O $C_{25}H_{30}CuN_5O_4S$	Brown 560.15	53.77 (53.61)	5.36 (5.40)	12.64 (12.50)		18.3	1.81
16	[Cu (HBATPpip)$_2$].(BF$_4$)$_2$ H$_2$O $C_{46}H_{52}B_2CuF_8N_{10}O_3S_2$	Brown 1094.26	50.26 (50.49)	4.65 (4.79)	12.76 (12.80)		22.5	1.88

a= Ω^{-1} mol^{-1} cm^2

Table 2. *Infrared spectra (cm^{-1}) of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-Substituted Thiosemicarbazones and their Copper(II) complexes.*

No.	Compound	ν [N(4)H)]	ν(C=N)	ν(C=S)	ν(M-N)	ν(M-S)	ν(M-Cl)
	HBATP4DH	3425(s) 3244(s)	1595(m)	840(s)	--	--	--
1	[Cu(HBATP4DH)Cl$_2$].2H$_2$O	3370(s) 3295(w)	1587(s)	840(s)	452(m)	368(m)	325(s), 312(m)
2	[Cu(HBATP4DH)Br$_2$]. H$_2$O	3367(m) 3288(w)	1582(m)	732(s)	448(w)	346(w)	--
3	[Cu(BATP4DH)(OAc)]$_2$.H$_2$O	3425(m) 3327(m)	1580(s) 1572(m)	720(s)	454(m)	344(w)	--
4	[Cu (HBATP4DH)$_2$].(BF$_4$)$_2$]	3445(s) 3226(m)	1677(m)	738(s)	452(w)	344(w)	--
	HBATP4M	3385(s)	1605(s)	852(m)	--	--	--
5	[Cu(HBATP4M)Cl$_2$]. H$_2$O	3342(m)	1587(s)	775(s)	455(m)	338(w)	318(s) 308(m)
6	[Cu(HBATP4M)Br$_2$]	3295(s)	1584(s)	785(s)	457(m)	320(m)	--
7	[Cu(BATP4M)(OAc)]$_2$	3264(m)	1588(s)	774(s)	458(w)	330(w)	--
8	[Cu (HBATP4M)$_2$].(BF$_4$)$_2$].H$_2$O	3324(m)	1580(s)	784(m)	462(m)	320(s)	--
	HBATP4DM	--	1600(s)	830(m)	--	--	--
9	[Cu(HBATP4DM)Cl$_2$]. H$_2$O	--	1576(m)	795(s)	456(m)	332(m)	318(s) 302(m)
10	[Cu(HBATP4DM)Br$_2$].2H$_2$O	--	1573(m)	780(s)	450(m)	338(w)	--
11	[Cu(BATP4DM)(OAc)]$_2$.H$_2$O	--	1568(m)	776(s)	447(m)	344(m)	--
12	[Cu (HBATP4DM)$_2$].(BF$_4$)$_2$	--	1570(m)	792(m)	450(w)	344(w)	--
	HBATPpip	--	1592(s)	840(s)	--	--	--
13	[Cu(HBATPpip)Cl$_2$]	--	1576(m)	775(m)	448(m)	342(w)	320(m) 302(w)
14	[Cu(HBATPpip)Br$_2$].H$_2$O	--	1573(s)	748(m)	456(w)	346 (w)	--
15	[Cu(BATPpip) (OAc)].H$_2$O	--	1580(s) 1564(m)	740(s)	450(m)	342(w)	--
16	[Cu (HBATPpip)$_2$].(BF$_4$)$_2$ H$_2$O	--	1570(s)	784(m)	448(w)	344(w)	--

The ^{1}H-n.m.r. spectra confirm the purity of the thiosemicarbazones. Both BATP4DM and HBATPpip exist as the Z-isomer with intramolecular hydrogen bonding in $CDCl_3$, based on the appearance of N(2)H resonance at δ (P.P.m) *ca*. 13.3. In [$^2H_6$]DMSO there is a mixture of the Z isomer, the E isomer with hydrogen bonding to the solvent (δ *ca*. 10.7) and a bifurcated tautomer (i.e. hydrogen bonding to carbonyl oxygen and thiolato sulfur) in which the N(2)H is transferred to N(1), resulting in a conjugated thiosemicarbazone moiety and yellow colour. Therefore, the resonance at δ = 11.2 in the spectrum of HBATP4M is assigned to N(2)H, which is hydrogen bonded to the [$^2H_6$]DMSO solvent; it and the resonance at δ = 7.8 disappear in the presence of D_2O, confirming the assignment of the latter as N(4)H. This resonance for N(2)H is considerably upfield from that found for HBATP4DH δ = 7.9 [16].

The stoichiometries of the copper(II) complexes of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-substituted thiosemicarbazones (HBATP4M, HBATP4DM and HBATPpip) are shown in Table 2. Complexes of the neutral ligands are generally formed unless OAc is included in the preparative mixture. However due to the bulkiness of both HBATP4DM and HBATPpip, two complexes, [Cu(HBATP4DM) (BATP4DM)] BF_4 and [Cu(HBATPpip) (BATPpip)]BF_4, are isolated with both neutral and anionic ligands. The neutral and anionic form of the ligand appears to coordinate in bidentate NS fashion and the carbonyl oxygen of the pyrazolone ring is not involved in coordination. Only the complexes prepared from copper(II)

tetrafluoroborate are electrolytes and the elevated molar conductivities found for some of the chloro complexes are probably due to partial decomposition in solution. The magnetic moments approach the theoretical value of 1.73 B.M. for mononuclear copper(II) complexes, except for the three binuclear copper(II) complexes derived from the acetate salts. These complexes have values in the 0.6-1.2 B.M. range, indicating significant interaction between copper(II) centres.

3.1. Infrared Spectra

The infrared spectral bands most useful for determining the thiosemicarbazon's mode of coordination are given in (Table 2).

Decreases in the ν(C=N) energy by 15-40 cm^{-1} on complexation are consistent with coordination of the azomethine nitrogen, as is the presence of a band at *ca*. 450 cm^{-1}, which is assigned to ν(M-N) for this nitrogen [17]. A second band assignable to ν(C=N) is expected in the spectra of those complexes having anionic thiosemicarbazone ligands, since the anionic ligand formally has a double bond between N(2) and C(3) of the thiosemicarbazone moiety [18]. The increase for the ν(N-N) frequency in the spectra of the complexes is probably due to enhanced double bond character through chelation, thus offsetting the loss of electron density via donation to metal ion, and is supportive of azomethine nitrogen coordination. Coordination of the thione/thiolato sulfur is indicated by a decrease in energy of the thioamide IV band, which derives considerable intensity from ν(CS), as well as a band in the the 330-360 cm^{-1} range, assignable to ν(Cu S) [19]. As expected, greater energy decreases in the thioamide IV band occur for the anionic form of the ligand due to C-S formally becoming a single bond [20]. A band in the 1640-1660 cm^{-1} region of the spectrum of the thiosemicarbazones is found essentially unchanged in the spectra of the complexes, which indicates that the carbonyl oxygen is not involved in coordination [21]. The spectra of the chloro complexes show two assignable, strong to medium intensity ν(Cu-Cl) bands in the 300-330 cm^{-1}, range indicative of terminal chloro ligands [22]. We are unable to assign ν(Cu-Br) bands with our spectrometer.

Extensive infrared spectral studies reported on metal acetate complexes [23] indicate that the acetate ligand may coordinate to a metal centre in a monodentate, bidentate or bridging manner. The $\nu_a(CO_2)$ and $\nu_s(CO_2)$ of the free acetate ions are at 1560 and 1416 cm^{-1}, respectively. For monodentate coordination the resulting ν (C=O) is found at a higher energy than $\nu_a(CO_2)$ and ν (C-O) is at lower energy than $\nu_s(CO_2)$. As a result, the separation between the two ν (CO) bands is much larger in monodentate complexes than for the free ion, but with bidentate acetate coordination (i.e. non-bridging Or bridging) the separation between ν (CO) bands is smaller than for the free ion. The two ν(CO) bands in the spectra of the acetate complexes under study have $\nu_a(CO_2)$ at *ca*. 1590 cm^{-1} with $\nu_s(CO_2)$ at *ca*. 1470 cm^{-1}, suggestive of bridging bidentate coordination, which results in the lower magnetic moment [24].

The absence of coordinated water molecules from the complexes under study is confirmed by the absence of the rocking, twisting and wagging vibrational modes which are normally activated at 970-930 cm^{-1} and 660-600 cm^{-1} and in the same time the presence of weak and broad band at ca. 3520 cm^{-1} indicating that the water in all of these complexes is lattice [25]. A broad band at ca. 1060 cm^{-1}, assignable to $\nu_3(BF_4)$, and a relatively sharp band at ca. 510 cm^{-1} due to $\nu_4(BF_4)$ indicate non-coordination [26] of the tetrafluoroborate ions in all compounds, in agreement with the molar conductivity results (Table 1).

3.2. Magnetic Susceptibilities

The magnetic moment values for the mononuclear copper(II) complexes are close to spin-only value for one unpaired spin (~ 1.7 B.M.) at room temperature. As magnetic susceptibilities of the complexes were not determined below room temperature, nothing can be said about the presence or absence of magnetic exchange. Dark green acetate complexes display a subnormal magnetic moment values (~ 1.2 B.M.) at room temperature which suggests that the compounds have dimeric structures in which magnetic exchange takes place probably by means of overlap of the $d_x2\text{-}y2$ orbitals and the spin exchange interactions between copper(II) ions may be explained on the basis of bridging by acetate ligand. A sulfur-bridged dimeric structure seems unlikely since sulfur-bridging leads to very strong antimagnetic interaction resulting in complete diamagnetism in copper(II) complexes.

3.3. Electronic Absorption Spectra

Listed in (Table 3) are the energies of the solid state electronic transition for the three thiosemicarbazones, as well as their copper(II) complexes. Omitted from Table 3 are the higher energy $\pi\rightarrow\pi^*$ transitions (*ca*. 34500 cm^{-1}) which are not significantly altered on complex formation. The $n\rightarrow\pi^*$ transition associated with the azomethine portion of the thiosemicarbazone portion of the thiosemicarbazone moiety is in the region 28000-31000 cm^{-1} in the spectra of the thiosemicarbazones and altered significantly on complexation (Table 3). A second $n\rightarrow\pi^*$ transition originating from the thioamide portion of the thiosemicarbazone moiety is found at somewhat lower energies (27000-30000 cm^{-1}). In the copper(II) complexes this latter band generally shifts to higher energies and sometimes merges with the $n\rightarrow\pi^*$ transition associated with the azomethine portion [27]. Also present at energies below 30000 cm^{-1} in the spectra of the copper(II) complexes are $S\rightarrow Cu^{II}$ charge transfer bands, as well as $Br\rightarrow Cu^{II}$ charge transfer bands [28]. The $Cl\rightarrow Cu^{II}$ bands are generally found in the 29000 cm^{-1} region of the spectrum [29]. This series of complexes has very broad bands due to the $n\rightarrow\pi^*$ transitions, and it is difficult to assign energies to the transition between 20000 and 30000 cm^{-1}. The four coordinate copper(II) complexes have a lower energy shoulder, $d_x2\text{-}_y2 \rightarrow d_{xz}$, on the main d → d composite

band consistent with an essentially square planar arrangement [30]. The d → d maximum of the main band, which is assigned to transitions to d_x2-$_y2$ from , d_{xz} , , d_{yz} , and , d_z2, is found at *ca*. 17000 cm^{-1}.

Table 3. *Solid state electronic spectra (cm^{-1}) of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-substituted thiosemicarbazones and their copper(II) complexes*

	Compound	Concentration				
		200[a]	400	600	1000	1600
	HBATP4DH	29840	24480			
1	$[Cu(HBATP4DH)Cl_2].2H_2O$	30110	24510	21460	14460	
2	$[Cu(HBATP4DH)Br_2].H_2O$	29860	24780	20480	14260	
3	$[Cu(BATP4DH)(OAc)]_2.H_2O$	29840	24470		17460	
4	$[Cu(HBATP4DH)_2].(BF_4)_2]$	29780	24260	18740	14940	13630(sh)
	HBATP4M	29920	24070	22180		
5	$[Cu(HBATP4M)Cl_2].H_2O$	30250	23460	22150	17210	16460(sh)
6	$[Cu(HBATP4M)Br_2]$	29960	24260		14370	
7	$[Cu(BATP4M)(OAc)]_2$	30430	23870		17560	14690(sh)
8	$[Cu(HBATP4M)_2].(BF_4)_2].H_2O$	29890	24710		18270	14320(sh)
	HBATP4DM	30160	28240	24610		
9	$[Cu(HBATP4DM)Cl_2].H_2O$	29980	27870	22040	15840	14040(sh)
10	$[Cu(HBATP4DM)Br_2].2H_2O$	30280	27980	23610	15880	
11	$[Cu(BATP4DM)(OAc)]_2.H_2O$	29840	27880	23480	17680	
12	$[Cu(HBATP4DM)_2].(BF_4)_2$	29780	27890	22760	17360	16240(sh)
	HBATPpip	31680	23840			
13	$[Cu(HBATPpip)Cl_2]$	31780	27430	24380	16480	
14	$[Cu(HBATPpip)Br_2].H_2O$	31670	26750		16870	
15	$[Cu(BATPpip)(OAc)].H_2O$	30860	27260	21380	17740	
16	$[Cu(HBATPpip)_2].(BF_4)_2 H_2O$	30540	27680	20480	16470	

sh: shoulder not resolved

Table 4. *Solution (DMSO) electronic spectra (cm^{-1}) of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-substituted thiosemicarbazones and their copper(II) complexes*

No.	Compound	Intraligand and charge transfer bands	d→d bands
	HBATP4DH	29780(4.41) 27810	
1	$[Cu(HBATP4DH)Cl_2].2H_2O$	29810(4.71) 27940 21870	14270(2.26)
2	$[Cu(HBATP4DH)Br_2].H_2O$	29750(4.78) 27880	14380(2.23)
3	$[Cu(BATP4DH)(OAc)]_2.H_2O$	29940(4.82) 27910	16450(2.32)
4	$[Cu(HBATP4DH)_2].(BF_4)_2]$	30120(4.86) 28140	15340(2.24)
	HBATP4M	30640(4.48) 27840	
5	$[Cu(HBATP4M)Cl_2].H_2O$	30670(4.52) 27910	1470(2.23)
6	$[Cu(HBATP4M)Br_2]$	29980(4.55) 27820	14840(2.28)
7	$[Cu(BATP4M)(OAc)]_2$	30120(4.62) 27860	17310(2.51)
8	$[Cu(HBATP4M)_2].(BF_4)_2].H_2O$	29780(4.69) 27810	15120(2.34)
	HBATP4DM	30280(4.39) 24640	
9	$[Cu(HBATP4DM)Cl_2].H_2O$	30170(4.42) 26740	15240(2.23)
10	$[Cu(HBATP4DM)Br_2].2H_2O$	29880(4.45) 27240	15160(2.27)
11	$[Cu(BATP4DM)(OAc)]_2.H_2O$	29480(4.64) 26480	16780(2.56)
12	$[Cu(HBATP4DM)_2].(BF_4)_2$	30120(4.73) 27020	15470(2.38)
	HBATPpip	29580(4.21) 24380	
13	$[Cu(HBATPpip)Cl_2]$	28540(4.32) 26480	15940(2.43)
14	$[Cu(HBATPpip)Br_2].H_2O$	29650(4.38) 27130	15230(2.38)
15	$[Cu(BATPpip)(OAc)].H_2O$	29470(4.52) 26540	17790(2.38)
16	$[Cu(HBATPpip)_2].(BF_4)_2 H_2O$	30140(4.54) 25890	15690(2.43)

The solution spectra (DMSO) of the 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-substituted thiosemicarbazones and their copper(II) complexes are presents in (Table 4). A peak associated with an n $\rightarrow\pi^*$ transition of the heterocyclic ring portion of the pyrazolin moiety is observed at about 35000 cm^{-1} in the spectra of the thiosemicarbazones and is unshifted in the spectra of their copper(II) complexes. A second band at *ca*. 3000 cm^{-1}, due to the n $\rightarrow\pi^*$ transition of the azomethine portion of the thiosemicarbazone moiety, has molar absorptivity, ε, of approximately 3×10^4 for the coordinated and uncoordinated ligand. Although a $Cl\rightarrow Cu^{II}$ charge transfer band might also be expected in this region of spectrum. A second $\pi\rightarrow\pi^*$ transition associated with the thione portion of the thiosemicarbazone moiety often appears as a low energy shoulder in the range of 23000-28000 cm^{-1}. In the complexes, this band generally merges with the $n\rightarrow\pi^*$ transition of the azomethine portion of the thiosemicarbazone moiety and, therefore, bands in this region of the complexes are assignable to $S\rightarrow Cu^{II}$ and other ligand to copper(II) charge transfer bands [31]. The solution d→d bands are altered from their energies in the solid state, suggesting that significant interaction with DMSO solvent molecules occurs. All

complexes exhibit a d → d band as weak shoulders in the visible region whose maximum of absorption lie in the visible region ~ 16000 cm^{-1}, such a feature is expected for a square planar chromophore in accordance with earlier reports [30, 32]. For the square planar complexes with $d_x2\text{-}_y2$ ground state, three spin allowed transitions are possible. In order to obtain additional information about the structure of the chelates, their spectra in pyridine were recorded. The presence of only one broad band at *ca*. 15000 cm^{-1} implies that the square planar configuration has been changed in a donor solvent, thus indicating that pyridine is coordinated [33].

3.4. Electronic Spin Resonance Spectral Studies

The powder ESR parameters of the copper(II) complexes measured at room temperature are shown in (Table 5). The lower $g_{//}$ values found for the bromo complexes are consistent with the greater covalency of the bromo compared to a chloro ligand as noted before in heteronuclear thiosemicarbazone complexes [34]. The lower the $g_{//}$ values of the chloro and acetato complexes suggest that the latter are likely four coordinate with acetato oxygen bridging. A lower $g_{//}$ values of the tetrafluoroborate complexes indicate more covalent planar bonding due to the presence of two sulfur donors; the two ligands are likely bidentate N, S donors [35]. The trend $g_{//} > g_{\perp} > 2.003$ observed for all complexes (for g tensors with orthorhombic splitting we take $g_{\perp} = (g_2 + g_3)/2$ indicates that the unpaired electron most likely resides in the $d_{x^2} - y^2$ orbital. Also, the g-tensor values of Cu(II) complexes can be used to derive the ground state. In tetragonally elongated octahedron the 3d unpaired electron for the Cu^{2+} ion lies in the $d_{x^2} - y^2$ orbital [36] ($^2B_{1g}$ as the ground state). The g values are then given by $g_{//} = 2(2 - 4\lambda / \Delta_1)$ and $g_{\perp} = 2(1 - \lambda / \Delta_2)$. On the other hand, for a tetragonally compressed octahedron, the electron lies in the d_{z^2} orbital ($^2A_1$ ground state). The g values are given by $g_{//} = 2$ and $g_{\perp} = 2(1 - 3\lambda / \Delta_3)$. Where Δ_1, Δ_2 and Δ_3 correspond to $d_{x^2} - y^2 \rightarrow d_{xy}$, $d_{x^2} - y^2 \rightarrow d_{xz}\, d_{yz}$ and $d_{x^2} - y^2 \rightarrow d_{z^2}$ excitations, respectively. From the observed g values (Table 6) it is clear that the unpaired electron lies predominantly in the $d_{x^2} - y^2$ and implying a $^2B_{1g}$ as a ground state. Kiveslson and Neiman [37] have suggested that the $g_{//}$ value in the Cu(II) complex can be used as a measure of covalent character of the metal-ligand bond. For the ionic environment it the $g_{//}$ value is normally 2.3 or higher and for the covalent environment it is less than 2.3. Using this criterion the data show considerable covalent character of the metal-ligand bond in the present complexes. The ESR parameters $g_{//}$, $g_{\perp}$ and the energies of the d-d transitions for the acetate complexes were used to evaluate the Racah parameters: $k_{//}^2$ and $k_{\perp}^2$, which may be regarded as measures of the covalency of the in-plane π–bonding and out-of plane π–bonding, respectively. In these complexes $g_{//} > g_{\perp} > 2.003$, which is consistent with $d_{x^2} - y^2$ ground state. Thus, the absorption band in the electronic spectrum at ca. 14000 cm^{-1} is due to Δ_1 and the one at *ca*. 17000 cm^{-1} is due to Δ_2 with the weaker Δ_3 transition between these two values. The following simplified expressions were used to calculate the bonding parameters $k_{//}^2$ and $k_{\perp}^2$ [38].

$$k_{//}^2 = (g_{//} - 2.0023)\Delta_2 / 8\lambda_{\circ}\ ,\ k_{\perp}^2 = (g_{\perp} - 2.0023)\Delta_1 / 2\lambda_{\circ}$$

Where λ_o is the spin-orbit coupling of the free copper(II) ion ($\lambda_{\circ} = -828\ cm^{-1}$). Hathaway [39] pointed out that for pure sigma bonding, $k_{//} \cong k_{\perp} \cong 0.77$ and for in-plane π–bonding, $k_{//} < k_{\perp}$; while for out-of-plane π–bonding, $k_{//} > k_{\perp}$. The acetate complexes under study it is observed that $k_{//} < k_{\perp}$ which indicates the presence of significant in-plane π–bonding [40].

Table 5. *E.s.r. spectral parameters of the copper(II) complexes of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-substituted thiosemicarbazones*

No.	Compound	Phase	Temp.	$g_{//}$	g_2	$g_{\perp}$ or g_3	g_{av} or g_o
1	$[Cu(HBATP4DH)Cl_2].2H_2O$	Solid	RT	2.206		2.049	2.101
2	$[Cu(HBATP4DH)Br_2].H_2O$	Solid	RT	2.186		2.044	2.091
3	$[Cu(BATP4DH)(OAc)]_2.H_2O$	Solid	RT	2.188		2.045	2.093
4	$[Cu(HBATP4DH)_2].(BF_4)_2]$	Solid	RT	2.166		2.036	2.079
5	$[Cu(HBATP4M)Cl_2].H_2O$	Solid	RT	2.213		2.052	2.106
6	$[Cu(HBATP4M)Br_2]$	Solid	RT	2.189		2.046	2.094
7	$[Cu(BATP4M)(OAc)]_2$	Solid	RT	2.184	2.058	2.094	2.112
8	$[Cu(HBATP4M)_2].(BF_4)_2].H_2O$	Solid	RT				2.054
9	$[Cu(HBATP4DM)Cl_2].H_2O$	Solid	RT	2.174	2.046	2.035	2.085
10	$[Cu(HBATP4DM)Br_2].2H_2O$	Solid	RT	2.153	2.052	2.027	2.077
11	$[Cu(BATP4DM)(OAc)]_2.H_2O$	Solid	RT	2.184	2.056	2.036	2.02
12	$[Cu(HBATP4DM)_2].(BF_4)_2$	Solid	RT	2.144	2.067	2.024	2.078
13	$[Cu(HBATPpip)Cl_2]$	Solid	RT	2.184	2.058	2.033	2.092
14	$[Cu(HBATPpip)Br_2].H_2O$	Solid	RT				2.065
15	$[Cu(BATPpip)(OAc)].H_2O$	Solid	RT	2.184	2.064	2.021	2.089
16	$[Cu(HBATPpip)_2].(BF_4)_2\ H_2O$	Solid	RT	2.142	2.057	2.019	2.073

Table 6. *TGA data for some copper(II) complexes*

No.	Complex	Temperature range °C	Weight loss Found/(Calcd.)	Assignment
1	[Cu(HBATP4DH)Cl_2].2H_2O	72-128	5.37 (5.91)	Loss two molecules of hydrated water
		194-287	13.95 (13.58)	i) Loss two coordinated chloride ion
		287-550	63.89 (64.66)	ii) Decomposed of organic ligand
		550°C	15.65 (15.24)	CuO
8	[Cu (HBATP4M)$_2$].(BF_4)$_2$.H_2O	69-130	1.52 (1.83)	Loss one molecule of hydrated water
		130-322	18.03 (17.61)	Loss two molecules of BF_4
		322-594	74.76 (74.12)	decomposed of organic ligand
		594-640	11.96 (12.13)	CuS+2C
10	[Cu(HBATP4DM)Br_2].2H_2O	78-136	5.19 (5.64)	Loss two molecules of hydrated water
		136-295	25.38 (25.01)	Loss two molecules of coordinated bromide Decomposed of
		295-586	59.37 (59.40)	organic ligand
		586-684	20.84 (20.61)	CuS+ 3C
15	[Cu(BATPpip)(OAc)].H_2O	64-131	3.51 (3.22)	Loss one molecule of hydrated water
		131-247	11.69 (10.54)	Loss of coordinated acetate
		247-570	74.76 (74.90)	Decomposed of organic ligand
		570-623	13.96 (14.20)	CuO

s.d: start of decomposition

3.5. Thermal Studies

Because the infrared spectra and elemental analyses show the presence of water molecules in the chemical structures of some metal complexes. The thermogravimetric analysis TGA was undertaken for the hydrated Cu(II) complexes and The TGA data and their assignments are summarized in Table (6). In general, the water of hydration can be considered either as crystal or coordinated water. According to Nikolav *et al* [41], water eliminated below 150 °C can be considered as crystal water, and that eliminated above 150 °C may be due to its coordination to the central metal ion. In the present study the water of hydration was eliminated below 150 °C, which suggests that the water of hydration was crystal water. The amount of water found from the weight loss in the thermogram approaches the theoretical value calculated for mono and dihydrates. A survey of the literature reveals that the order of decomposition by pyrolysis of the constituents of solid complexes is: water, anion, ligand and final residue, corresponding to either metal oxide or free metal. In the present study copper(II) complexes follow this order where the first step (70–130 °C) for all complexes represented the dehydration process. The second step (200 – 460 °C) for all complexes is the elimination of the chloride, bromide, acetate or tetrafluoroborate group. The third step (400 – 680 °C) is the complete decomposition of the complexes which ended with copper oxide formation.

3.6. Antifungal Studies

Table 7. *Activity of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-substituted thiosemicarbazones and their copper(II) chloride and copper(II) bromide complexes against Aspergillus niger*

	Compound	Concentration				
		200[a]	400	600	1000	1600
	HBATP4DH	6.0	6.0	6.0	6.0	6.0
1	[Cu(HBATP4DH)Cl_2].2H_2O	6.0	6.0	6.0	6.0	6.0
2	[Cu(HBATP4DH)Br_2]. H_2O	6.0	6.0	6.0	6.0	6.0
	HBATP4M	6.0	6.0	6.0	6.0	6.0
3	[Cu(HBATP4M)Cl_2]. H_2O	6.0	6.0	6.0	6.0	6.0
4	[Cu(HBATP4M)Br_2]	6.0	6.0	6.0	6.0	6.0
	HBATP4DM	7.9	13	15.4	20.2	23.2
5	[Cu(HBATP4DM)Cl_2]. H_2O	6.0	6.0	6.0	12.5	15.5
6	[Cu(HBATP4DM)Br_2].2H_2O	6.0	6.0	6.0	6.0	6.0
	HBATPpip	6.0	12.4	15.6	17.4	20.5
7	[Cu(HBATPpip)Cl_2]	7.4	11.6	14.6	18.2.	22.4
8	[Cu(HBATPpip)Br_2].H_2O	6.0	7.0	12.3	14.5	14.8

a) μ/ml; and
b) mm diameter of the growth inhibition zone (6.0 – no inhibition).

Table 8. *Activity of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)-substituted thiosemicarbazones and their copper(II) chloride and copper(II) bromide complexes against Paecilomyces variotii.*

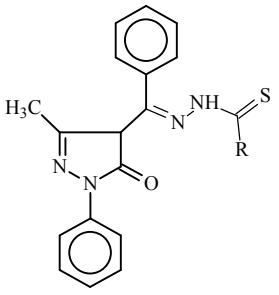
	Compound	Concentration				
		200[a]	400	600	1000	1600
	HBATP4DH	6.0[b]	6.0	6.0	6.0	6.0
1	[Cu(HBATP4DH)Cl_2].2H_2O	6.0	6.0	6.0	6.0	6.0
2	[Cu(HBATP4DH)Br_2]. H_2O	6.0	6.0	6.0	6.0	6.0
	HBATP4M	6.0	6.0	6.0	6.0	12.0
3	[Cu(HBATP4M)Cl_2]. H_2O	6.0	6.0	6.0	6.0	6.0
4	[Cu(HBATP4M)Br_2]	6.0	6.0	6.0	6.9	6.4
	HBATP4DM	9.4	20.2	22.7	30.3	34.6
5	[Cu(HBATP4DM)Cl_2]. H_2O	6.0	6.8	7.4	9.8	12.7
6	[Cu(HBATP4DM)Br_2].2H_2O	6.0	6.0	6.5	8.2	8.6
	HBATPpip	6.0	13.2	14.6	18.7	21.8
7	[Cu(HBATPpip)Cl_2]	16.5	20.7	21.7	23.6	28.3
8	[Cu(HBATPpip)Br_2].H_2O	7.4	9.5	12.7	14.8	16.3

a) μ/ml; and
b) mm diameter of the growth inhibition zone (6.0 – no inhibition).

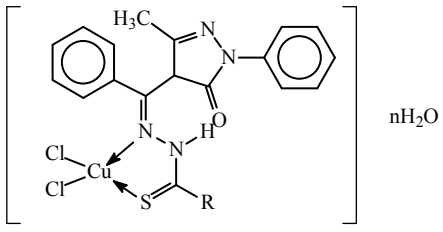
Thiosemicarbazones and some of their copper(II) complexes were assayed for their antifungal activity in order to obtain quick information about their potential use for antitumor agents. Two pathogenic human fungi were used for the assay, Paecilomyces variotii and Aspergillus niger. (Tables 7 and 8) lists the results of antifungal tests of thiosemicarbazones and their copper(II) chlorides and bromides complexes, against Aspergillus niger and Paecilomyces variotii. Against Aspergillus niger, neither of

the HBATP4DH and HBATP4M exhibit any activity until the highest concentration, 1600 µg/ml, presumably due to a lack of hydrogen bonding. HBATP4DM shows a considerable amount of activity, comparable to that of nystatin, a commercially available antifungal agent. The copper(II) complex, $[Cu(HBATP4DM)Cl_2]$, was inactive at the lowest three concentrations, but possess some activity at the two highest dilutions. The bromo complexes were completely inactive. This is consistent with the previous findings where the complexes of the smaller thiosemicarbazones were relatively inactive. Against Paecilomyces variotii HBATP4DH and HBATP4M were inactive except at the highest concentration tested. The dialkyl thiosemicarbazone, HBATP4DM, showed a tremendous amount of activity at the highest concentration tested (34.0 mm of growth inhibition at 1600 µg/ml) and was active even at the lowest concentrations tested. Once again, the HBATP4DH and HBATP4M are inactive due to a lack of hydrogen bonded isomers. Copper(II) complexes of HBATP4DM showed a decrease in activity compared to the uncomplexed thiosemicarbazone [42]. This decrease in activity is attributed to either an increase in the size of the compound or a deviation from planarity.

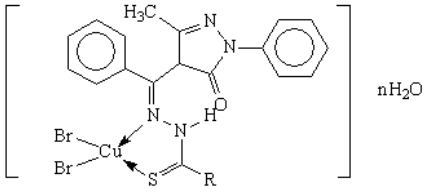
The obtained data are consistent with the proposed chemical structures of the organic ligands and their copper(II) complexes as shown in scheme 1.



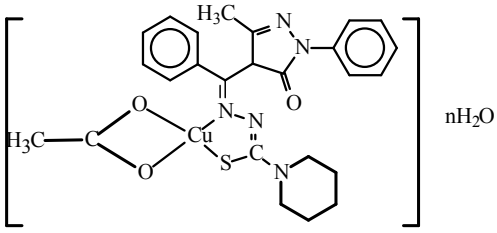
$R = NH_2$	HBATP4DH
$R = NH(CH_3)$	HBATP4M
$R = NH(CH_3)_2$	HBATP4DM
$R = N(C_2H_5)_2$	HBATP3pip

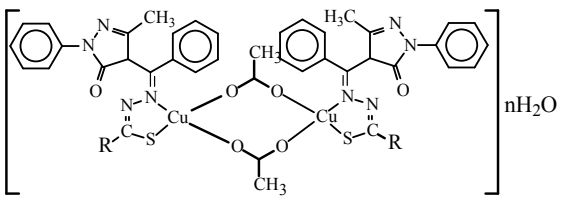


R	n
NH_2	2
$NH(CH_3)$	1
$N(CH_3)_2$	1
$N(C_2H_5)_2$	-

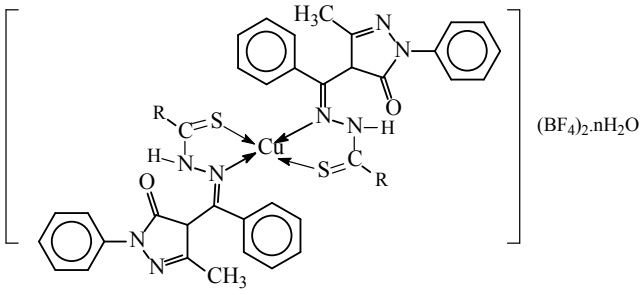


R	n
NH_2	2
$NH(CH_3)$	-
$N(CH_3)_2$	2
$N(C_2H_5)_2$	1





R	n
NH_2	1
$NH(CH_3)$	-
$NH(CH_3)_2$	1



R	n
NH_2	-
$NH(CH_3)$	1
$N(CH_3)_2$	-
$N(C_2H_5)_2$	1

Scheme 1. *Structural representation of the organic ligands and their copper(II) complexes*

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