Synthesis and structure studies of Co(II), Ni(II), Cu(II), Pd(II), Ru(II), Ag(I), Cd(II) and dioxouranium(VI) complexes with 1-acetoacet-o-toluidide-4-phenyl-3-thiosemicarbazone

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The synthesis of the new 1-acetoacet-o-toluidide-4-phenyl-3-thiosemicarbazone (H₂aatpt) complexes: [M(H₂aatpt)(H₂O)₄] (M(II) = Co, Cd, n = 0; M(II) = Ni, Cu, n = 2), [Cu(H₂aatpt)(AcO)(H₂O)₂], [M(H₂aatpt)(Cl)(H₂O)₄] (M (II) = Cu, n = 0; M(II) = Ru, n = 2), [Pd(H₂aatpt)(Cl)₂], [Ag(H₂aatpt)(H₂O)₃]NO₃ and trans-[UO₂(H₂aatpt)₂] is reported. Their elemental analyses, molar conductivities, thermal, magnetic measurements, IR, ¹H NMR and UV-vis spectroscopy have been investigated. Growth inhibition of B. subtilis and Micrococcus sp. by H₂aatpt and its Ni(II) and Pd(II)-complexes is reported.

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Thiosemicarbazones and their complexes exhibit a great variety of biological activity. In recent years, thiosemicarbazones have been used for the analytical determination of metals. We have earlier described the chelation behaviour and electronic properties of aromatic and aliphatic thiosemicarbazones obtained by organic moieties with biological interest. As a part of continuing work on O, N, S and O, N, S donor ligands, we report here the synthesis and spectroscopic studies of the new complexes of 1-acetoacet-o-toluidide-4-phenyl-3-thiosemicarbazone (H₂aatpt) with some first and second row transition elements. Also, the growth inhibition activity of H₂aatpt and its Ni(II) and Pd(II) complexes against B. subtilis (gram-negative bacteria) and Micrococcus sp. (gram positive bacteria) has been achieved.

Materials and Methods
All used chemicals were analytically grade. 1-Acetoacet-o-toluidide-4-phenyl-3-thiosemicarbazone (H₂aatpt) was prepared by mixing 4-phenyl-3-thiosemicarbazide (1.67 g, 0.01 mol) with acetoacet-o-toluidide (1.91 g, 0.01 mol) in ethanol (40 mL) and 5 M HCl was added (2 mL). The reaction mixture was stirred at room temperature for 1.5 h and the white solid filtered off, washed, recrystallized from ethanol and dried over anhydrous calcium chloride.

The complexes [M(H₂aatpt)(H₂O)₄] (M(II) = Co, Cd, n = 0; M=Ni(II), n=2), [Cu(H₂aatpt)(AcO)(H₂O)₂] and trans-[UO₂(H₂aatpt)₂] were synthesized by mixing ethanolic solutions of both H₂aatpt (0.001 mol) and the corresponding metal acetates (0.001 mol; 35 mL). The reaction mixtures were boiled under reflux for 2-3 h. The solid complexes were separated out either during reflux or after cooling. [Cu(H₂aatpt)Cl] was produced by the same procedure using equimolar ratio of H₂aatpt (0.001 mol) and CuCl₂·2H₂O (0.001 mol). The same method was applied for the isolation of [Ru(H₂aatpt)(Cl)(H₂O)₂] with 2:1 molar ratio (H₂aatpt:RuCl₃·3H₂O). The complex [Cu(H₂aatpt)(H₂O)₂] was isolated by refluxing H₂aatpt (0.001 mol) and CuSO₄·5H₂O (0.001 mol) in ethanol-aqueous (3:2 molar ratio) solution. The complexes [Pd(H₂aatpt)(Cl)₂] and [Ag(H₂aatpt)(H₂O)₃]NO₃ were prepared by adding H₂aatpt (0.001 mol) in ethanol and aqueous solution of K₂PdCl₄ or AgNO₃ (0.001 mol). The solid complexes were isolated after stirring for 1 h [in dark in case of Ag(I) complex]. The complexes obtained were filtered, washed with ethanol, ether and dried in vacuo. The complexes obtained were recrystallized from hot acetonitrile solution upon cooling.

Antimicrobial studies
The cup-diffusion method was used to study the ligand (H₂aatpt) and the complexes, [Ni(H₂aatpt)(H₂O)₂] and [Pd(H₂aatpt)Cl₂]. The test organisms were B. subtilis (gram-negative bacteria)
and Micrococcus sp. (gram positive bacteria). The activity of these compounds against the tested bacteria was compared with that of two standard antibiotics (penicillin and streptomycin).

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]₂ as calibrant. Electronic spectra in DMSO were recorded using a Unicam UV 2.1(Kl) uv-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 α-Al₂O₃ as a reference, on a Shimadzu thermogravimetric analyzer TGA-50 (Mansoura University). Conductometric measurements were carried out at room temperature on YSI Model 32 conductivity bridge.

Results and Discussion

The physical and analytical data of the complexes, together with their elemental analyses are given in Table I. All the complexes are stable in air and insoluble in common organic solvents and most of them are completely soluble in DMSO. The molar conductivities (Λ_m) in DMSO at 25°C for all the complexes are in the range of 2-10 ohm⁻¹ cm² mol⁻¹ indicating their non-electrolyte nature.¹⁵

IR and 'H NMR studies

The main vibrational bands (cm⁻¹) of H₂aatpt and its complexes are reported. The IR spectrum of the free ligand (H₂aatpt) shows band in the 3320-3430 cm⁻¹ region assigned to the stretching vibration of the NH groups.¹⁰ The strong band at 1650 cm⁻¹ is attributed to ν(C=O) stretching vibration thirteen while the medium intensity at 1615 cm⁻¹ is due to ν(C≡N)¹³. The medium intensity band at 1013 cm⁻¹ is assigned to ν(N-N) vibration while that at 840 cm⁻¹ is attributed to ν(C=S) stretch¹³,¹⁷. 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 H₂aatpt in the thione/keto form¹⁹ (Structure I).

The ¹H NMR spectral data of H₂aatpt in DMSO-d₆ have been analyzed. The aromatic protons appear at δ 7.05-7.52 ppm region, the CH₃ protons give a singlet at δ 2.20 (N=C-CH₃)¹⁹ and 3.06 (Ph-CH₃) ppm. The N(3)H, N(1)H and N(4)H protons appear as singlets at δ 10.3, 9.6 and 9.2 ppm, respectively.¹¹

The characteristic absorption bands of the free ligand are shifted on complexation and new vibrational bands characteristic of complexation appeared showing that H₂aatpt behaves in a bidentate and/or tridentate manner due to the type of the metal salt used, the preparation conditions and the pH of the medium.

The IR spectrum of [Pd(H₂aatpt)Cl₂] shows that H₂aatpt behaves as a neutral bidentate ligand coordinates to Pd(II) ion via the carbonyl oxygen (C=O) and azomethine (C=N) centers (Structure II). This mode of chelation is suggested due to the shift of ν(C=O) and ν(C≡N) stretches to lower wave numbers²⁰,²¹ and the shift of ν(C=S) and ν(N-N) vibrations to higher indicating that the latter groups are not participate in complexation. The complex shows extra IR bands at 520, 440 and 285 cm⁻¹ are attributed to ν(Pd-Cl)²², ν(Pd-N)²² and ν(Pd-C)²², respectively. This feature is further supported by the ¹H NMR spectrum of [Pd(H₂aatpt)Cl₂], which shows three siglets at δ 10.25 (10.35), 9.6 (9.65) and 9.15 (9.23) ppm, almost the same as that of the free H₂aatpt. Further more, the presence of two resonances for each proton, suggesting a cis arrangement of this complex.²⁰

In the IR spectrum of [Ag(H₂aatpt)(H₂O)₂][NO₃] complex, the strong bands at 1615 and 840 cm⁻¹ in the free ligand arising from ν(C=O) and ν(C≡N) are affected upon coordination and shifted to lower wave number while ν(C=O) is shifted to higher wave number upon complexation, as expected since the thione sulphur center is involved in coordination.¹³,¹⁹ This means that H₂aatpt behaves as a neutral bidentate. This complex shows a new band at 1385 cm⁻¹, which may be assigned to ν(NO₃) vibration proving the presence of NO₃⁻ as a free ion.²³

The IR spectra of the complexes [Cu(Haatpt)(AcO)(H₂O)₂] and [M(Haatpt)(H₂O)₆] (M=Ni(II), n=2; M=Cd(II), n=0), show that H₂aatpt is acting as a mononegative bidentate coordinating via the deprotonated thiol sulfur (C-S⁻) and azomethine nitrogen (C=N) atoms (Structure III). This mode of chelation is supported by the disappearance of ν(C=O) with the appearance of new bands in the 610-645 and 1630-1636 cm⁻¹ probably arising from ν(C-S) and ν(C=N) vibrations, respectively. The shift of
Table 1—Characterization of H₂aatpt and its complexes

<table>
<thead>
<tr>
<th>(Empirical Formula), yield (%)</th>
<th>Color</th>
<th>m.p.(°C)</th>
<th>% Cale (found)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂aatpt (C₁₈H₂₅N₅O₃S₂), 85</td>
<td>White</td>
<td>173</td>
<td></td>
</tr>
<tr>
<td>[Co(H₂aatpt)₂]H₂O</td>
<td>Brown</td>
<td>235°</td>
<td></td>
</tr>
<tr>
<td>[Co(C₁₈H₂₅N₅O₃S₂)], 60</td>
<td>Brown</td>
<td>230°</td>
<td></td>
</tr>
<tr>
<td>[Ni(H₂aatpt)₂(H₂O)₂]</td>
<td>Brown</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>[Cu(H₂aatpt)(AcO)(H₂O)], 65</td>
<td>Green</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>[Cu(H₂aatpt)(H₂O)₂]·4H₂O</td>
<td>Brown</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>[Cu(H₂aatpt)(Cl)(H₂O)], 65</td>
<td>Dark-brown</td>
<td>&gt; 300</td>
<td></td>
</tr>
<tr>
<td>[Ru(H₂aatpt)Cl(H₂O)], 65</td>
<td>Orange</td>
<td>&gt; 300</td>
<td></td>
</tr>
<tr>
<td>[Pd(H₂aatpt)Cl]</td>
<td>Pale-brown</td>
<td>&gt; 300</td>
<td></td>
</tr>
<tr>
<td>[Ag(H₂aatpt)(H₂O)]NO₃</td>
<td>White</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>[Cd(H₂aatpt)₂]</td>
<td>Yellow</td>
<td>&gt; 300</td>
<td></td>
</tr>
<tr>
<td>[UO₂(H₂aatpt)₂]·4H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[M(H₂aatpt)Cl(H₂O)] [M(II) = Cu, n = 0; M(II)=Ru, n=2] and trans-[UO₂(H₂aatpt)₂]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*decomposition of complexes

**v(C=N)** vibration to lower wave number and the shift of **v(N-N)** vibration to higher wave number. Also, the complexes show new bands near 440 and 330 cm⁻¹ may assign to **v(M-N)** and **v(M-S)**, respectively. These features are further supported by the ¹H NMR spectrum of [Cd(H₂aatpt)₂] complex as the singlet at δ 10.30 ppm is disappeared due to the deprotonation through N(3)H. The IR spectrum of the complex, [Cu(H₂aatpt)(AcO)(H₂O)], shows two extra bands at 1560 and 1450 cm⁻¹ attributed to ν₈(OCO) and ν₁(OCO) of the acetate group, respectively, indicating asymmetric bidentate coordination of the acetate group [ν(OCO) between ν₈(OCO) and ν₁(OCO)] is in the 140 cm⁻¹ region.

In the IR spectrum of [Cu(H₂aatpt)(H₂O)₂], the stretching vibration **v(C=O)** of the free ligand is missing in the complex indicating the participation of the deprotonated enolic carbonyl oxygen (=C=O) in coordination. Also, the **v(C=N)** stretch of the free ligand is shifted to lower wave number while **v(N-N)** is shifted to higher one upon complexation. These features are further supported by the observation of new band at 1140 cm⁻¹ due to **v(C-O)** vibration. The complex shows extra IR bands at 510 and 450 cm⁻¹ are assigned to **v(Cu-0)** and **v(Cu-N)**, respectively.

The IR spectral data of [M(H₂aatpt)Cl(H₂O)] [M(II) = Cu, n = 0; M(II)=Ru, n=2] and trans-[UO₂(H₂aatpt)₂] suggested that H₂aatpt behaves as a mononegative tridentate ligand coordinating the metal ion via the deprotonated thiol sulfur, azomethine nitrogen and carbonyl oxygen centers (Structure IV). This mode of complexation is suggested due to the disappearance of **v(C=S)** stretch with the simultaneous appearance of new bands at 605-640 and 1620-1630 cm⁻¹ attributed to **ν₁(OCO)** and **ν₈(OCO)** of the acetate group, respectively.
IBRAHIM et al.: STUDY OF $\text{H}_2\text{aatpt}$ COMPLEXES

Structure I

Structure II

Structure III

Structure IV

cm$^{-1}$ regions that may be assigned to $\nu$(M-O)$^{9,13,20}$, $\nu$(M-N)$^{13,32,35}$, $\nu$(M-S)$^9$ and $\nu$(M-Cl)$^{34}$, respectively.

The complex trans-$\text{UO}_2(\text{Haatpt})_2$ shows a strong IR band at 920 cm$^{-1}$ assigned to $\nu^a$(U=O) of the trans-O-U-O group$^{9,13,33,36}$.

The IR spectral data of the complex, [Co(Haatpt)$_2$]$_2$, show that H$_2$aatpt 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 $\nu$(C=O) vibration of the free ligand with the observation of new band at 1111 cm$^{-1}$ due to $\nu$(C-O) in the complex$^8$. The $\nu$(C=S) and $\nu$(C=N) stretches shift to lower wave numbers upon coordination$^8$. Also, the complexes show extra IR bands at 500, 430 and 330 cm$^{-1}$ regions which are assigned to $\nu$(Co-O)$^{12,37}$, $\nu$(Co-N)$^{12,37}$ and $\nu$(Co-S)$^{12,37}$, respectively.

Magnetic and electronic spectral studies

The electronic spectrum of H$_2$aatpt in DMSO showed that this ligand has $n$-$\pi^*$ transition in the 31750-33670 cm$^{-1}$ region assigned to the phenyl ring$^{38}$. The energies are raised by ca 1000 cm$^{-1}$ in the complexes$^{39}$. The 25320-25900 cm$^{-1}$ region bands are assignable to the $n$-$\pi^*$ transition of the thiosemicarbazone thioamide moiety, and are shifted to higher energies in the complexes$^{25}$.

The electronic spectrum of [Ni(Haatpt)$_2$(H$_2$O)$_2$] complex shows two absorption bands at 15385 and 25975 cm$^{-1}$ assignable to $\text{A}_{2g}$-$\text{T}_{1g}(F)$ and $\text{A}_{2g}$-$\text{T}_{1g}(P)$ transitions$^{40,41}$, respectively. The ligand field parameters, $D_{q}$, $B$, $\beta$, $\epsilon$ (994, 863, 0.829, 9490) as well as the magnetic moment ($\mu_{\text{eff}} = 2.80$ B.M.) are consistent with Ni(II) octahedral geometry$^{8,12,41}$.

The complex [Co(Haatpt)$_2$] is paramagnetic with magnetic moment ($\mu_{\text{eff}} = 2.40$ B.M.). The electronic spectrum of this complex shows two bands at 14080 and 17090 cm$^{-1}$. The magnetic moment with the position of the absorption bands suggest low-spin octahedral geometry around the Co(II) complex$^{29}$.

The electronic spectra of the complexes, [Cu(Haatpt)$_2$(H$_2$O)$_2$] and [Cu(Haatpt)(AcO)(H$_2$O)$_2$] show broad bands near 17000 cm$^{-1}$ with a shoulder near 14100 cm$^{-1}$, which may be assigned to $^2\text{B}_{1g}$-$^2\text{E}_g$ and $^2\text{B}_{1g}$-$^2\text{A}_1g$ transitions, respectively, in a tetragonal distorted octahedral configuration$^{30,37}$.

The reported Cu(II) complexes are found to be paramagnetic with magnetic moments (2.0 and 1.8 B.M., respectively) which is normal for Cu(II) complexes (the $d^9$ system contains one unpaired electron$^{44}$).
The electronic spectrum of \([\text{Ru(Haatpt)}\text{Cl(H}_2\text{O})_2]\) shows three bands at 18587, 23310 and 32150 cm\(^{-1}\), which may be arisen from \(1A_{1g} \rightarrow 1T_{1g}\), \(1A_{1g} \rightarrow 1T_{2g}\) and ligand (\(\pi \rightarrow \pi^*\)) transitions, respectively\(^{8,9,13,44}\). This indicates a low-spin octahedral arrangement around the diamagnetic Ru(II)\(^{8,44}\).

The electronic spectrum of the diamagnetic \([\text{Pd(H}_2\text{aatpt)}\text{Cl}_2]\) complex exhibits a band at 25250 cm\(^{-1}\) due to \(1A_{1g} \rightarrow 1B_{1g}\) transition in a square-planar configuration\(^{13,25}\).

The electronic spectrum of \([\text{Ag(Haatpt)}\text{(H}_2\text{O})_2]\)NO\(_3\) complex shows two absorption bands at 17587 and 28571 cm\(^{-1}\), which may be attributed to a square-planar stereochemistry\(^8,13\).

The electronic spectrum of trans-\([\text{UO}_2(\text{Haatpt})_2]\) shows two bands at 23810 and 27500 cm\(^{-1}\) may be due to \(\Sigma_{1e}^+ \rightarrow 2\pi_a\) and \(n \rightarrow \pi^*\) charge transfer, respectively\(^{37}\).

**Thermal studies**

The thermal decompositions of the complexes, \([\text{Ni(Haatpt)}_2\text{(H}_2\text{O})_2]\) and \([\text{Pd(H}_2\text{aatpt)}\text{Cl}_2]\) were studied using the TG and DTG technique as shown in Scheme 1 and 2, respectively.

The thermogram of \([\text{Ni(Haatpt)}_2\text{(H}_2\text{O})_2]\) is thermally stable up to 175°C, above which point it shows the first endothermic weight loss between 175 and 210°C, which may correspond to the elimination of two coordinated water molecules\(^{9,11}\) (Found 4.9; Calcd. 4.7%). The second endothermic weight loss step (Found 65.9; Calcd. 66.2%) between 210 and 445°C may be attributed to the elimination of the loosely bound \(\sigma\)-methylphenylimino (MePhNH\(_2\); C\(_7\)H\(_7\)N) and phenylthiouridine (PhNHCSNH; C\(_7\)H\(_8\)N\(_2\)S) fragments from both ligands\(^{8,9,12,13}\). The third TG inflection was observed between 445 and 555°C, the endothermic weight loss in this inflection may arise from the removal of two C\(_7\)H\(_7\)N fragments and 1/2 O\(_2\), leaving NiO representing (Found 9.9; Calcd. 9.7%).

The thermogram of \([\text{Pd(H}_2\text{aatpt)}\text{Cl}_2]\) shows a great thermal stability up to 205°C, above which the weight loss occurs. The first endothermic weight loss step (205-335°C) is probably correlated to the elimination of \(\sigma\)-methylphenylimino (MePhNH\(_2\); C\(_7\)H\(_7\)N) and a chlorine molecule\(^8\) (Found 34.5; Calcd. 34.3%) in the TG and DTG curves. The second weight loss, between 335 and 450°C, may be attributed to the release of phenylthiouurdido (PhNHCSNH; C\(_7\)H\(_8\)N\(_2\)S) fragment as well as the removal of the remaining C\(_7\)H\(_7\)N fragment (Found 41.8; Calcd. 42.2%).

The last step at 450°C may be due to the formation of PdO (Found 23.6; Calcd. 23.4%).
Evaluation of kinetic parameters

The complexes [Ni(Haatpt)₂(H₂O)₃] and [Pd(Haatpt)Cl₂] exhibit well-defined and non-overlapping second (Pd) and third (Ni) stage pattern. These stages are chosen for detailed study.

The kinetic parameters were evaluated using the Coast-Redfern and Horowitz-Metzger equations. The kinetic parameters, order of reaction (n) and activation energy (E) for the chosen stages have been determined. The order of the reaction in complexes was found to be n=0, E=109.63 KJmol⁻¹ (Ni) and n=2, E=204.60 KJmol⁻¹ (Pd).

Antimicrobial activity studies

The free ligand (H₂aatpt) and its complexes [Ni(Haatpt)₂(H₂O)₃] and [Pd(Haatpt)Cl₂] (200 µL of 10 mg mL⁻¹ DMSO) show antimicrobial activity towards the growth of B. subtilis (gram negative bacteria) and Micrococcus sp. (gram positive bacteria). The Ni(II) and Pd(II) complexes are more active than the free ligand H₂aatpt against the studied organisms (B. subtilis: 1.4 cm (H₂aatpt), 6.1 cm (Ni complex) and 1.9 cm (Pd complex) and Micrococcus sp. (1.8 cm (H₂aatpt), 6.0 cm (Ni complex) and 2.1 cm (Pd complex). An important aspect of the growth inhibition of the coordinated, deprotonated H₂aatpt is the formation of the conjugated -C=N-N=C(S)N moiety as well as the central ion. This feature is observed clearly in case of Ni(II) complex. The low antimicrobial ability of the cis-[Pd(H₂aatpt)Cl₂] complex may be due to the presence of two chloro ligands in a cis-configuration which inhibits the growth of the tested organisms by altering their cell walls. It has been reported that trace amount of cis-dichloroplatinum(II) and cis-dichloromercury(II) causing this biological effects. This feature is supported by comparing the activity of these complexes with that of two standard antibiotics (penicillin and streptomycin). The Pd(II) and Ni(II) complexes exhibit lower activity against B. subtilis and Micrococcus sp. than penicillin (22.3, 31.8 cm) and streptomycin (24.5, 35.7 cm).

References

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