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Synthesis And Spectral Characterization Of 1-Acetoacetanilide-4-Phenyl-3-Thiosemicarbazone Complexes



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ABSTRACT

The new 1-acetoacetanilide-4-phenyl-3-thiosemicarbazone (H_2aapt) complexes; $[M(Haapt)(AcO)(H_2O)_n]$ ($M = Co(II)$, $n=1$; $M=Ni(II)$, $n=2$; $M(II)=Cu$, Cd , $n=0$), $[M(Haapt)Cl(H_2O)_n]$ ($M(II)=Cu$, Ru , $n=2$; $M=Cd(II)$, $n=1$), $[Cu(Haapt)_2]$, $[Pd(H_2aapt)Cl_2]$, $[Ag(H_2aapt)(H_2O)_2]$ NO_3 and $trans-[UO_2(Haapt)_2]$ are presented and studied by IR, 1H -NMR and electronic spectra, magnetic and thermal studies. The cyclic voltammetry was applied to study the electrochemical behavior of $[Ru(Haapt)Cl(H_2O)_2]$ complex, which was found to be an efficient catalyst for the organic oxidation of primary alcohols, secondary alcohols, aldehydes and diols. The formation of complexes in solution was studied pH-metrically and the order of their stability constants ($\log k_1$ and $\log k_2$) were found to be $Cu(II) > Ni(II) > Zn(II) > Cd(II) > Co(II)$ and $Zn(II) > Cu(II) > Ni(II) > Cd(II) > Co(II)$, respectively. © 2007 Trade Science Inc. -INDIA

KEYWORDS

Complexes;
Spectra;
Oxidation;
Thermal studies;
Stability constant.

INTRODUCTION

Thiosemicarbazones and their complexes exhibit a broad spectrum of biological properties, including, anticarcinogenic^[1,2] and virus growth inhibitors^[3]. In our laboratory, many studies on transition metal complexes with thiosemicarbazone derivatives have been reported^[4-10]. In continuation of our previous studies on O, N^[11], and O, N, S^[4-10,12,13] donor ligands,

we now report the synthesis and characterization of the new complexes of 1-acetoacetanilide-4-phenyl-3-thiosemicarbazone (H_2aapt ; Figure 1) with some first and second row transition elements. Also, we report their magnetic and thermal studies as well as the electrochemical behavior of $[Ru(Haapt)Cl(H_2O)_2]$ complex. The catalytic oxidation of primary alcohols, secondary alcohols, aldehydes and diols by $[Ru(Haapt)Cl(H_2O)_2]$ complex have been examined.

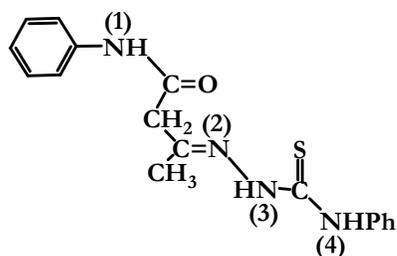


Figure 1: Structure of 1-acetoacetanilide-4-phenyl-3-thiosemicarbazone (H_2aapt)

The stability constants of some of the reported complexes in solution have been identified pH-metrically.

EXPERIMENTAL

Instrumentation

Microanalyses were determined by the micro analytical Unit of Cairo University. Magnetic moments at 25°C were recorded using a Johnson Matthey magnetic susceptibility balance with $Hg[Co(SCN)_4]$ as calibrant. Electronic spectra in DMSO were recorded using a Unicam UV₂₋₁₀₀ U.V.-vis. spectrometer. IR spectra were measured as KBr discs on a matson 5000 FT-IR spectrometer. 1H -NMR spectra were measured on a varian gemini WM-200 spectrometer (Laser Centre, Cairo University). Thermal analysis measurements were made in the 20-800°C range at the heating rate of 10°C min⁻¹, using $\alpha-Al_2O_3$ as a reference, on a Shimadzu thermogravimetric analyzer TGA-50. Conductometric measurements were carried out at room temperature on a YSI Model 32 conductivity bridge. The pH-metric measurements were performed using a Metrohm E₅₃₆ potentiograph equipped with a Dosimat (Metrohm, Herisau, Switzerland). Cyclic voltammetry was performed on a potentiostat wave generator (Oxford press) equipped with a 7000 AM X-Y recorder. The electrochemical cell assembly consists of a spiral Pt wire (0.5 mm diam) as auxiliary electrode, with glassy carbon and Ag/AgCl as working and reference electrodes, respectively.

Preparation of ligand

1-Acetoacetanilide-4-phenyl-3-thiosemicarbazone (H_2aapt) was prepared by stirring a mixture of 4-phenyl-3-thiosemicarbazide (1.67 g, 0.1 mol) with acetoacetanilide (1.77 g, 0.1 mol) in EtOH (40 ml)

and 5 M HCl was added (2 ml). The reaction mixture was stirred at room temperature for 4 h. The white precipitate was filtered off, washed, recrystallized from EtOH and dried *in vacuo*.

Preparation of complexes

[Ru(H_2aapt)Cl(H_2O)₂]

Hydrated ruthenium trichloride (0.065 g, 0.25 mmol) in EtOH (25 ml) was added with stirring to H_2aapt (0.165 g, 0.5 mmol). The reaction mixture was boiled under reflux for 4 h producing a dark green precipitate. It was filtered off while hot, washed with hot EtOH and dried *in vacuo*.

[Pd(H_2aapt)Cl₂]

To a stirred solution of H_2aapt (0.33 g, 1 mmol) in EtOH (15 ml), K_2PdCl_4 (0.33 g, 1 mmol) in H_2O (5 ml) was added. The reaction mixture was stirred for 0.5 h. The red brown complex was filtered off, washed with water, EtOH, Et₂O and dried *in vacuo*.

[Ag(H_2aapt)(H_2O)₂] NO_3

Silver nitrate (0.087 g, 0.5 mmol) in H_2O (1 ml) was added to H_2aapt (0.165 g, 0.5 mmol) in EtOH (10 ml) to produce a pale yellow solid. It was stirred and left in dark for 1 h, filtered off, washed with little H_2O , EtOH, Et₂O and dried in dark *in vacuo*.

[M($Haapt$)(AcO)(H_2O)_n] (M=Co(II), n=1; M=Ni(II), n=2; M(II)=Cu, Cd, n=0)

These complexes were synthesized by mixing of both H_2aapt (0.33 g, 1 mmol) and the corresponding metal acetate (1 mmol) in EtOH (25 ml). The reaction mixture was boiled under reflux for 2-3 h. The solid complexes were separated out either during reflux or after cooling. The fine gray (Ni), brown (Co, Cu) and yellow (Cd) complexes were filtered off, washed with EtOH, Et₂O and air-dried.

[M($Haapt$)Cl(H_2O)_n] (M=Cu(II), n=2; M=Cd(II), n=1)

Hydrated copper chloride (0.17 g, 1 mmol) or cadmium chloride (0.23 g, 1 mmol) in EtOH (10 ml) was added to H_2aapt (0.33 g, 1 mmol) in EtOH (20 ml). The reaction mixture was boiled under reflux for 2 h. The brown (Cu) or yellow (Cd) precipitate was filtered off, washed with EtOH, Et₂O and dried *in vacuo*.

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[Cu(Haapt)₂]

An aqueous solution of copper sulfate (0.25 g, 1 mmol) was added to H₂aapt (0.33 g, 1 mmol) in EtOH (20 ml). The reaction mixture was boiled under reflux upon which a green-brown precipitate was isolated. It was filtered off, washed with EtOH, Et₂O and air-dried.

Trans-[UO₂(Haapt)₂]

Hydrated uranyl acetate (0.21 g, 0.5 mmol) in MeOH (10 ml) was added to H₂aapt (0.165 g, 0.5 mmol) in MeOH (15 ml). The resulting solution was boiled under reflux for 3 h in a steam bath. The orange solution was reduced in volume until the precipitate separated out. It was filtered off, washed with little ice-cold MeOH and dried *in vacuo*.

Catalytic oxidation

For the catalytic oxidation of primary alcohols, secondary alcohols, aldehydes and diols by the [Ru(Haapt)Cl(H₂O)₂] complex, the organic substrate (1.0 mmol) was added to KIO₄ (2.5 mmol) in CH₃CN - water (1 : 2; 15 ml) and the complex (0.02 mmol). The reaction mixture was stirred under reflux at 348 K, then cooled to room temperature and extracted with Et₂O (3 × 25 ml). The ethereal layer was dried with anhydrous Na₂SO₄. The aldehyde or ketone content was qualified as its 2, 4-dinitrophenyl hydrazone derivatives. The aqueous layer was acidified with 5 M H₂SO₄ (pH = 2), extracted with Et₂O (3 × 25 ml), dried and evaporated to give either carboxylic or dicarboxylic acids.

pH-Metric measurements

The protonation constant of H₂aapt and the formation constants of some of its reported complexes at 298.15 K were determined pH-metrically^[14]. The following solutions mixtures (A, B, C) were titrated pH-metrically with standardized 9.2 × 10⁻³ M NaOH at constant ionic strength (M KNO₃). (A) 5 ml of 5.4 × 10⁻³ M HCl + 2.5 ml of M KNO₃, (B) Mixture (A) + 1 ml of 5 × 10⁻³ M H₂aapt and (C) Mixture (B) + 0.1 ml of 1 × 10⁻² M aqueous solution of the metal ions Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)). These solutions were completed to 25 ml with the appropriate volume of H₂O - EtOH (3:7- V/V).

RESULTS AND DISCUSSION

The elemental analyses and some physical properties of the isolated complexes are listed in TABLE 1. The data obtained are in agreement with the suggested formulae. The molar conductivity values of the complexes in DMSO showed them to be non-electrolytes^[15].

Vibrational spectra

TABLE 2 shows the IR spectral data of H₂aapt and its complexes with provisional assignments of selected vibrations. In the IR spectrum of H₂aapt, the bands in the 3320-3430 cm⁻¹ region assigned to the stretching vibration of NH groups^[10, 16]. The strong band at 1653 cm⁻¹ is attributed to ν(C=O) stretching vibration^[13] while the medium intensity one at 1610 cm⁻¹ is due to ν(C=N) stretch^[13]. The medium intensity band at 1030 cm⁻¹ is assigned to ν(N-N) vibration while that at 805 cm⁻¹ is attributed to ν C=S stretch^[13,17]. The absence of bands above 3500 cm⁻¹ or in the 2500-2600 cm⁻¹ region which would be due to ν(OH) and ν(SH) vibrations, respectively; indicating the presence of H₂aapt in the thione/keto form^[18].

A comparison of the IR spectra of H₂aapt and the reported complexes shows that H₂aapt behaves as a neutral bidentate in case of [Ag(H₂aapt)(H₂O)₂]NO₃ and [Pd(H₂aapt)Cl₂], mononegative bidentate as shown in [M(Haapt)(AcO)] (M = Cu, Cd) and [Cd(Haapt)Cl(H₂O)], and as a mononegative tridentate in the other reported complexes.

The IR spectral data of [Pd(H₂aapt)Cl₂] shows that H₂aapt coordinates to Pd(II) ion via the thione sulfur (C=S) and azomethine (C=N) centers as a neutral bidentate ligand forming a five membered ring including the metal ion (Figure 2). This mode of chelation is suggested by the shift of the ν(C=S) and ν(C=N) stretches to lower wave numbers^[4,13]. The shift of ν(C=O) vibration to higher wave number indicating that this group is not participate in complexation. The complex shows extra IR bands at 375, 325 and 270 cm⁻¹ are attributed to ν(Pd-N)^[19], ν(Pd-S)^[19] and ν(Pd-Cl)^[19] stretches, respectively.

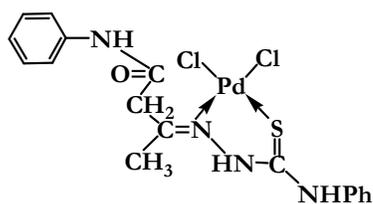
In case of [Ag(H₂aapt)(H₂O)₂]NO₃ complex, the strong bands at 1653 and 1610 cm⁻¹ in the free ligand

TABLE 1: Analytical data of H₂aapt and its complexes

Compound	% Calc (found)				$(\Lambda_m)^*$ in DMSO
	C	H	M	Cl	
H ₂ aapt	62.6 (62.6)	5.5 (5.6)	-	-	--
[Co(Haapt)(AcO)(H ₂ O)]·2H ₂ O	45.9 (45.9)	5.3 (5.2)	11.8 (12.1)	-	8
[Ni(Haapt)(AcO)(H ₂ O) ₂]·2H ₂ O	44.3 (44.0)	5.5 (5.8)	11.4 (11.0)	-	3
[Cu(Haapt)(AcO)]·4H ₂ O	43.9 (43.5)	5.4 (5.1)	12.2 (12.8)	-	6
[Cu(Haapt)Cl(H ₂ O) ₂]·2H ₂ O	41.1 (41.1)	5.1 (5.1)	12.8 (12.7)	7.1 (7.2)	7
[Cu(Haapt) ₂]·2H ₂ O	54.4 (54.7)	5.1 (5.0)	8.5 (8.9)	-	3
[Ru(Haapt)Cl(H ₂ O) ₂]	41.0 (41.0)	4.3 (4.1)	--	7.1 (6.8)	9
[Pd(H ₂ aapt)Cl ₂]	40.5 (40.1)	3.6 (3.8)	21.1 (21.4)	14.1 (14.1)	4
[Ag(H ₂ aapt)(H ₂ O) ₂]NO ₃ ·4H ₂ O	33.8 (33.4)	5.0 (4.7)	-	-	P. S
[Cd(Haapt)Cl(H ₂ O)]·H ₂ O	40.1 (39.8)	4.2 (3.9)	22.1 (22.4)	7.0(6.6)	5
[Cd(Haapt)(AcO)]	45.9 (45.4)	4.1 (4.2)	22.6 (23.0)	-	6
Trans-[UO ₂ (Haapt) ₂]·2H ₂ O	42.7 (43.0)	4.0 (3.8)	24.9 (25.0)	-	P. S

* in DMSO in ohm⁻¹ cm² mol⁻¹, P. S. = partially solubleTABLE 2: IR Spectral data of H₂aapt and its complexes

Compound	ν (C=O)	ν (C=N)	ν (C=N ³)	ν (N-N)	ν (C=S)	ν (C-S)	ν (C-O)	ν (M-O)	ν (M-N)	ν (M-S)	ν (M-Cl)
H ₂ aapt	1653	1610	--	1030	805	--	--	--	--	--	--
[Co(Haapt)(AcO)(H ₂ O)]·2H ₂ O	--	1588	--	1037	790	--	1110	503	410	320	--
[Ni(Haapt)(AcO)(H ₂ O) ₂]·2H ₂ O	--	1591	--	1044	788	--	1110	510	405	330	--
[Cu(Haapt)(AcO)]·4H ₂ O	--	1591	--	1055	821	--	1120	502	320	--	--
[Cu(Haapt)Cl(H ₂ O) ₂]·2H ₂ O	1645	1592	1620	1057	--	631	--	516	420	330	270
[Cu(Haapt) ₂]·2H ₂ O	--	1594	--	1051	790	--	1135	502	407	313	--
[Ru(Haapt)Cl(H ₂ O) ₂]	1640	1590	1615	1040	--	610	--	503	433	345	315
[Pd(H ₂ aapt)Cl ₂]	1669	1592	--	1035	785	--	--	--	375	325	270
[Ag(H ₂ aapt)(H ₂ O) ₂]NO ₃ ·4H ₂ O	1640	1587	--	1060	825	--	--	500	430	--	--
[Cd(Haapt)Cl(H ₂ O)]·H ₂ O	--	1591	--	1060	820	--	1150	510	405	--	286
[Cd(Haapt)(AcO)]	1664	1588	1615	1035	--	620	--	--	440	368	--
Trans-[UO ₂ (Haapt) ₂]·2H ₂ O	--	1600	--	1035	792	--	1135	910*	430	330	--

* $\nu^{as}(\text{UO}_2)$ stretchFigure 2: Structure of [Pd(H₂aapt)Cl₂]

arising from $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ are affected upon coordination and shifted to lower wave number while $\nu(\text{C}=\text{S})$ stretch is not affected, as expected since the carbonyl oxygen center is involved in coordination^[20]. This means that H₂aapt behaves as a neutral bidentate. This complex shows a new band at 1385 cm⁻¹, which may be assigned to $\nu(\text{NO}_3)$ stretching vibration prov-

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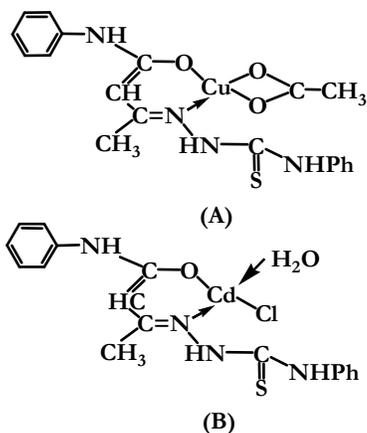


Figure 3: Structure of [Cu(Haapt)(AcO)] (A), [Cd(Haapt)Cl(H₂O)] (B)

ing the presence of NO₃⁻ as a free ion^[13,21].

In the IR spectra of [Cu(Haapt)(AcO)] and [Cd(Haapt)Cl(H₂O)] complexes, the stretching vibration $\nu(\text{C}=\text{O})$ of the free ligand is missing in the complexes indicating the participation of the deprotonated enolic carbonyl oxygen ($=\text{C}-\text{O}^-$) in coordination^[13]. Also, the $\nu(\text{C}=\text{N})$ stretch of the free ligand is shifted to lower wave number while $\nu(\text{N}-\text{N})$ is shifted to higher one upon complexation. These features are further supported by the observation of new bands at 1120-1150 cm⁻¹ region due to $\nu(\text{C}-\text{O})$ stretch^[13,22,23]. The complexes show extra IR bands at 500-510 and 320-405 cm⁻¹ regions are assigned to $\nu(\text{M}-\text{O})$ ^[12], $\nu(\text{M}-\text{N})$ ^[12,24] stretches, respectively. The complex, [Cd(Haapt)Cl(H₂O)], shows IR band at 286 cm⁻¹ may be due to $\nu(\text{Cd}-\text{Cl})$ stretch^[25] (Figure 3).

The IR spectrum of the [Cd(Haapt)(AcO)] complex shows that H₂aapt is acting as a mononegative bidentate coordinating Cd(II) ion through the deprotonated thiol sulfur and azomethine nitrogen atoms (Figure 4). This mode of chelation is supported by the disappearance of $\nu(\text{C}=\text{S})$ stretch with the appearance of new bands at 620 and 1615 cm⁻¹ probably arising from $\nu(\text{C}-\text{S})$ and $(\text{C}=\text{N}^3)$ ^[26] stretches, respectively, the shift of $\nu(\text{C}=\text{N})$ vibration to lower wave number and the shift of $\nu(\text{N}-\text{N})$ vibration to higher wave number. Also, the complex shows new bands at 440 and 368 cm⁻¹ may assign to $n(\text{Cd}-\text{N})$ and $\nu(\text{Cd}-\text{S})$ stretches, respectively^[25].

The IR spectral data of [M(Haapt)Cl(H₂O)₂] (M(II)=Cu, Ru) suggested that H₂aapt behaves as a mononegative tridentate ligand coordinating the

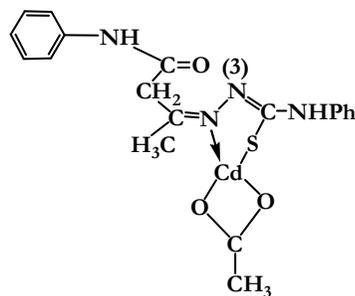


Figure 4: Structure of [Cd(Haapt)(AcO)]

metal ion via the deprotonated thiol sulfur, azomethine nitrogen and carbonyl oxygen centers. This mode of complexation (Figure 5) is suggested due to the disappearance of $\nu(\text{C}=\text{S})$ stretch with the simultaneous appearance of new bands at 610-631 and 1615-1620 cm⁻¹ regions attributed to $\nu(\text{C}-\text{S})$ and $\nu(\text{C}=\text{N}^3)$ stretches^[26]. The $\nu(\text{C}=\text{O})$ stretch is shifted to lower wave number^[13] and the shift of $\nu(\text{N}-\text{N})$ to higher wave number while $\nu(\text{C}=\text{N})$ is shifted to lower wave number^[13]. Also, the appearance of new bands at 503-516, 420-433, 330-345 and 270-315 cm⁻¹ regions that may be assigned to $\nu(\text{M}-\text{O})$ ^[4,13,20], $\nu(\text{M}-\text{N})$ ^[13,27,28], $\nu(\text{M}-\text{S})$ ^[4] and $\nu(\text{M}-\text{Cl})$ ^[29] stretches, respectively.

Finally, the IR spectral data of the complexes [M(Haapt)(AcO)(H₂O)_n] (M = Co, n = 1; M = Ni, n = 2), [Cu(Haapt)₂] and trans-[UO₂(Haapt)₂] show that H₂aapt behaves as a mononegative tridentate ligand coordinating the metal ions through the deprotonated enolic carbonyl oxygen, the azomethine nitrogen and the thione sulfur atoms. This feature is supported by the missing of $\nu(\text{C}=\text{O})$ stretching vibration of the free ligand with the observation of new band in the 1110-1135 cm⁻¹ due to $\nu(\text{C}-\text{O})$ in the complexes^[13]. The shift of $\nu(\text{C}=\text{S})$ and $\nu(\text{C}=\text{N})$ stretches to lower wave numbers upon coordination^[4]. Also, the complexes show extra IR bands at 503-510, 420-405 and 320-330 cm⁻¹ regions are assigned to $\nu(\text{M}-\text{O})$ ^[12,30],

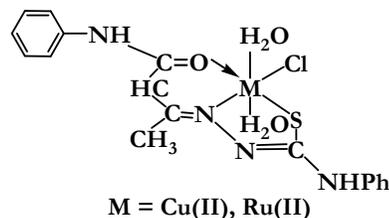


Figure 5: Structure of [M(Haapt)Cl(H₂O)₂] (M(II) = Ru, Cu)

$\nu(\text{M-N})^{[12,30]}$ and $\nu(\text{M-S})^{[12,30]}$ stretches, respectively. The complex $\text{trans-}[\text{UO}_2(\text{Haapt})_2]$ shows a strong IR band at 910 cm^{-1} assigned to $\nu^{\text{as}}(\text{UO}_2)$ of the trans-O=U=O group^[13,31,32]. The IR spectra of the complexes, $[\text{M}(\text{Haapt})(\text{AcO})(\text{H}_2\text{O})_n]$ ($\text{M} = \text{Co(II)}$, $n = 1$; $\text{M(II)} = \text{Cu, Cd}$, $n = 0$) show two extra bands at 1537 and 1410 cm^{-1} attributed to $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ of the acetate group, respectively, indicating asymmetric bidentate coordination of the acetate group ($\Delta(\text{OCO})$ between $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ is in the 140 cm^{-1} region)^[13,33].

¹H-NMR spectra

The ¹H-NMR spectral data of H_2aapt in d_6 -DMSO and some complexes have been analyzed, and are in close agreement with the reported data^[10]. In the free ligand, the aromatic protons appear at δ 7.1-7.6 ppm, the CH_2 protons give a singlet at δ 3.64 ppm while the CH_3 protons appear as a singlet at δ 3.21 ppm. The N(3)H, N(1)H and N(4)H protons appear as singlets at δ 10.7, 10.5 and 9.9 ppm, respectively^[4,10]. The ¹H-NMR spectrum of $[\text{Pd}(\text{H}_2\text{aapt})\text{Cl}_2]$ complex shows three singlets at δ 10.75, 10.5 and 9.8 ppm, almost the same as that of the free H_2aapt ^[10]. Furthermore, the presence of two resonances for each proton, suggesting a cis arrangement of this complex^[10]. The ¹H-NMR spectrum of $[\text{Cd}(\text{Haapt})\text{Cl}(\text{H}_2\text{O})]$ complex shows singlets at δ 3.75, 3.25, 10.8, 10.5 and 9.95 ppm corresponding to CH, CH_3 , N(3)H, N(1)H and N(4)H protons, respectively. The shifts to downfield values indicate the decrease in the electron density caused by withdrawing of electrons by Cd(II) from the coordination centre^[31].

Electronic spectra and magnetic measurements

The magnetic moments, electronic absorption bands (in DMSO) and ligand field parameters of some of the reported complexes are listed in TABLE 3.

The electronic spectrum of H_2aapt in DMSO showed that this ligand has $n \rightarrow \pi^*$ transition in the 300-325 nm region assigned to the phenyl ring^[34]. The energies are raised by ca 10 nm in the complexes^[35]. The 390-395 nm region bands are assignable to the $n \rightarrow \pi^*$ transition of the thiosemicarbazone thioamide moiety, and are shifted to higher energies in the complexes^[36].

The electronic spectrum of $[\text{Ni}(\text{Haapt})(\text{AcO})(\text{H}_2\text{O})_2]$ complex shows two absorption bands at 614 and 370 nm assignable to ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$ transitions^[37], respectively. The ligand field parameters, D_q , B , β (TABLE 3) as well as the magnetic moment ($\mu_{\text{eff}} = 2.84\text{ B.M.}$) are consistent with Ni(II) octahedral geometry^[12,37]. The complex $[\text{Co}(\text{Haapt})(\text{AcO})(\text{H}_2\text{O})]$ is paramagnetic with magnetic moment ($\mu_{\text{eff}} = 4.80\text{ B.M.}$). The electronic spectrum of this complex shows two bands at 690 and 588 nm which may be assigned to ${}^4T_{1g} \rightarrow {}^4A_{2g}(\text{F})$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$ transitions, respectively. The magnetic moment with the position of the absorption bands suggest octahedral geometry around the cobalt(II) complex^[20].

In the electronic spectrum of $[\text{Cu}(\text{Haapt})(\text{AcO})]$ complex, a broad band was observed with a maximum at 670 nm due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition, suggesting a square-planar configuration^[36,38]. The electronic spectra of the complexes, $[\text{Cu}(\text{Haapt})_2]$ and $[\text{Cu}(\text{Haapt})\text{Cl}(\text{H}_2\text{O})_2]$ show a broad band near 570 nm with a shoulder near 675 nm, which may be assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively, in a tetragonal distorted octahedral con-

TABLE 3: Magnetic moments, electronic spectra and ligand field parameters of H_2aapt and its complexes

Compound	μ_{eff} (B.M.)	Band Position (nm)	B	β	D_q	ν_1
$[\text{Co}(\text{Haapt})(\text{AcO})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$	4.8	690, 588	757	0.78	757	7570
$[\text{Ni}(\text{Haapt})(\text{AcO})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	2.84	614, 370	898	0.86	988	9880
$[\text{Cu}(\text{Haapt})(\text{AcO})] \cdot 4\text{H}_2\text{O}$	2.0	670	-	-	-	-
$[\text{Cu}(\text{Haapt})\text{Cl}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	1.74	680, 580, 410 (CT)	-	-	-	-
$[\text{Cu}(\text{Haapt})_2] \cdot 2\text{H}_2\text{O}$	1.8	674, 561	-	-	-	-
$[\text{Ru}(\text{Haapt})\text{Cl}(\text{H}_2\text{O})_2]$	Dia	594, 395, 320	-	-	-	-
$[\text{Pd}(\text{H}_2\text{aapt})\text{Cl}_2]$	Dia	476	-	-	-	-
$[\text{Ag}(\text{H}_2\text{aapt})(\text{H}_2\text{O})_2] \cdot \text{NO}_3 \cdot 4\text{H}_2\text{O}$	Dia	546, 364	-	-	-	-
$\text{Trans-}[\text{UO}_2(\text{Haapt})_2] \cdot 2\text{H}_2\text{O}$	Dia	458, 360	-	-	-	-

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figuration^[20,30]. The latter complex show extra absorption band at 410 nm which is attributed to Cu → Cl charge transfer^[39]. The reported Cu(II) complexes are found to be paramagnetic with magnetic moments (1.74 - 2.0 B. M.) which is normal for copper(II) complexes (the d⁹ system contains one unpaired electron^[42]).

The ground state of ruthenium(II) in an octahedral environment is ¹A_{1g} and only two spin allowed transitions, ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g} are expected^[40]. The electronic spectrum of [Ru(Haapt) Cl(H₂O)₂] shows three bands at 594, 395 and 320 nm which may be raised from ¹A_{1g} → ¹T_{1g}, ¹A_{1g} → ¹T_{2g} and ligand (π → dπ) transitions, respectively^[4,13,40], this indicates a low-spin octahedral arrangement around the diamagnetic Ru(II)^[4,40].

The electronic spectrum of the diamagnetic [Pd(H₂aapt)Cl₂] complex shows 476 nm due to ¹A_{1g} → ¹B_{1g} transition in a square-planar configuration^[13,19].

The electronic spectrum of [Ag(H₂aapt)(H₂O)₂]⁺ complex shows two absorption bands at 546 and 364 nm, which may be attributed to a square-planar stereochemistry^[13].

The electronic spectrum of trans-[UO₂(Haapt)₂] shows two bands at 458 and 360 nm may be due to S_g¹⁺ → ²π_u and n → π* charge transfer, respectively^[30].

Thermal studies

The thermal decompositions of the complexes, [Pd(H₂aapt)Cl₂] and [Ni(Haapt)(AcO)(H₂O)₂].2H₂O were studied using the TG and DTG technique. The thermogram of [Ni(Haapt)(AcO)(H₂O)₂].2H₂O shows the first weight loss between 100 and 145°C, which may correspond to the release of hydrated water molecules (Found, 6.9; Calcd., 7.0%)^[13]. The second weight loss endotherm step (Found, 54.4; Calcd., 54.2%) between 145 and 388°C may be attributed to the elimination of two coordinated water molecules, phenylimino (PhNH; C₆H₆N) and phenylthiourido (PhNHCSNH; C₇H₇N₂S) fragments^[4,12,13]. There are two other TG inflections in the ranges 388-510 and 510-570°C, the first endothermic weight loss in these inflections may arise from the removal of the acetate species (Found, 11.3; Calcd., 11.5%)^[41,42]. The last decomposition step which occurs gradually in the TG curve, may interpret as the loss of the remaining fragment (C₄H₄N)

of the ligand molecule (Found, 12.5; Calcd., 12.8%), leaving NiO representing (Found, 14.8; Calcd., 14.5%).

The thermogram of [Pd(H₂aapt)Cl₂] shows a great thermal stability up to 200°C, above which the weight loss occurs. The first endothermic decomposition step (200-310°C) is probably correlated with the elimination of phenylimino (PhNH; C₆H₆N) and a chlorine molecule (Found, 32.4; Calcd., 32.2%).

The second weight loss, between 310-490°C, may be attributed to the release of phenylthiourido (PhNHCSNH; C₇H₇N₂S) fragment (Found, 29.7; Calcd., 30.0%)^[4,12,13]. In the temperature range 490-650°C, the third weight loss may be corresponding to the removal of the remaining fragment (C₄H₄N) of the ligand molecule (Found, 13.5; Calcd., 13.3%), followed by PdO representing (Found, 24.5; Calcd., 24.3%).

Electrochemical studies

The electrochemical behavior of the complex, [Ru(Haapt)Cl(H₂O)₂] (10⁻³ M) in 0.5 M (n-Bu₄N)PF₆ as supporting electrolyte at room temperature in DMF was investigated by cyclic voltammetry versus Ag/AgCl electrode. The voltammogram shows a well defined cathodic wave at -0.8 V coupled with a well definite anodic wave at -0.35 V. Another anodic process is observed at 0.92 coupled with a well defined cathodic one at 0.42 V. The peak at 0.92 is assigned to Ru^{II/III} while that formed in the reverse at 0.42 V is presumably due to Ru^{III/II} reduction process. The irreversible anodic peak at 1.48 V, which may arise from Ru^{III/IV} oxidation. The value of E_{1/2} of the electrode (0.45 V), with good agreement with the reported data for [Ru(HHBP_{pip})₂] complex^[4].

Catalytic oxidation

We reported that the [Ru(HL)₂(H₂O)₂] complexes (H₂L = 1-(phenylacetyl and phenoxyacetyl)-4-phenyl-3-thiosemicarbazide) catalytically oxidized primary alcohols to aldehydes and carboxylic acids, secondary alcohols to ketones and aryl halides to aldehydes and acids in CCl₄ - CH₃CN - H₂O (1:1:2) at 70°C in the presence of NaIO₄ as co-oxidant^[13]. We tested the reported [Ru(Haapt)Cl(H₂O)₂] complex for organic catalytic oxidation by using 0.02 mmol of the catalyst in CH₃CN - H₂O (1 : 2) solution with KIO₄ (2.5 mmol) as co-oxidant with 1.0 mmol of the substrate (primary alcohols, secondary alcohols,

TABLE 4: The catalytic oxidation [Ru(Haapt)Cl (H₂O)₂] complex^a

Substrate	Yield %	Turn Over
Benzyl alcohol	30 ^{ald} , 60 ^{ac}	55
Cinnamyl alcohol	25 ^{ald} , 55 ^{ac}	50
3,4-Dimethoxybenzyl alcohol	26 ^{ald} , 40 ^{ac}	48
α -Tetralol	97 ^k	49
Benzohrdrol	80 ^k	44
Benzaldehyde	88 ^{ac}	60
Cinnamaldehyde	71 ^{ac}	52
1,2-Cyclooctanediol	39 ^{dk}	21
Trans-Cyclohexanediol	33 ^{ad}	26
Cis-Cyclohexanediol	27 ^{ad}	27

^a Oxidation reactions were carried out for 3 h (4.5 h in case of diols), all at 348 K by using 0.02 mmol of the catalyst, 2.5 mmol KIO₄ (co-oxidant) in in CH₃CN - H₂O (1 : 2, 15 mL).

^{ad}Corresponding aldehyde, ^{ac}corresponding carboxylic acid, ^kcorresponding ketone, ^{dk}1,2-cyclooctanone, ^{ad}adipic acid

aldehydes and diols). The oxidation reactions being carried out for 3 h (4.5 h in case of diols), all at 348 K. Aldehydes and ketones were detected and quantified as 2,4-dinitrophenyl hydrazone derivatives while carboxylic acids and dicarboxylic acids isolated and weighed as such (TABLE 4). With both cinnamyl alcohol and cinnamaldehyde, the oxidation product was benzoic acid with cleavage in the double bond^[43].

Control experiments were conducted under similar conditions in the absence of the catalyst, in all cases very small amounts of oxidation products were found.

pH-Metric measurements

The pH-metric titration of 5×10^{-3} M H₂aapt with 9.2×10^{-3} M NaOH in the presence of 5.4×10^{-3} M HCl in water-EtOH (3:7, by volume) was carried out at 298.15 K. The average number of protons dissociated from the ligand n_A , was determined at different pH values by applying Irving-Rossotti equation^[44]. The values of n_A were plotted against the pH values, and the ligand protonation constant values, $\log k_1$ and $\log k_2$ were determined by the interpolation at half n_A values (0.5, 1.5).

$$n_A = Y + \frac{(V_1 - V_2)(N^0 + E^0)}{(V_0 + V_1)T_L}$$

Y = 2 (the number of dissociated protons in the ligand); E⁰ = molar concentration of HCl; N⁰ = molar concentration of NaOH; V₁ and V₂ are the volumes

TABLE 5: The formation constants of H₂aapt and its complexes

Central metal ion	pK _{a1}	pK _{a2}
H ⁺	11.80	5.85
Co(II)	8.00	4.80
Ni(II)	11.60	6.95
Cu(II)	14.30	7.95
Zn(II)	11.25	8.40
Cd(II)	9.30	6.30

of NaOH required to reach definite pH value in free HCl and the mixture of HCl and H₂aapt titrations, respectively; V₀ = 25 mL (the initial volume of the titrated solution); and T_L is the molar concentration of the ligand.

As expected, the maximum n_A values were found to be two owing to the presence of two dissociable protons of the enolized carbonyl oxygen and enolized thiol centers. The pK_{a1} and pK_{a2} values of H₂aapt were determined by interpolation at half n_A values (0.5, 1.5) to be 11.8 and 5.85, respectively.

The metal-ligand stability constants were obtained from the relation between n and pL.^[44] The calculated stability constants are summarized in TABLE 5. It is clear that, for all the reported complexes under this study $\log k_1 > \log k_2$, as the vacant sites of the central metal ions are more freely available to bind the first ligand molecule with respect to the second one. The order of the stability constants for ML and ML₂ were found to be Cu(II) > Ni(II) > Zn(II) > Cd(II) > Co(II) and Zn(II) > Cu(II) > Ni(II) > Cd(II) > Co(II), respectively.

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